

Comparison of approaches for assessing sustainable remediation of contaminated sites

Søndergaard, Gitte Lemming; Binning, Philip John; Bjerg, Poul Løgstrup

Published in:

14th International Conference on Sustainable Use and Management of Soil

Publication date:

2017

Document Version

Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):

Søndergaard, G. L., Binning, P. J., & Bjerg, P. L. (2017). Comparison of approaches for assessing sustainable remediation of contaminated sites. In 14th International Conference on Sustainable Use and Management of Soil: Book of abstracts (pp. 242-242). Lyon, France.

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14th International Conference on
Sustainable Use and Management of
Soil, Sediment and Water Resources

26–30 June 2017 • Lyon • France

BOOK OF ABSTRACTS



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Special Sessions (SpS)

SpS 2b.4: (Bio)availability vs. reactivity of organic pollutants in soils and sediments

Pierre Faure¹; Coralie Biache²; Stéphanie Ouvrard³; Jose Julio Ortega-Calvo⁴; Joop Harmsen⁵; Kirk Semple⁶

¹ CNRS / GISFI; ² Laboratoire Interdisciplinaire des Environnements Continentaux; ³ Laboratoire Sols et Environnement; ⁴ Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC); ⁵ Alterra; ⁶ Lancaster University, FR

The (bio)availability of organic chemicals in soil and sediment is an important area of scientific research. Reactivity of organic contaminants can be defined by their responses to biological or chemical constraints (water leaching, degradation, transformation...). Reactivity, under environmental conditions (natural attenuation) or facing remediation treatments, is mainly controlled by contaminant availability. To better predict the behavior of contaminant, it is essential to improve our knowledge on the link between both (bio)availability and reactivity.

The aim of this session is to discuss recent research in this field and provide some scientifically-based propositions to incorporate the availability in the description of mechanisms involved in environmental matrix fate over time. The presentations proposed in the session illustrate by several examples, the interaction between (bio)availability and reactivity in the context of chemical processes (remediation treatments) and biological processes (plant and microorganisms action) and the link between availability and risk assessment. The presentations will provide a discussion (30 to 45 min) forum for existing availability concepts and methods, for their introduction in reactivity mechanisms as well as pathways for their implementation into risk assessment.

Names of presenters and titles of presentations (20 min of presentation + discussion)

- Pierre Faure, CNRS – Lorraine University, Vandoeuvre les Nancy (France): How availability controls reactivity of hydrophobic contaminants in soils?
- J.-Julio Ortega-Calvo, IRNAS-CSIC, Seville (Spain) : Microbial processes affecting bioavailability of hydrophobic chemicals in soil
- Stéphanie Ouvrard, INRA - Université de Lorraine, Vandoeuvre les Nancy (France): Evaluation of combined availability tools and modeling approach for PAH plant uptake prediction
- Coralie Biache, CNRS – Lorraine University, Vandoeuvre les Nancy (France): Thermal method as a new approach to link organic pollutant availability and reactivity in contaminated soils
- Joop Harmsen, Alterra, Wageningen (The Netherlands) : Risk assessment of non-extractable residues in soil
- Kirk Semple, Lancaster University (United Kingdom) : From bioavailability science to regulation of organic chemicals

SpS 2b.5: REMEDIATE – Improved decision making for contaminated land site investigation and risk assessment

*Frederic Coulon*¹; *Rory Doherty*²; *Siobhan Cox*²; *Sabrina Cipullo*¹; *Peter Brennan*³; *Coren Pulleyblank*³; *Stacie Tardif*; *Kristian Koefoed Brandt*⁴; *Brian Kelleher*³; *Domenico Antonio De Luca*⁵; *Neha Mehta*; *Breda Moore*; *Tatiana Cocerva*; *Alex Gottschalk*

¹ Cranfield University; ² Queen's University Belfast; ³ Dublin City University; ⁴ University of Copenhagen; ⁵ University of Turin, GB

The EU has allocated over €3.1 billion to the rehabilitation of industrial sites and contaminated land in the last 6 years and over €2 billion is spent annually on site risk management. However the systematic monitoring and protection of soil quality across Europe has still to be attained. Remediation of contaminated sites is necessary to limit the volume of land take for industrial, housing and roads development, and involves a number of EU Directives. The primary objective of the Soil Framework Directive is to protect European soil. Historic land contamination is among the long-term causes of water contamination and the Water Framework Directive encourages increased remediation of contaminated sites to assist Member States achieve water quality targets by 2015. The Groundwater Daughter Directive has also introduced measures to prevent or limit inputs of pollutants into groundwater and the Waste Framework Directive requires that waste be managed without endangering human health and harming the environment. Contaminated sites and the presence of contaminants (for example, metals, NAPLs, chlorinated hydrocarbons) in soil present a potential risk to humans, water and ecosystems. Depending on the future use of that site, risk management measures, or site remediation, will be required. Currently, remediation techniques mainly follow the traditional route of excavation and off-site disposal. Potential contaminated sites exist where unacceptable soil contamination is suspected but not verified, thus requiring investigation to verify the risk to receptors. Legal requirements for general protection of soil or to reduce soil contamination are not yet available – however, costs involved and human health/ ecosystem risks make this topic a socio-economic priority for the EU. As the EU further develops a common framework for the management of contaminated sites, the burden on sustainability, characterisation, risk management and remediation is increasing. There is therefore considerable pressure to develop new innovative and cost effective solutions to the challenges facing the sector.

The REMEDIATE session will not address specific remediation technologies but will instead address the overarching multidisciplinary demands needed for enhanced leadership and decision-making, to ensure that in future the optimal remediation technologies are employed on a site specific basis. Key topics to be covered include:

1. Environmental chemistry & toxicology approaches to site assessments
2. Rapid Molecular Microbiology assessment approaches to assessing bioremediation
3. Geophysical approaches to site assessment
4. Computational modelling & prediction approaches to estimate contamination profile, forecast contamination development & assessing remediation options

Effects of physiochemical factors on hydrocarbons and metals bioavailability in soil: implication for risk assessment

Cipullo S., Prpich G., Campo Moreno P., Coulon F.

Cranfield University, School of Water, Energy and Environment, Cranfield, UK

Environmental contamination comprises a complex mixture of both organic and inorganic contaminants and therefore understanding their distribution, behaviour and chemical interactions is key to provide the evidence necessary to make informed decision and implement robust remediation strategies. However, most of the current risk assessment frameworks used to manage land contamination are based on total contaminant concentrations and the exposure assessments embedded within them do not explicitly address the partitioning and bioavailability of chemical mixtures. This inability may contribute to an overestimation of the risks posed by chemical mixtures. In turn, this may limit the efficacy of the risk frameworks to inform targeted and proportionate remediation strategies. In order to address these issues and therefore provide a more rationale understanding of the factors that drive uncertainty in determining bioavailability, a series of soil mesocosms containing contaminated soils with heavy metals and/or hydrocarbons mixtures was setup under a range of various conditions where the influence of pH, moisture, soil organic carbon content, soil texture and temperature on the fate and behaviour of the mixtures was assessed. Mesocosms were incubated under aerobic conditions for 360 days. The bioavailable and total concentrations of hydrocarbons and heavy metals were determined at T0, 3, 6 and 12 months. The petroleum hydrocarbons were extracted using either a sequential cyclodextrin and acetone:dichloromethane extraction (bioavailable hydrocarbons fraction), methanol:water mixture (readily available hydrocarbons fraction) and hexane:dichloromethane (total extractable petroleum hydrocarbons TEPH). All extracted fractions were subsequently analysed by gas chromatography coupled to mass spectrometry using a combination of full scan mode and single ion monitoring event. The distribution and availability of the metal elements were determined using a multi-elemental sequential extraction associated with a chemometric identification of substrates and element distributions (CISED). Preliminary results on petroleum hydrocarbons from soil samples collected at T0, 3, and 6 months showed that soils where no pre-treatment was done (absence of binder and stabilizer) had the most significant reduction in the aromatic and aliphatic hydrocarbon fractions over time. In comparison the hydrocarbon fractions composition and concentration barely changed in the treated soils as the hydrocarbons were mostly sorbed to the soils due to the presence of the stabilizer. . Among the variables tested, pH seems to be the main driver affecting contaminant availability when comparing pre and post-treatment samples; however more data are needed to understand if the contaminants reduction observed is due to sorption or degradation process. The metals data are currently underway. Overall, this research will provide valuable knowledge concerning distribution, behaviour and ageing of complex chemical mixtures in soil on a range of conditions not previously investigated. The output will help understanding antagonistic (or synergistic) effects capable of reducing (or enhancing) contaminants availability, in order to develop uniform basis for estimating risk. Overcoming uncertainties associated with bioavailability measurement can lead to the development of a more informative site-specific risk assessment, enabling a proportionate evaluation of risk and cost-effective land management.

Characterization of oral bioaccessibility of Potentially Toxic Elements (PTEs) in urban area of Belfast

Tatiana Cocerva¹; Siobhan Cox¹; Mark Cave²; Rory Doherty¹; Ulrich Ofterdinger¹

¹ Queen's University Belfast; ² British Geological Survey

Urban environments have been modified significantly since the industrial revolution, due to the release of many Potentially Toxic Elements (PTEs) and their accumulation in topsoil. Belfast, the largest city in Northern Ireland, is historically recognised for both linen production and shipbuilding. A recent study using the Tellus geochemical dataset (McIlwaine et al., 2016) demonstrated the relationship between historical development zones in Belfast and PTEs concentrations, suggesting the PTEs are of both geogenic and anthropogenic origin. In some areas of the city, concentration of PTEs including As, Cd, Cr, Pb, Ni, V, Zn exceed current "Suitable 4 Use Levels" (Nathanail et al., 2015) for the protection of human health. However, not all these contaminants in soil are available for uptake by humans. Oral bioaccessibility testing can be used to refine the risks posed to human health by measuring the fraction of a contaminant that is released in the digestive tract.

A subset of 100 samples from across the metropolitan area of Belfast was selected from the archive of Tellus samples held by Geological Survey of Northern Ireland (GSNI). This subset was chosen to include soils overlying the main bedrock formations, a wide variety of contaminant concentrations and different land uses. The Unified BARGE Method (UBM), an in-vitro method which simulates the human gastro-intestinal tract and validated against in-vivo studies for As, Cd, Pb, and Sb (Denys et al., 2012) was used to undertake bioaccessibility testing on selected samples.

The outcomes of this research are used to provide data on the behaviour of PTEs and their oral bioaccessibility in urban soil across Belfast and to improve decision making regarding contaminated land management.

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The use of BioElectrochemical Systems (BESs) to remediate and monitor contamination in groundwater plumes.

R Doherty¹, C Mendonca², P Kirimizakis¹, R Costeria³, S Puig-Rodes¹, L Kulakova², CCR Allen², M Larkin²

¹ School of the Natural and Built Environment, Queen's University Belfast, ² University of São Paulo, Department of Geophysics, Rua do Matão, Brazil, ³School of Biological Sciences, Queen's University Belfast

The application of BioElectrochemical Systems to the remediation of waste water and contaminant plumes in groundwater has long been recognised. The scaling up of such systems from lab to pilot or field study can be a difficult procedure due to a focus on power output rather than remediation efficiency. Here we present a conceptual model of a groundwater plume at a gasworks site and show how the BES can be designed to primarily manage the risks with associated with groundwater contamination. We present a series of lab studies using contaminated groundwater from the centre and fringe of the contaminant gasworks plume and highlight degradation efficiency of the BES compared with a series of controls. Electrical output of the BES was monitored over time with analysis of the contaminants by GCxGC FID, and assessment of microbial ecology of the gasworks groundwaters and BES systems using 16S sequencing. We show the design of a field scale system that can be used to monitor degradation in near real time.

Mining waste management : A Risk Analysis Approach

Neha Mehta¹, Giovanna Antonella Dino¹, Franco Ajmone-Marsan², Manuela Lasagna¹, Chiara Romè², Domenico Antonio De Luca¹

¹ Department of Earth Sciences, University of Turin, ² Department of Agricultural, Forest and Food Sciences, University of Turin

Abandoned mine sites continue to present a serious environmental hazard as the heavy metals associated with mining waste are continuously released into the environment that threaten the human life and environment. Remediation of sites affected by mining waste is a complex, lengthy and costly process. Thus in most of the European countries a site is considered for remediation when it poses risk to the human health and surrounding environment. To evaluate the effects posed by mining waste risk analysis approach was used for an abandoned mine site in North Italy.

The site is present in Campello Monti in Valstrona comune in the province of Verbano-Cusio- Ossola in the Italian region of Piedmont. It is located in basement of Southern Italian Alps in the Ivrea Verbano Zone. Campello Monti is composed of large and voluminous mafic rocks intruded by mantle periodite. The mafic formation consists of a sequence of cumulate peridotites, pyroxenites, gabbros and anorthosites, together with a large, relatively homogeneous body of gabbro-norite, grading upwards into gabbro-diorite and diorite. Mines here were used for nickel exploitation from 9th Century and continued until 1940s. The long history of mining has left the mining waste contaminated with nickel and cobalt in the mountains scattered over an area of 2 Km. The area around the site is used for housing, shows the presence of domestic animals like goats, and has Strona creek passing through it. Thus the mining waste may present risk to local inhabitants and water resources.

The risk analysis of the site was performed by preparing preliminary conceptual model after gathering information about the site from earlier research done in the field of geology, hydrogeology, hydrography, mine activity and use of soil. The preliminary model contained information on the potential contamination sources, pathways and receptors.

This conceptual model formed the basis for sampling activities. The samples were then collected from different environmental matrices (waste, soil, groundwater, superficial water) and were analyzed for physical and chemical parameters.

The risk assessment procedure including the environmental monitoring of metals and the exposure assessment of population residing nearby to the mine sites contributes to the analysis and prognosis of health related risks. This information forms the basic understanding of the current situation at the sites affected by mining waste and will also serve to help in suggesting the future actions to be taken for successful management of mining waste. The information collected during the whole procedure will also help in finding routes for reuse of mining wastes.

Quantitative environmental sustainability of contaminated land remediation

D. Santos, A. Gottschalk, S. Tlatlik

SUPREN GmbH, Dortmund, DE

The selection of remediation strategies for contaminated site management has evolved from mainly cost and risk-based to a more holistic approach that includes the assessment of the environmental impacts caused by remedial actions. This presentation will focus on the environmental implication of remediation activities using a life cycle approach in line with international standards (ISO 14040 and 14044, 2006) and according to the rules of the International Reference Life Cycle Data System. For each remediation technology, the key processes must be designed to establish a meaningful operating scenario. Process elements such as equipment size and energy demand were either theoretically or numerically modelled to determine the necessary input and output flows to be used in the life cycle inventory (LCI). The developed LCI datasets were then used to aggregate the environmental impacts over the life cycle of contaminated land remediation. Furthermore, the presentation will discuss how to consider the potential effects of remedial actions when managing contaminated sites. First available decision models and tools for remediation sustainable appraisal are summarized. It includes qualitative decision models such as guidelines and frameworks that are commonly used to support the selection of remediation technologies. However, this qualitative approach can be judgemental and requires considerable expertise knowledge or past experience in site remediation. In contrast a quantitative decision framework provides a basis for balancing the trade-offs of a proposed remedial action. Existing quantitative-based models incorporate sustainability measures into the decision making process. A predictive model that allows for reasonable estimates at the decision level is useful to conclude on the environmental sustainability of future remedial actions. By taking into account the environmental impacts over the entire life cycle of contaminated land remediation, the decision making process may be improved resulting in more sustainable cleanup strategies.

Approach of theory of porous media (TPM) is used to simulate groundwater remediation through oxidation via slow release of permanganate

S.M.Seyedpour, T. Ricken

TU Dortmund University, DE

The contamination of groundwater is a wide spread and persistent problem which admits no easy analysis or solution and has become a growing concern. Relative to this matter, chemical contaminants remain as an important issue because the procedure of water purification from these material is expensive and time consuming; hence, the ever increasing emphasis on protection and preservation of natural resources through regional planning is evident today [1]. In Situ Chemical Oxidation (ISCO) is a popular technology used to treat contaminated groundwater. ISCO is the delivery of chemical oxidants, typically through injection, to groundwater to degrade contaminants. One of the challenging issues regarding to standard ISCO is the quick reaction and dissolution in environment. A method to address this challenge is the use of a encapsulated passive, slow-release oxidant, which is inserted and allowed to dissolve and intercept the contaminant over numerous years. Encapsulation prevents instant dissolution of the entire oxidant mass into the environment [2, 3]. Slow release of permanganate is an emerging approach in order to remediate groundwater, in which the cylinders with only few centimeters in diameter are placed in wells or pushed directly into the subsurface. This study has been focused on simulation and modeling of remediation groundwater via slow release of permanganate in frame work of theory of porous media considering mixture theory. A two phasic model (soil and groundwater) including a contaminant and oxidant in the liquid phase is proposed for the phenomenological description of contaminated site. We consider the transport of solute concentrations including diffusion and advection. A finite element implementation of theory of porous media framework is used to provide an illustrative example, describing the spatial and time-depending reaction and process between contaminant and permanganate and transport of them in water.

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Legacy effects of chromated copper arsenate contamination on soil bacterial communities

Stacie Tardif¹, Yi Zhao¹, Peter E. Holm¹, Yong-Guan Zhu², Kristian Koefoed Brandt¹

¹ Department of Plant and Environmental Sciences, University of Copenhagen, DK, ² Institute of Urban Environment, Chinese Academy of Science, China

Multi-element contaminated soils are complex habitats confronting microbial life with a range of stresses, but it remains a challenge to elucidate the main factors shaping microbial communities in such environments. Total metal contamination is a poor predictor of effects on soil microbiota as metal toxicity depends on chemical metal speciation. Hence, it is crucial to use a multi-disciplinary approach to elucidate the major determinants of microbial community structure and functioning in contaminated soils. This study investigates the long-term effects of multi-metal contamination on soil bacterial community diversity, function and metal resistance. Top soil contaminated with varying concentrations of chromium, copper and arsenic due to the use of chromated copper arsenate (CCA) more than 40 years earlier were sampled at a former wood impregnation site in Denmark and characterized by soil physical and chemical tools as complemented by the use of recombinant, whole-cell bacterial bioreporters. Bacterial community composition, function and metal resistance were characterized with molecular and microbiological tools such as next-generation Illumina sequencing of the 16S rRNA gene, high throughput qPCR array targeting microbial biogeochemical cycling genes and pollution-induced community tolerance (PICT) assays. Preliminary results have shown that increased contamination concentrations result in decreased bacterial community activity. Furthermore, it is expected that CCA contamination will affect community diversity, function as well as result in increased community metal resistance as contamination concentrations increase. Insights from this study are expected to provide valuable knowledge on the intricate interactions between soil physicochemical properties, contamination and microbial communities and provide baseline knowledge for subsequent attempts to test different remediation strategies at the studied site.

High-throughput profiling of arsenic resistance genes in multi-metal contaminated soils

Yi Zhao¹, Jian-qiang Su², Stacie Tardif¹, Yong-Guan Zhu², Kristian Koefoed Brandt¹

¹ Department of Plant and Environmental Sciences, University of Copenhagen, DK, ² Institute of Urban Environment, Chinese Academy of Science, China

Arsenic is one of the most prevalent environmental toxic elements and represents risk to human health and ecosystem. Many microorganisms have evolved different arsenic resistance mechanisms for arsenic detoxification to cope with widespread arsenic contamination, and some bacteria even exploit dissimilatory arsenic biotransformation processes for their energy generation. The genes encoding arsenic resistance and dissimilatory arsenic cycling play important roles in the biogeochemical cycling of arsenic. Understanding the diversity, abundance, and distribution of all these genes constitute a promising avenue for predicting the fate of arsenic and for assessing environmental risks and remediation strategies in arsenic contaminated environments. In this study, we aim to design an arsenic smart chip based on high-throughput qPCR enumeration of arsenic resistance and transformation genes and to apply this novel approach to profiling arsenic resistance genes of a former wood impregnation site in Denmark contaminated with chromium, copper and arsenic four decades ago.

Key words: bioremediation, arsenic, arsenic resistance, microorganisms, arsenic contamination, arsenic biotransformation.

SpS 2c.2: Emerging issues with PFAS risk assessment workshop

Dorte Harrekilde; Hans Bengtsson; Marianne Wilton

Ramboll, DK

Background

Poly- and Perfluorinated substances (PFAS) have been identified as emerging contaminants as a result of widespread presence in the environment and a growing concern with respect to human health and ecological effects. This class of compounds includes perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), the two most commonly researched PFAS, and reportedly, the most prevalent in the environment. These chemicals are widespread around the globe, primarily due to their manufacturing, processing and use, and disposal practices. PFAS are widespread in the environment in part because they are persistent – that is, they do not break down when exposed to air, water or sunlight. Regulations for investigating and monitoring for PFAS and establishing acceptable environmental threshold values have been evolving in many countries, although the approach to addressing these topics varies widely from country to country. Further, given the range of compounds present in this class of contaminant, there is uncertainty about their fate and transport properties in the environment, as well as the human and ecological toxicity.

Objectives

This workshop will discuss the regulatory trends in managing this class of emerging contaminant, and the associated technical challenges, including the following topics.

- Overview on PFAS; issue and terminology, PFAS sources, chemical and physical properties
- Toxicology and ecotoxicology
- State of the Practice for investigating, analysing and remediating PFAS

The objective of this workshop is to provide participants with a common understanding from which to discuss best practices and future developments. A short talk will be given on each of the three elements (10-15 minutes) followed by group discussions on each topic (10-15 minutes). The group discussions will be initiated by a list of questions aiming at discussing best practices and differences in national approaches. The last discussion will focus on illuminating the expected path forward.

We suggest that knowledge and experiences on the following aspects could be addressed:

PFAS sources and issues. What are PFAS and precursors and what are their characteristics? Where do they come from? What happens when PFAS are emitted to the environment?

Toxicology and ecotoxicology. Where do we find PFAS and which human and ecological exposure route is the most critical? What is the basis for setting acceptable threshold values and how do these threshold values vary between countries? What are the regulatory drivers?

State of the practice – analytical methods and treatment options. Which PFAS can be analysed in environmental samples and which methods are available in your country? How much do we actually know about treatment options, how effective are they. What do you think is the expected way forward?

SpS 3b.5: Free session - Silphes project

" SILPHES is a Research, Development and Innovative project dedicated to the development of in-situ remediation solutions for groundwater contaminated with chlorinated compounds. This project benefits from French public funds (ADEME, French Agency of Environment and Energy Management) and extends over 4 years (2013-2017).

The main objective of SILPHES is to develop solutions from the laboratory scale to the in-situ pilot scale under a continuous cost-benefit approach.

It integrates several demonstrators, companies and laboratory such as chemical company (INOVYN), remediation operators (SERPOL, SOL Environment), soil remediation engineering companies (INTERA, MAHYTEC, SOLDATA), remediation products developer (BIOREM Engineering), Public laboratory / University (LCE/CNRS, UTINAM/CNRS) and the French geological survey (BRGM).

The pilot site is a large chloroalkali chemical plant located near Dole in eastern France. From the 1980s to 2007, a historical DNAPL pool of several hectares was physically confined and monitored. A steady-state plume of chlorinated solvents has however formed downstream the source zone within a shallow sandy aquifer located above clayey bedrock at 10 meters depth. DNAPL thicknesses of 20 cm to 150 cm have been observed following the morphology of the substratum at the source zone. The DNAPL is composed of a mix of heavy chlorinated compounds: hexachlorobutadiene (55%), hexachloroethane (14%), perchloroethylene (8%), carbon tetrachloride (4%), trichloroethylene (2%), hexachlorobenzene (1%) and others (16%).

The main objective of SILPHES project is to combine characterization tools and techniques for remediation of organochlorine compounds. The complementarity of different techniques gives to the project an innovative and structuring type of dimension chain that will build on:

The development and validation of pollution characterization techniques "source areas" and "plume zones" in order to optimize the design of pollution control units and ensure their management (Geophysical and PITT tracers, Phytoscreening / Dendrochemistry, isotopic analysis...), . The development and validation of in situ remediation solutions with the demonstration of their technical and economical efficiency (upwelling, soil mixing, jet grouting, surfactant and foam, innovative reducers), . The development of a new decision support tools for future projects."

Delineation of chlorinated solvent sources at a chlor-alkali facility using phytoscreening

Michel Chalot¹; Loic YUNG; Matt Limmer; David Cazaux

¹ Université de Bourgogne Franche-Comté, FR

Chlorinated ethenes (CEs) are among the most common volatile organic compounds (VOC) that contaminate groundwater, representing currently a major source of pollution worldwide. Indeed, when entirely present in the subsurface, they persist for decades and act as long-term sources of contamination. Site characterization is often time consuming and a financial burden for the site owners, which raises a demand for rapid and inexpensive global (pre)screening methods. Phytoscreening has been employed and developed through different applications at numerous sites, where it was generally useful for detection of subsurface chlorinated solvents. Within the research and development SILPHES project (French acronym for Innovative Solutions to Fight Halogenated Compounds in Groundwater), we aimed at delineating subsurface CE contamination at a chlor-alkali facility using phytoscreening. Our tree core data were compared with soil data to ascertain correlations between the two datasets, while taking into account variations of biological and pedogeological parameters. Standardized sampling and analytical protocols are keys in elaborating a phytoscreening program, as already detailed in published guides (Chalot and Balouet, 2015 ; Nielsen and Trapp, 2014 ; Olaf Holm et al., 2011 ; Vrobley, 2008). For this investigation a total of 165 trees from experimental zones were sampled and further analyzed for perchloroethene (PCE) and trichloroethene (TCE) concentrations, determined by solid phase microextraction gas chromatography coupled to mass spectrometry. Within the panel of tree genera sampled, *Quercus* and *Ulmus* appeared to be some efficient biomonitors of subjacent TCE and PCE contaminations, in addition to the well known and widely used *Populus* and *Salix* genera. Among the 25 trees located above the dense non-aqueous phase liquid (DNAPL) pool zone, 19 tree cores contained detectable amounts of CE, with concentrations ranging from 25 to 3000 µg/L. Our tree core dataset was found to be well correlated to soil gas sampling results, although more informative. Our data further emphasized the need for choosing the relevant tree species and sampling periods, as well as taking into consideration the nature of the soil and its heterogeneity. Overall, this low-invasive screening method appeared useful to delineate contaminants at a small-scale site, impacted by multiple sources of chlorinated solvents.

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Injection and soil mixing for in situ treatment: from design to works

Delphine Kaifas¹; Aurélien Triger¹; Antoine Joubert²; Alain Dumestre²; David Cazaux³; Stéfan Colombano⁴; Nicolas Fatin-Rouge⁵; Julien Maire⁵; Benoît Castermans⁶; Pierre-Yves Klein¹

¹ Sol Environment; ² SERPOL; ³ INOVYN; ⁴ BRGM; ⁵ Université de Franche-Comté, UMR 6213-UTINAM; ⁶ Biorem Engineering, FR

Many polluted sites show a contamination of groundwater by organochlorine products. These pollution involve negative impacts right to these sites and outside (sustainable degradation of soil and groundwater quality, restriction of use and reconversion of these areas, etc.) and represents a real challenge on a national and European level.

Among the multitude of remediation techniques, in-situ treatments have many benefits such as the reduction of environment and worker exposure to pollutants (by limiting their displacement), the removal rates, the range of pollutants treated etc. The key success of an in-situ treatment is an effective contact between the reactant and the pollutant. Sol Environment leads several project on this subject so as to develop its expertise and to promote the use of in-situ technologies.

In this context Sol Environment takes part in SILPHES project which aim is to develop innovative and complementary remediation technics and tools or characterization methods to treat soil and groundwater contaminated by DNAPL, at both source and plume levels.

As part of the component « source area treatment », Sol Environment was in charge of in situ implementation of innovative reductant for residual DNAPL treatment. Project was realized following several steps:

- Characterization of reactant and evaluation of their workability. Physico-chemical properties of the reactants and their matrix was studied
- Injection and soil-mixing tests at laboratory level: Aim of these tests is to evaluate efficiency of different implementation technics and to obtain designing data (pressure, flowrate, distribution radius, radius of influence etc.)
- Pilot test implementation: Data obtained at laboratory scale were used to design in situ implementation at pilot scale. Impregnation injection by Manchette Tubes (TAM[®]) was tested. An innovative tool (combining two soil mixing tools, Springsol[®] and Jet Grouting[®]) was also developed for the project and tested during pilot tests. Objective of the pilot test is to evaluate injection and soil-mixing technics on real conditions and to compare their performance. Results obtained at laboratory and pilot scale were also compared so as to determine consistency of laboratory tests.

This communication aims to present results of this project at each steps highlighting approach used by Sol Environment so as to provide answers to technical locks encounter with injection and soil-mixing treatment.

Remediation of Chlorinated Organic Compounds: Single- and Multi-Component Approaches

Romain Rodrigues¹; Stéphanie Betelu¹; Stéfan Colombano¹; Guillaume Masselot²; Théo Tzedakis³; Ioannis Ignatiadis¹

¹ BRGM; ² ADEME; ³ LGC, FR

Chlorinated organic compounds (COCs) represent a major concern and are widespread distributed in soil and groundwater. Due to their strong hydrophobicity and their density higher than water, these COCs infiltrate through aquifers and form DNAPL pools. A large part of DNAPL can be removed by physical technologies (mainly pumping), but an important part will remain trapped and adsorbed in the aquifer matrix. In situ remediation technologies have been then developed in order to destroy in situ the remaining COCs.

This study aims at characterizing the chemical reductive dechlorination of a mixture of COCs, mainly composed of hexachlorobutadiene (HCBD) and hexachloroethane (HCA). Many studies have shown the great efficiency of bimetallic Pd/Fe particles for the remediation of COCs (Colombo et al., 2015; Kim and Carraway, 2003; Lien and Zhang, 2007). Preliminary studies have been conducted in order to select the most appropriate reactants, which are Pd/Fe microparticles dispersed in a polyacidic hydrophobic matrix (Rodrigues et al., 2015).

First, HCBD and HCA were individually investigated in a monophasic single-component system, i.e. in presence of one dissolved pollutant in deionized water:methanol (99.9:0.1% v/v) solutions. Several analytical parameters were studied: pollutant/reactant ratios, temperatures and presence or absence of surfactants. Similar experiments were performed in a monophasic multi-component system, containing dissolved HCBD and HCA, to characterize the impact of a hydrophobic mixture.

Then, as most part of the pollutant is present as a DNAPL in groundwater, HCBD and HCA were investigated in a polyphasic single-component system, i.e. in presence of one pure pollutant in deionized water. This second approach combines both reduction reactions and transport processes, especially solubilization. The aim is to understand the influence of temperature and the presence of a surfactant in a polyphasic system to define the rate-determining step of the global remediation process. Finally, polyphasic multi-component systems were performed in presence of a mixture of HCBD and HCA, and in presence of a DNAPL taken from a polluted site.

These two approaches allowed the determination of degradation pathways and kinetic laws for the two compounds individually and in mixture.

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Drainage-imbibition tests and pumping heavy chlorinated solvents in saturated porous media: measures and modeling of the effects of thermal and chemical enhancement

Stéfan Colombano¹; Hossein Davarzani¹; Eric van Hullebusch²; Ioannis Ignatiadis¹; David Huguenot³; Dominique Guyonnet¹; Jacques Deparis¹

¹ BRGM, FR; ² UNESCO-IHE Institute for Water Education, Delft, NL; ³ Université Paris-Est, UPEM, FR

Recovery of chlorinated solvents (CSs) as a free product is mainly based on pumping and pumping/skimming (Perez et al., 2014). However, this technique is time consuming and does not allow significant recovery of CSs in the form of free product and associated dissolved emissions (McGuire et al., 2006). Our study focuses on the beneficial effects of thermal and chemical enhancements for recovering free product composed of heavy chlorinated compounds (Hexachlorobutadiene, Hexachloroethane, Perchloroethylene, Pentachlorobenzene, Trichloroethylene...).

This study is part of the SILPHES project, financially supported by ADEME (French Environment and Energy Agency) in the framework of the Investing for the Future ("Investissements d'Avenir").

1. Materials and methods

The rheological parameters of the DNAPL were characterized: density, dynamic viscosity, interfacial tension (water/DNAPL) and contact angles (water/DNAPL). First, the imbibition-drainage tests were conducted in small columns to determine the capillary pressure-saturation functions. Then, the tests were elaborated in a one-dimensional large column, in order to validate the numerical model. Finally, pumping tests at different flow rates were carried out in a 2D tank, in order to improve the processes. These tests were carried out using glass beads of different diameters (0.1 to 1 mm) at different temperatures (10 °C and 45 °C) and with application of different surfactants (SDBS, Triton X-100, Aerosol MA-80, Tween 80). DNAPL flow was monitored using Time Domain Reflectometry (TDR) probes, geophysical probes (induced polarization) and also imaging technique (Light Reflected Method-LRM).

Numerical models have been developed using COMSOL Multiphysics® for 1D and 2D cases and the experimental results were compared with simulations.

2. Results and Discussion

The results show that increasing the temperature from 10 to 45 °C decreases the dynamic viscosity of DNAPLs (respectively from 5.5 (±0.2) to 2.8 (±0.08) mPa.s) and has a limited influence on the interfacial tension (12 mN/m) and the contact angles (70 °). However, surfactants reduce the interfacial tensions (from 12 mN/m to 1 mN/m, depending on surfactant nature and concentration).

Retention curves of the two-phase system (capillary pressure as a function of water saturation) obtained using small column are compared to various analytical models (Chen et al., 2006). The best correlations are obtained with the van Genuchten - Mualem model and the Brutsaert - Burdine model.

These retention curves show that: (i) The residual saturation of DNAPL decreases by 30% with increasing the temperature from 10 to 45 °C; (ii) Adding the surfactants globally decreases the irreducible saturation of water by 25% (i.e., the surfactants can, at constant pressure, increase the mobility of DNAPLs) and; (iii) Aerosol MA-80 decreases the residual saturation by 24%.

The pumping experiments using 2D tanks are under way to confirm these data and to estimate the radius of influence and the optimal pumping rate.

Finally, the developed two-phase pressure-pressure numerical model accurately reproduces the experiments, in particular, the movements of the water-DNAPL interface.

Sps 3c.3: Geophysical monitoring of optimized DNAPL extraction techniques

Emilie Nodot¹; Antoine Joubert²; Jacques Deparis¹; Benjamin Francois¹; Thomas Invernizzi²; Alain Dumestre²; Nicolas Fatin-Rouge³; Julien Maire³; Delphine Kaifas⁴; Aurélien Triger⁴; Pierre-Yves Klein⁴; Quentin Giraud⁵; Benoît Paris⁵; David Cazaux⁶; Jean Christophe Gourry¹; Stéfan Colombano¹

¹ BRGM; ² SERPOL; ³ Université de Franche-Comté, UMR 6213-UTINAM; ⁴ Sol Environment; ⁵ INTERA; ⁶ INOVYN, FR

Soil contaminated by Chlorinated solvents represent an environmental issue as it impacts on ecosystems and aquifers. This kind of pollution is heavy (it is a DNAPL), not too mobile, not readily degradable and very toxic. They relate to 16% of the polluted sites surveyed by public administration. Conventional In situ monitoring of the treatment is expensive, invasive and can be insufficient as the information provided is restricted to vertical profiles at discrete locations.

In the last few decades, Geophysical methods are the subject of intensive research in order to study environmental problems and determine the interaction between pollution and geophysical signal. Among the wide range of geophysical methods available, electrical geophysical tools, (i.e. Electrical Resistivity (ER) and Induced Polarization (IP)), is well adapted in order characterized the pollution and to monitor migration of DNAPL through saturated porous medium. ER and IP measurements are made by injecting an electrical current into the ground between two current electrodes and making measurements of the induced voltages between two receiving electrodes in order to measure resistivity (ER measurements) and the chargeability (IP measurements). These parameters depend, amongst others, on DNAPL presence and concentration.

This study is part of the SILPHES project, financially supported by the ADEME (French Environment and Energy Agency) in the framework of the Investissements d'Avenir (Future Investments).

The site had been equipped to monitor time-lapse changes in electrical properties of the subsurface with electrical resistivity (ER) and time domain induced polarization (TDIP) by systematic 2D tomography. The electrical measurements were carried out using 96 stainless steel electrodes with a spacing of one meters implanted along a line. The measurement were carried out using a Syscal Pro resistivity meters (from IRIS Instruments©, Orleans, France). Moreover, piezometrical level of the water/DNAPL interface was measured during the depollution process. Three successive pumping phases have been carried out in order to overcome as far as possible technical limits. First step consists of pumping DNAPL in a static state, then groundwater are pumped, in a so called process "upwelling", to induce an hydraulic pressure decrease in the pumping well hence optimizing DNAPL accumulation. During this step, injection of pumped (salt) water was carried at the extremity of the site. Finally, low concentration of surfactant was injected in such pumping process to decrease interfacial tension and optimize DNAPL extraction again.

The result shows that the resistivity decreases along time around 8 meters depth, which matches the polluted zone defined by geochemical borehole analyses. Indeed, the salt water takes the place of the DNAPL. In fact salt water being less resistive than the DNAPL, which explains why we observe a decrease of the resistivity. Our results argue that electrical measurements is able to monitor DNAPL depollution process and will allow us to give a practical non-intrusive method of monitoring and evaluating in situ remediation.

SpS 4a.1: Implementation of Treatment Technologies and Innovative Remediation Practices in the USEPA Superfund Program

Carlos Pachon¹; Dymont Stephen

¹ Superfund Program, US

Since the inception of the Superfund program in the United States, federal, state, and local governments, and private industry have invested billions of dollars annually to clean up sites contaminated with hazardous waste and petroleum products. A technology innovation program was established early in Superfund for the advancement of promising state-of-the-art technologies and tools for streamlining and improving the cost, performance and duration of site cleanups. In this session, EPA experts from the technology innovation program present a summary of recent analyses on trends in the use of innovative technologies and engineering practices at Superfund sites.

The 90-minute session includes recent insights on the selection of treatment technologies, including an analysis of how remedies are combined and managed to gain maximum leverage their strengths. Combined remedies address site contamination spatially and temporally to capitalize on synergies between technologies and help meet remedial action objectives. The session will also summarize findings from over two hundred remedy optimization efforts conducted at major Superfund remediation projects. An analysis of more than 700 unique optimization recommendations identified five major recommendation categories; remedy effectiveness, technical improvement, cost reduction, site closure and green remediation.

SpS 4a.2: A case study on the development and regulatory approval of a mass discharge remedial target for MTBE at a fuel release site

Ged Sojka¹; David Granger¹; Alan Hill²

¹ AECOM; ² Shell International Petroleum Co. Ltd, GB

Historical release of methyl tertiary-butyl ether (MTBE) into a chalk aquifer from a petrol filling station (PFS) in the UK resulted in a MTBE groundwater plume approximately 750m long and MTBE impact at a public water supply (PWS) well. Between 2005 and 2013 non-aqueous phase liquid (NAPL) skimming, soil vapour extraction (SVE) and total fluids extraction (TFE) were undertaken and removed circa 60,000 litres of hydrocarbon. Closure criteria for BTEX, naphthalene, MTBE, tertiary amyl methyl ether (TAME) and tertiary butyl alcohol (TBA) were agreed with the regulators in 2012. The SVE and TFE systems were removed from the PFS site in 2013, once asymptotic recovery was reached. Regulatory approval for completion of remediation at the PFS was received in 2014 following validation that remedial criteria for the PFS had been met. In December 2010 a hydraulic containment system (HCS) was installed approximately 100m down hydraulic gradient of the site and was designed to break the MTBE pathway between the source and the PWS. The discharge from the HCS contains only MTBE and TAME. Once the HCS was started, MTBE concentrations at the PWS rapidly reduced to below method detection limit and have remained so since December 2012. Whilst remediation closure objectives were met for the PFS, and there is no risk to human health, there is a need to manage the remaining MTBE plume to prevent impact based on taste and odour at the PWS. Achievement of the concentration-based remedial target for MTBE (3.3mg/l) across the large source area with numerous wells installed at different depths with varying concentrations over time was considered difficult and an overly conservative metric for protecting the PWS. Between 2014 and 2015 detailed groundwater modelling determined that the HCS captures all of the dissolved MTBE plume (and MTBE source area) between the PFS and HCS. Mass discharge at the HCS is therefore easily calculated to a much greater accuracy than inferring source zone activity from measured source zone groundwater concentrations that are highly variable. A mass discharge remedial target (MDRT) for assessing remedial close-out for the MTBE plume was developed by adopting the 10th percentile abstraction rate of 9,358m³/d for the PWS (e.g. 90% of the time the PWS will be pumping at volumes greater than assumed target rate) and an agreed ceiling concentration based on taste and odour within the blended PWS water of 7µg/l. The calculated MDRT of 65g/d equates to a concentration of approximately 227µg/l in the discharge from the HCS. The MDRT was agreed with the regulators and stakeholders including the water supply company in July 2015. This is believed to be the first time a mass discharge remedial has been agreed with the UK regulators. The groundwater model was also used to assess the effects of source-zone depletion and remediation on plume longevity and timescales to reach the MDRT at HCS. A number of scenarios were modelled which indicated natural source zone depletion would take 8-12 years from 2016 and a range of remedial actions could reduce the time frame of HCS operation from between 2 to 9 years.

SpS 4b.1: Exploring Opportunities for rehabilitating brownfield land in emerging economies for renewable energy and other self-sustaining re-use strategies

Paul Bardos¹; Frederic Coulon; Alfonso Rodriguez; Quing Hu; Yongguan Zhu

¹ University of Brighton, Brighton, UK, r3 Environmental Technology Ltd., GB

This special session build on the outcomes from two Strategic Partnership Fund projects on rehabilitating brownfield land for renewable energy and other self-sustaining re-use strategies in Colombia and China. Specifically a range of case studies were carried out to investigate the opportunities of soft reuse services and interventions needed for the redevelopment of gold mining areas impacted by mercury contamination in Colombia and large derelict industrial areas contaminated by coal and heavy metals in China. Both projects adopted UK, EU and US EPA thinking on brownfields rehabilitation for renewable energy and other soft re-uses which offered a broad range of services that have both improved the overall sustainability and enhanced economic value of the sites investigated.

Both projects combined structural and policy level research supported by specific case studies. The functions of the special session is therefore to:

- Present the process to support decision-making and design of reuses for brownfields
- Provide a more detailed understanding of the decision tools developed for the services and interventions needed for the regeneration/development decision and their application in Colombia and China
- Provide a comparison with European case studies and approach
- Discuss broader guidance on opportunities to maximising the sustainability and value of restoring contaminated land in emerging economies
- Based on China and Colombia's case studies discuss the next steps for future works and research needs in emerging economies and provide an opportunity for interested parties to debate the findings, but also to get involved in future work in Colombia, China and other emerging countries

Sps 4b.2: Making sustainable remediation real: A hands-on sustainability assessment

Nicola Harries¹; Jonathon Smith²; Paul Bardos³

¹ CL:AIRE; ² Shell Global Solutions (UK) Ltd; ³ University of Brighton, Brighton, UK, r3 Environmental Technology Ltd., NL

This session will involve an interactive and hands-on sustainable remediation case study exercise, where delegates will come together to evaluate the relative sustainability of shortlisted options to remediate a contaminated site.

The session will follow the approaches set out in ISO Standard and SuRF-UK Framework and its associated tools. Delegates will be presented with pertinent information and working in small groups will undertake a sustainability assessment of their own.

Delegates will learn some of the intricacies of sustainable remediation assessment, and gain confidence to undertake similar appraisals on other projects.

SpS 4c.1: Environmental Due Diligence Special Session; Best practice sharing and improving consistent approaches

Pieter Dols¹; MSc. Wouter Gevaerts²; Craig Carson³

¹ Shell Global Solutions International B.V., NL; ² Arcadis Europe; ³ ERM France

Environmental liabilities can materially impact transactions of sites. Environmental Due Diligence plays an important role to identify risks, reduce uncertainties and quantify liabilities in order to manage these risks appropriately before, during and after transactions. This special session will aim to share knowledge and best practices on Due Diligence efforts (both strategic and practical) and Risk & Liability Management from the perspective of the different parties involved; policy makers, legal professionals, service providers and industry stakeholders. The long-term objective is to achieve common guidelines/ways of working that can help facilitate better transactions and reduce risks. The session will be a combination of short introductory presentations from key stakeholder representatives and a moderated Panel Discussion

SpS 5a.1: Prioritization strategies & tools for regional brownfield redevelopment: Perspectives & Feedback on existing tools and approaches

Elsa Limasset¹; Stephan Bartke²; Corinne Merly¹; Blandine Clozel¹; Sonia Doisy³; Anne Dubromel⁴; Lisa Pizzol⁵; Stanislav Martinát⁶; Petr Klusáček⁶

¹ BRGM; ² Helmholtz-Zentrum für Umweltforschung GmbH – UFZ, DE; ³ DREAL Grand Est; ⁴ Conseil régional Auvergne-Rhône-Alpes; ⁵ University Ca' Foscari Venice; ⁶ Institute of Geonics Brno, FR

The ability for a prioritization and targeted selection of brownfields is increasingly understood as being critical for regional development. Several European companies, communities and regions have built brownfield registers to steer brownfield investments. Having different brownfield redevelopment options, a proper selection of most promising sites is a pre-requisite to efficiently allocate the limited financial resources. Authorities are in need of strategies and tools to screen wide areas with a large number of brownfields to identify locations with best potentials for redevelopment.

So far, only a few tools have been developed to support “regional brownfield prioritization” strategies. These are mainly spatial decision support tools based on multi-criteria analysis (MCA). Noteworthy is the Timbre Brownfield Prioritization Tool (TBPT), a freely available web-based tool assisting stakeholders in prioritizing brownfields. It was developed under the FP7 R&I project TIMBRE.

A similar prioritization tool relying on a MCA is being developed and tested for the French Alsace Regional authority. This tool is required as part of a regional strategy to encourage transparent decision-making process in sites prioritization and selection, especially for those where groundwater is potentially contaminated and would benefit from state funding for remediation. The Auvergne-Rhone Alpes region, through its regional brownfield initiative called “ID Friche”, is developing an approach to provide tools to inform decision makers in how to improve efficiency of brownfields redevelopment.

The aims of this session are to share knowledge and experience on regional prioritization approaches and to discuss lessons learned on best ways to develop prioritization tools by avoiding challenges identified in previous projects and utilizing potentials of innovative approaches already developed.

The session, facilitated by Stephan Bartke (UBA & UFZ), will consist of three parts:

Part 1 – Introduction and Background (15 min)

- S. Bartke, PhD (UBA & UFZ, DE): Objective: Understanding the challenges and opportunities for regional brownfield prioritization
- L. Pizzol, PhD (UNIVE and GD, IT): Setting the scene: Status-quo of risk-based approaches for brownfields prioritization at regional scale

Part 2 – Examples of Recent Prioritization Approaches (30 min)

- P. Klusáček, PhD (IoG, CZ): Challenges and obstacles in transdisciplinary research: The TIMBRE Brownfield Prioritization Tool's application in 5 countries
- E. Limasset (BRGM, FR): Development of a brownfield prioritization tool for the French Alsacian local authority based on available data
- C. Merly (BRGM, FR): Co-Design of a brownfield prioritization approach for the French Auvergne Rhône Alpes Regional Council from a stakeholders' needs perspective

Part 3 – World Café – Exchange on Improving Prioritization Tools (45 min)

- Participants will discuss in separate groups for 3 slots of 10 minutes on expectations, experiences, opportunities and concerns related to effective regional brownfield prioritization strategies and tools.
- Topics, from which participants choose, will include:

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- End-user needs and orientation
 - Data availability and quality
 - Effective stakeholder engagement
 - Understanding drivers of regeneration success
 - Applicability of ecosystem services concept
 - Financing and application costs for tools

The session will close with a 2-min report from report from each table back to the plenum.

SpS 5c.1: Benchmarking of Excavated Soil Reuse Management in Europe: what is the position five years after national implementation of the Waste Framework Directive in EU countries?

Céline Blanc; Nicholas Willenbrock; Andy Heurckmans; Jonathon Atkinson; Jean-Yves Richard, FR

Organizer : BRGM

Moderator : CL:AIRE

With the support of NICOLE and AXELERA

The sustainable management of excavated soil remains a problem for a number of European Member States. In 2008, the revision of the EU Waste Framework Directive defined the legal framework applicable to excavated soil at EU level. However, its implementation at the national level is based on technical conditions of reuse of this land which differ between European countries.

Most development projects in urban areas or remediation projects on contaminated and brownfield sites have to face the challenge of the reuse of the excavated soils. After 5 years of national implementation, it's time to assess progress.

The sustainability benefits which can be achieved through the careful management of excavated soils can be extremely significant, yet when it comes to measuring sustainability the focus of the construction sector is often focused on a sites build phase. Sustainable management of soils can be the key to a developments sustainability credentials. Is sustainable soils management given the priority in the construction sector it warrants or is it too frequently a last resort consideration?

The special session gives an overview of the evolutions of national policies in order to improve excavated soil reuse by maximizing the use of good data to prove and improve genuine sustainable development. In particular the session will cover the following issues:

TOPIC 1 - Management of big data for characterization and re-use of excavated material

1a. the traceability of excavated soils: a trigger towards valorization & circular economy - Andy Heurckmans, Grondbank.

1b. Improving data collection and management to improve soil transport & regulator confidence– UK experience– Jonathan Atkinson – UK Environment Agency

TOPIC 2 - How can a circular economy approach facilitate a regulatory framework for excavated materials management / How can a circular economy approach ease excavated material management in sometimes a controversial / difficult regulatory context?

2. Valtex : how to offer an industrial platform of excavated soil management in the context of waste legislation regarding circular economy purposes ? – Jean Yves Richard – Suez Environnement

TOPIC 3 - What standardisation is needed for ensuring quality and efficiency of procedures?

3. Revision of the ISO standard "Characterization of excavated soil and soil materials intended for re-use", an opportunity to standardize procedures? ISO members.

A round table discussion will follow this set of presentations in order to compare the approaches and identify the locks and successes of excavated soil reuse management.

SpS 5c.2: Water self-sufficiency in large scale industrialized areas

Koen Wetser¹, Hans van Duijn²

¹Wageningen University, ²Deltares, NL

Main idea of the session:

The availability of fresh water is under pressure in coastal and (semi-)arid regions due to growing demand, climate change and saltwater intrusion. Attempts to find solutions are fragmented and often connected with high costs and poor sustainability. Existing solutions cannot create sufficient water quantities to solve the scarcity. A genuine breakthrough requires a radically different approach. The ambition of the 5 year program Water Nexus (www.waternexus.nl) is to reach this breakthrough by developing integral solutions for problems with water scarcity for large volume sectors (agri/horticulture and industry). Water self-sufficiency requires a paradigm shift to consider saline and used water as a resource and not as a threat.

The goal of this session is to identify existing conceptual and organizational barriers for reaching large scale water self-sufficiency in (agro) industrialized areas. In the session, we will also look for the required next steps to overcome these barriers.

The session will include four presentations and a discussion (details in table below). In the discussion, the existing conceptual and organizational barriers for large scale water self-sufficiency will be addressed from two perspectives: industrial and governmental. We will start the discussion with questions and issues that industries and governments face within their water management. The discussion will result in barriers and risks associated with large scale water self-sufficiency. We will end the discussion with suggestions for the required next step to apply the Water Nexus integral solutions and achieve water self-sufficiency.

The industrial perspective:

Many industries are developing new strategies for sustainable supply of water. These industries also produce wastewater, which can be upgraded to support agriculture, green infrastructure and ecosystems. New concepts for climate adaptive water management and new technologies to (re)use saline and used water need to be tailored to local situations. Local partners and governments are needed to arrange such water supply systems. Are industries and governments ready for this approach and how should they share responsibilities?

The governmental perspective:

Governments can facilitate local/regional arrangements to arrange self-sufficiency for water supply, e.g. by allowing water storage and treatment in subsurface and green infrastructure. How can the industry help the governments with these arrangements?

Title	Presenter	Time (min)
General introduction of Water Nexus	Huub Rijnaarts	10
Global resource analysis and regional water management	Daniel Zamrsky	10
Including the local context in determining the sustainability of water use	Joeri Willet	10
Integrated solutions to use saline and used water as an alternative to fresh water	Koen Wetser	10
Discussion		45
Conclusions and closure	Huub Rijnaarts	5

SpS 6a.1: INSPIRATION – Linking Europeans’ Strategic Research Agenda on Spatial Planning and Land Use Management with AquaConSoil themes

Stephan Bartke¹, Paul Nathanail², Linda Maring³, Sandra Boekhold⁴, Uwe Ferber⁵, Franz Makeschin⁶, Valérie Guerin⁷, Detlef Grimski¹

¹ German Environment Agency, DE; ² University Nottingham, UK; ³ Deltares, NL; ⁴ RIVM, NL; ⁵ StadtLand U.G., SE; ⁶ Dresden International University; DE; ⁷ BRGM, FR

The way Europeans steward their soil and manage the use of land is central to ensuring Europe’s transition to a sustainable future. Research and knowledge dissemination are fundamental prerequisites for informed land use and evidence-based policies. Smarter use of the services provided by land and the soil-sediment-water system may provide ongoing and new solutions for meeting societal needs without exasperating societal challenges.

With partners from 17 countries across Europe, the INSPIRATION project has developed a Strategic Research Agenda (SRA) for spatial planning, managing land and using soil-sediment-water system services sustainably. The SRA’s topics were identified through a unique bottom-up process of engaging with over 500 key experts from academia, research funders and end-users from industry, policy making, regulators, municipalities and citizen groups.

This session will:

- Share information about INSPIRATION's Strategic Research Agenda (SRA) focusing on research needs related to integrated spatial planning, urban and contaminated land management;
- Identify priorities of AquaConSoil community, in particular potential funders and end-users, where to co-invest in specific themes;
- Facilitate a match-making towards implementation of these topics.

Participants will be invited to become part of the wider INSPIRATION community and to liaise with INSPIRATION’s activities in their home country.

Session outline

1. Introduction: The unique INSPIRATION approach - Stephan Bartke (UBA, DE), project coordinator
2. Key note: The importance of the soil-water-sediment system for land management - Linda Maring (Deltares, NL).
3. INSPIRATION’s Strategic Research Agenda, highlighting identified research topics related to integrated spatial planning, urban and contaminated land management - Paul Nathanail (UNOTT, UK)

SpS 6a.3: Groundwater energy: policies, integrated technologies & management

Tim Grotenhuis¹; John Flyvbjerg²; Nanne Hoekstra³

¹ Wageningen University, NL; ² The Capital Region of Denmark, DK; ³ Deltares, NL

In the transition to sustainable energy systems the demand for space heating and cooling is of crucial importance, as it requires 50% of all the energy we use. Subsurface storage of heat utilizes abundantly available heat with demand at another time (e.g. summer-winter, or day/night). Aquifer Thermal Energy Storage (ATES), also called 'Groundwater Energy', provides a cost-effective solution: heat and cold can be stored for six months or more.

Storing thermal energy in aquifers and acquiring heat and/or cold from extracted groundwater is in the Netherlands a popular sustainable energy technology, because of its cost-efficiency, delivering on average approximately 60% less CO₂-emissions and substantial savings (ROI < 5 – 10 years) compared to sole use of fossil energy. In the pan-European Climate-KIC project Europe-wide Use of Sustainable Energy from aquifers (E-USE(aq)) we showed before that in the rest of Europe, socio-economical, legislative and some technological barriers prevent widespread application so far, but that these can be overcome.

ATES can function as stand-alone technology, be integrated in energy grids with other cooling/heating technologies, combined with sustainable power production or with reuse of surplus heat and cold from e.g. industrial plants. ATES systems may offer, especially in combination with cooling, very cost-effective solutions with savings up to a factor 4 compared to conventional systems.

Currently, in Europe scarce awareness on ATES systems as well as regulatory and knowledge barriers hamper the wide adoption of such systems. In this session technical specialists are connected with decision makers in an interactive discussion about a wide range of solutions for these difficulties including policy contributions.

At the start of the session Sara Picone (ASTER, It) will present a short overview on how barriers are overcome in demonstration projects of different ATES applications from the EU project E-USE(aq) which aims at boosting market application of ATES in Europe.

Five hot topics will be addressed in three minute pitches, each pitch will result in a statement about how to realize Europe-wide implementation of Groundwater Energy.

The statements of the pitches will be the basis for discussions by an international panel of experts in which the audience can participate, led by Ruud Cino (Ministry Economic Affairs, NL).

The topics of the pitches are:

- 1) Optimal use of subsurface space with ATES requires 'smart energy grids'. (Martin Bloemendal, TUD/KWR, NL)
- 2) The use of ATES to stimulate biodegradation of VOCI contaminated groundwater. (Zhuobiao Ni, SYSU, China)
- 3) The dilemma on water scarcity and development of sustainable technologies (Dynamic Closed Loop (DCL) for heating and cooling. (Alicia Andreu Gallego, Instituto de Tecnología Cerámica, Spain)
- 4) New generation solar cells to improve electricity production plus production of heat: PVT cells (Nicholas Simmons, Naked Energy, UK)
- 5) Creation of attractive business cases for groundwater energy (Matteo Mazzoni, Nomisma Energia, It)

In the international panel (John Flyvbjerg (Capital region of Denmark, DK), Johan Ceenaeme (Ovam, B), Wouter Gevaers (Arcadis ,B), Attilio Raimondi (Emilia-Romagna Region, Energy Service, It)) opposite opinions of a variety of stakeholders will discuss the changes and hick-ups for societal implementation of the proposed technologies. The chair of this special session will stimulate interaction with the public.

Thematic Session (ThS)

ThS 1a.1: Adaptive monitoring based on real time data, model driven

Using 3D Modelling to Choose Among Several Conceptual Models at a Site Contaminated by Chlorinated Solvents

Olivier Atteia¹; Clément Portois¹; Nathalie Guiserix²

¹ENSEGID, FR; ²RENAULT, FR

Since the 80's the past disposal in tanks of degreasing solvents in an active factory results in a contamination of soil and groundwater below the factory. The pollution is characterized by high concentrations of chlorinated solvents in groundwater near the old deposit tanks (source zone) and significant concentrations in groundwater at the factory boundary. The geology is quite complex with interlaced multilayers clays and sand beds. Previous studies highlighted a Chlorinated Solvents contamination in two aquifers (Upper Aquifer (UA) and Lower Aquifer (LA)) without apparent communication between them. Recent investigations (without using Geoprobe) evidenced a high heterogeneity in the two aquifers with some layer of coarse sand inducing local preferential flow path. The spatial distribution of the chlorinated solvents suggests several infiltration areas between the two aquifers. Several points were to be clarified in order to build the required conceptual model.

In order to find the main sources and the flow directions a progressive study implementing joined drillings and modeling. In a first stage a 2D modeling approach using Modflow and MT3DMS was built using heads and concentrations as fitting parameters. The analysis of the remaining uncertainty showed that some places were gathering a high uncertainty and were thus chosen as the places to drill new wells. After this step the number of data was sufficient to build a 3D model. This model was also built at first for only transport. However for this model we used the information on the concentrations of the different chlorinated solvents. It appeared that a small part of the plume in the UA was containing mainly TCE while the main part was degrading and thus contained also cis-DCE and Vinyl Chlorid. In the LA at the bottom of the source zone the main contaminant is cis-DCE while the plume is mainly composed of TCE. This indicated that there was not a general communication from the UA to the LA despite the head difference. After a long fitting period it was possible to model the transport in both aquifers that was able to reproduce the observed concentrations, with the use of PHT3D.

At first, the source zone is extremely local as compared to the previous estimates. Secondly, it was located in a zone with a variability higher than three orders of magnitude in permeability. In fact later drilling in this area shows that the UA contains clay zones located at the place suggested by the model. Thirdly, the flow from the UA to the LA is very located at some silty-sand holes in the aquitards. This explains the transfer of only TCE to the LA. Finally, the use of the 3D modeling, including the fitting of contaminant concentrations, was able to provide a satisfying conceptual model for a site where concentrations were quite complex. It enhances the high variability of the permeability at the local scale, but also shows that, despite this high variability, it was possible to model it. Although the process is tedious it showed that when the concentrations of several species are correctly simulated the model can lead to substantial gains in the cost of investigation and source zone treatment.

Evaluating vis-NIR reflectance spectroscopy sensitivity to weathering for enhanced assessment of oil contaminated soils

Reward Douglas; Said Nawar; Frederic Coulon; Abdul Mouazen

Cranfield University, GB

This study investigated the sensitivity of visible-near infrared diffuse reflectance spectroscopy (vis-NIR DRS) to detect and characterise fresh and weathered crude oil composition and concentration in 5 different soil types collected from 10 sites located in Bedfordshire, UK. The performance and sensitivity of the vis-NIR DRS was further compared to gas chromatography-mass spectrometry (GC-MS) analysis. Soil types included sandy loam, sandy clay loam, clay loam, sandy clay and clay. A series of soil mesocosms was then set up where each soil sample collected was spiked with 10 ml of Alaskan crude oil and allowed to equilibrate at room temperature for 48 h before running the first vis-NIR DRS scanning and collecting the first samples for GC-MS analysis. The mesocosms were incubated for 2 year at room temperature in the dark. Soils scanning and GC-MS analysis were carried out at T0, 4, 8, 12, 16, 20 and 24 months. The soil scanning was done simultaneously using an AgroSpec spectrometer with a spectral range of 350 to 2200 nm (tec5 Technology for Spectroscopy, Germany) and Analytical Spectral Device (ASD) spectrometer (ASDI, USA) with a spectral range of 305 to 2500 nm to assess and compare the sensitivity and response of the two instruments against GC-MS data. Three standardized spectral pre-processing approaches including (1) maximum normalisation, (2) maximum normalisation plus first derivative, and (3) maximum normalization plus first derivative plus smoothing were applied on the spectral data obtained from tec5 and ASD spectrometers using Unscrambler® version 9.8 (186-200 CAMO software) followed by principal component analysis (PCA). The results demonstrated that vis-NIR DRS is a promising tool for assessing a range of key soil properties including soil texture, CEC, pH, total C and organic compounds such as petroleum hydrocarbons. It further provides an integrative soil contamination assessment and allowed to differentiate and discriminate fresh versus weathered/aged contaminated soils. The sensitivity of the two spectral devices tested was comparable to those of GCMS and the first standardized spectral pre-processing method where maximum normalisation was carried out provided the best performance. Overall, the results demonstrate that vis-NIR DRS is a promising tool for rapid site investigation and monitoring without the need of collecting soil samples and lengthy hydrocarbon extraction for further analysis.

Analyzing Groundwater Quality Data and Contamination Plumes with GWSDAT

Wayne Jones; *Matthijs Bonte*

Shell International Petroleum Co. Ltd, NL

The Groundwater Spatiotemporal Data Analysis Tool (GWSDAT) is a user-friendly, open source software tool used to analyze and report trends in groundwater quality monitoring data. GWSDAT is based on the open source statistical programming language R and Microsoft Excel. GWSDAT's primary use is for interrogation and interpretation of groundwater monitoring data derived from contaminated sites. It has specific functionality for analyzing dissolved-phase concentration and light non-aqueous phase liquid (LNAPL) thickness trends and spatiotemporal smoothing to delineate dynamic contamination plumes. The software can handle large data sets with multiple monitoring locations, variable sampling events, and differing chemical constituents. GWSDAT has been used extensively in the assessment of soil and groundwater conditions at numerous assets around the world, including retail and manufacturing sites.

The main functionalities of GWSDAT include trend analyses, data smoothing, spatiotemporal smoothing, and determination of contamination plume characteristics. Groundwater quality observation data for individual monitoring points can be fitted to a linear or log linear regression model, where the significance of a trend can be determined by using the Mann-Kendall approach, which is widely used for trend detection in groundwater and surface water studies. Further details on the input and output features of GWSDAT can be found in Jones et al. (2015). Additional information on each of the methodologies (including descriptions of the R packages used, but excluding the plume metrics, which are added in the latest version of GWSDAT) can be found in Jones et al. (2014). The software is freely available from: <http://www.claire.co.uk/projects-and-initiatives/gwsdat>

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Use of Adaptive Management Investigation Techniques for the Refinement of Landfill Waste Volumes Required for Remediation

Laurence Rebenne¹; James Day¹; Philippe Menoud

¹CH2M

A groundwater plume containing agro-pharmaceutical compounds was detected downgradient of a manufacturing facility in Western Europe. An iterative/adaptive investigation plan was developed and implemented to identify the source. The general source location was first estimated using a numerical groundwater flow model to be within a 13ha area on an undeveloped portion of the Site.

A review of historical documents, aerial photos and personnel interviews indicated that the area was historically an exploratory quarry backfilled incrementally between the 1930s and 1980s with construction debris, industrial/solid waste, WWII debris and soil impacted by agro-pharmaceutical compounds.

This information was supplemented with two geophysical surveys using electromagnetic (EM) methods to map shallow (up to 5.5m deep) subsurface features, including a former burn pit and quarry areas. Six phases of soil and groundwater investigations were then undertaken from 2012 to 2015 to identify and delineate the impacted soils. Each phase of investigation used a “real-time” approach with soil and grab groundwater samples analyzed using on-site analytical capabilities to focus on features identified by the historical review and geophysical survey. Four discrete impacted areas each with specific features were identified. Overall 97 locations in the unsaturated zone were investigated using geoprobe, sonic drilling and test pitting techniques and 10 monitoring wells were installed. The main agro-pharmaceutical compound was analyzed in 270 soil samples.

Through this integrated and adaptive characterisation, the source volume necessary for remediation was reduced from an initial estimate of up to 20000m³ down to 5000m³. All of the characterisation data was incorporated into a 3D modelling software (environmental visualization software, EVS) to visualize and quantify the extent of contamination above remedial objectives. This 3D model enabled a focused evaluation of the extent of contamination and allowed further optimization of remediation volume using extrapolation/interpolation techniques to estimate the contaminant mass within different areas. This additional optimization enabled a further reduction of source volume to 3500m³ while still meeting remedial objectives.

Full-scale remediation (ex situ soil washing) of the source area was recently completed. Additional segregation techniques were used to fully characterise discrete volumes of the excavated soil during remediation. Composite samples were collected from small volumes (60m³) excavated during remediation and analyzed. This approach did not result in further reduction of source volume, but allowed tracking a detailed inventory of soil concentrations. This project represents a highly successful example of how integrative and adaptive characterisation techniques can significantly reduce the volume of soil requiring treatment and provide accurate treatment cost forecasts. Investigation efforts represented 25% of total project cost, and allowed cost savings of over 300%.

ThS 1b.1: Passive Samplers & Passive Flux Samplers

Assessing the impact of contaminated sites on karst - Feedback on the exposure of integrative passive samplers in 17 springs of the Jura mountains

Hélène Demougeot-Renard¹; Celia Trunz²; André Bapst³; Philippe Renard²; Laurence Fischer²; Didier Lambert³; Julien Michel⁴

¹ eOde Sàrl; ² University of Neuchâtel; ³ MFR Géologie Géotechnique SA, CH; ⁴ INERIS

In Switzerland, many potentially contaminated sites are located in karst, especially in the north-west part of the country, in the Jura mountains. A large part of the contamination is made of chlorinated hydrocarbons used by the watch industry and microtechnology factories.

Showing the impact of contaminated sites in these environments is challenging because pollutants often travel very rapidly over long distances (several km), leading to very low and highly fluctuating concentrations in the springs that form the outlets of the karst watersheds. These springs are nevertheless often the only points where groundwater pollution can be monitored, due to the difficulty to reach karstic conduits and the pollution with boreholes, within or at short distances from the contaminated sites.

Since 2011, the Swiss federal office for the environment is funding the Chlorokarst project on this topic. The purpose of the project is 1) to test and experiment devices that may be helpful to assess the impact of contaminated sites on karst groundwater, and 2) to elaborate a regulatory approach for estimating the need of monitoring or remediating these sites in these specific environments.

Among all the tested devices, integrative passive samplers were found to be useful to measure very low levels of chemicals, despite strong variability with time, over exposure periods of 2 months. Compared to the 2 other types of samplers that were tested in the springs, the Sorbicell® were found to show the best performances for detecting the chlorinated hydrocarbons.

A large set of Sorbicell were then installed in 2016 in 17 springs of the Jura mountains, where a hydraulic connection with contaminated sites was suspected or proven. Samplers were exposed in 2 periods of 2 months, in low and high water conditions. Beside the chlorinated hydrocarbons, a broad range of organic and inorganic chemicals were analyzed. Standard snapshot samples were also collected during the period.

In the first series of analyzes (low water), chlorinated hydrocarbons were measured in 3 of the 17 springs, at very low levels, close to the limits of quantification (LOQ). Moreover, inorganic chemicals (i.e. lead, mercury, boron, phosphorus) were found in all the springs at low levels (results of the second series are expected in the late 2016). These results show evidence of human disturbance on water, even if it is at very low concentrations.

In conclusion, the Sorbicell samplers were found to be very useful to detect the low and highly fluctuating levels of chemicals in karst springs, provided that the limits of quantification were sufficiently low. The LOQ vary for each passive sampler unit, because they mainly depend on the volume of water that percolates in the sampler during the exposure period: the highest the volume, the lowest the LOQ. It is thus important to control exposure conditions in order to get the higher percolation volume without exceeding the maximal capacity of the device.

Advances in characterization of water and contaminant flux in porous media

Michael Annable

University of Florida, US

A passive method for quantifying contaminant mass flux and ground water flow, developed at the University of Florida, has been field-tested at a number of sites. Those sites range from military facilities to industrial sites including drycleaners and represent a range of hydrogeologic conditions. The contaminants at the sites have primarily consisted of DNAPL's (PCE and TCE) but also include contaminants such as MTBE, nitrate and perchlorate. Deployment strategies have included flux transects down gradient of source zones; multiple transects within plumes and profiles through the center of plumes. This presentation provides a summary of the results and a status of the technology focusing on applications targeted at quantifying mass loads in contaminated aquifers. Assessments will include both site characterization and remedial technology performance assessment. Recent applications in sediments and fractured media will also be discussed.

Integrated passive flux measurement in groundwater: field cases with iflux samplers

Goedele Verreydt¹; Patrick Meire¹; Jan Bronders²; Ilse Van Keer²; Piet Seuntjens²

¹ Universiteit Antwerpen; ² VITO, BE

The monitoring and management of soil and groundwater is a challenge. Current methods for the determination of movement or flux of pollution in groundwater use no direct measurements but only simulations based on concentration measurements and Darcy velocity estimations. This entails large uncertainties which cause remediation failures and higher costs for contaminated site owners. On top of that, the lack of useful data makes it difficult to get approval for a risk-based management approach which completely avoids costly remedial actions.

The iFLUX technology is a key development of Dr. Goedele Verreydt at the University of Antwerp and VITO. It is supported by the passive flux measurement technology as invented by Mike Annable and his team at the University of Florida. The iFLUX technology includes an in situ measurement device for capturing dynamic groundwater quality and quantity, the iFLUX sampler, and an associated interpretation and visualization method.

The iFLUX sampler is a modular passive sampler that provides simultaneous in situ point determinations of a time-averaged target compound mass flux and water flux. The sampler is typically installed in a monitoring well where it intercepts the groundwater flow and captures the compounds of interest.

The sampler consists of permeable cartridges which are each packed with a specific sorbent matrix. The sorbent matrix of the water flux cartridge is impregnated with known amounts of water soluble resident tracers. These tracers are leached from the matrix at rates proportional to the groundwater flux. The measurements of the contaminants and the remaining resident tracer are used to determine groundwater and target compound fluxes. Exposure times range from 1 week to 6 months, depending on the expected concentration and groundwater flow velocity.

The iFLUX sampler technology has been tested at several field projects. Currently, 4 cartridges are tested and available: 1 waterflux cartridge to monitor speed and direction of flow and 3 cartridges to monitor different sources of pollution – VOC's, heavy metals and nutrients. The modular design enables to sample several types of pollution at the same time.

The principles of the iFLUX technology will be presented, together with the results from field cases.

Passive Flux Samplers – Comparison of Methods and Possibilities

Lars Bennedsen; Kristian Raun¹; Bjørn Pedersen¹

¹ Region of Southern Denmark, DK

Contaminant flux is often used as a supplement to measurements of groundwater concentrations, since the flux generally can provide a better estimate of the groundwater risks related to a contaminated site. The last couple of years passive flux samplers have been used in several case studies in Denmark to determine the flux of contaminants. Different commercial available flux samplers exist including the Passive Flux Meter (PFM) from Enviroflux and the Fluxsampler from Sorbisense. Despite that these samplers have been used in several field measurements in Denmark, it is still not clear, when these samplers can be used to replace the traditional flux estimates based on Darcy velocities and measured groundwater concentrations. To investigate this further, a technology development project financed by the Danish Environmental Protection Agency and The Region of Southern Denmark was carried out in 2015-2016.

The objectives of this project were to screen the market for different commercially available methods/techniques for flux measurement, choose promising techniques for passive flux measurement and test these at a number of different contaminated sites. Other similar projects have been carried out in Denmark in the same period.

First phase of the project was a literature review of methods and possibilities for flux measurement. Based on this review, it was decided to test the Fluxsampler from Sorbisense and the Passive Flux Meter from Enviroflux at 4 different well described locations contaminated with chlorinated ethenes.

At each location flux estimates were performed in three wells with both the Sorbisense Fluxsampler, the PFM and with traditional measurements of Darcy velocity and groundwater concentrations. The Sorbisense Fluxsamplers were installed 1-6 weeks. Before, between and after the passive flux measurements, traditional groundwater samples were collected. The test included deep wells, artesian wells and a wide range of chlorinated ethene (and degradation products) concentrations from a few µg/l to more than 10 mg/l. For each of the 12 PFM's, measurements were performed in three intervals to study the vertical variations in contaminant flux in the monitoring wells. The Sorbisense Fluxsampler was also used to determine the groundwater flow direction.

The project created an interesting data set with results from a total of 24 passive flux measurements under different conditions, which can be used to evaluate in which cases the passive flux samplers can provide value for a project.

A simple field deployment of a sampler provides many data and the two different samplers tested both provided results comparable with the traditional flux estimates. The estimated flow directions did not match the expected directions. Also some general differences between the methods were observed. The difference in detection limits for the methods are also important when choosing which method to use.

Overall, the data from the project provides a good basis for a discussion on where and when the passive flux samplers are applicable.

An innovative combination of tools to measure fluxes of contaminants in aquifers

Elyess Essouayed¹; Olivier Atteia

¹ INNOVASOL, FR

Background.

French regulations on Polluted Sites require the study and the treatment of pollution including both the technical and economical aspects. Efficiency of this treatment depends on the localization of Source Zones, which are the most important Discharge of Pollutant. Indeed, several studies showed that 90% of the pollution discharge is located on only 10 or 15% of the total surface of the site. It is therefore important to have efficient method to measure the direction and magnitude of the contaminant fluxes. Passive Flux Meters are presently the major tools to measure flux magnitude, and have been tested at several sites. However this tool requires the apparatus to remain in the well during 2 or 3 weeks and does not give information on the velocity direction.

Approach.

Two new tools are used for determining magnitude and fluxes of contaminants. At first, we use a focused sampler that allows measurement of vertical concentrations of contaminants in a unique screened well. This tool is based on small packers and one or several immersed pumps. The other tool, the directional velocity tool (DVDT), allows measuring the magnitude and direction of groundwater velocity in the well rapidly by a dilution test. This tool is based on a thin but long window limits the entering of the groundwater to only a single place in a well, its surroundings being sealed. Then the velocity is measured in a small tube that is the only output of the groundwater entering the window. This allows for measuring the velocity in some tens of minutes. By varying the angle of the window, it is possible to identify the major direction of the groundwater movement, but well screens do not span the whole perimeter of the well which introduces a certain degree of error. Several tests of both were done in the laboratory and in the field.

Results.

The focused sampler has been validated by measuring the head variations in and around the tool. The concentrations correspond to the groundwater ones only if the sampled water come from the same elevation as the pumped interval. This was done at several wells and showed that significant concentration gradients can be measured in a fully screened well. The measure takes only a few minutes for each measurement. The DVDT has first been tested in the laboratory, showing a linear response to changes in velocity in the range of 2 to 50 cm/d for the pore velocity. It is thus relevant technique for slow velocities for which few tools are available. The tool has also been tested in the field, and particularly at a site with very high variations in the velocities. The measurements were compared to PFM measurements. These measured velocities agree with the groundwater model developed for the site. This can allow the use of the measured velocities as constraining data for inverse modeling, and thus leading to improved localization of source zones.

ThS 1b.2: On-site & In-situ characterization - Real-time monitoring

On site GCMS soil gas screening and EnISSA-MIP profiling: a thorough triad approach to support high resolution site characterization.

Pieter Buffel¹; John Ulrik Bastrup²; Samuel Van Herreweghe; Mark Van Straaten

¹ EnISSA; ² GEO, BE

The success of soil investigations and remediation designs is highly depended on a dynamic conceptual site model (CSM) and detailed visualization of the contaminants. It will also help the soil expert to recognize and identify the many data gaps and uncertainties. A qualitative characterization of source and plume zone based on conventional soil samples and monitoring wells is an intensive and time consuming task. Since the soil is a very heterogeneous medium and contaminants can have a complex occurrence and distribution, high data densities are required to obtain an assured CSM. With conventional methods this high density cannot be obtained in a cost nor time efficient way. In situ screening methods like the membrane interphase probe (MIP) are great method to provide a higher data density in a so called High Resolution Site Characterization (HRSC). In this approach the scale of measurement matches the scale of the contaminant distribution and soil characteristics. This leads to a greater certainty of the CSM, supporting appropriate risk assessment and faster and more effective site remediation.

To increase sensitivity and selectivity of the conventional MIP system, the EnISSA-MIP has been developed. This enhanced MIP system uses a modified GCMS system which is connected to the MIP system. The advantages of using a GCMS detector, are the low intrinsic detection limits of the detector and the capabilities to measure individual compounds, hence bringing the lab into the field. Field evaluations demonstrated that the EnISSA MIP is capable of measuring soil profiles for individual compounds with detection limits near 10-20 µg/l.

Recently a Danish consultant (GEO), collaborated with EnISSA to provide High Resolution data at three neighboring industrial sites located in the Copenhagen area. In the first phase > 400 sub-slab and 0.9 m-bgl soil gas were collected with soil vapor probes and a vacuum box and subsequently analyzed in the field lab to identify hot-spots/ source zones. Based on those horizontal screening results, the EnISSA-MiHPT locations were targeted to gather more detailed information of the contaminants and geology with depth. During the EnISSA-MiHPT probing, instant analytical results were evaluated and discussed with the consultant to optimize the sampling plan. The Hydraulic Profiling Tool (MiHPT) showed to be very interesting in interpreting the contaminant distribution in this typical glacier sediments. Formation with low permeability (max HPT pressure) were alternated with high permeability materials (HPT pressure close to zero). The EnISSA GCMS MIP results indicate little degradation at this locations. The contamination is mainly TCE and only small amounts of cis-1,2-DCE were detected.

The horizontal soil gas screening as well as the 37 vertical MIP soundings showed to be complementary methods to implement the triad approach for site characterization. The results, available in the field allow the soil expert to apply a dynamic sampling plan and to build a detailed CSM with just a single investigation phase. A traditional approach probably would have taken different consecutive phases stretched over more than a year.

Real-time and in situ monitoring of aquatic environments using indigenous microbial community - based biosensors

Jean-Michel Monier¹; Olivier Sibourg

¹ ENOVEO, FR

Increasing contamination of aquatic environments by organic loads or toxic chemicals has resulted in the need for real-time monitoring tools to be used in pollution detection and risk assessment. While monitoring aquatic environments is critical to ensure their quality and sustainability, monitoring strategies often relies on the collection of individual spot samples followed by ex situ analyses under laboratory conditions. Such approach, usually costly and time-consuming, only provides a snapshot that may often fail to detect localized transient contamination events and describe the dynamic changes of the monitored environment. The objective of our work was to develop a cost-effective event detection system to monitor aquatic environment in real-time, inform targeted sampling by conventional means (ie spot sampling) and act as a decision support tool.

This novel biosensor uses microorganisms naturally occurring in the targeted environment as bioindicators and exploits their ability to convert chemical energy into an exploitable electrical signal. The electrical signal generated by the sensor is proportional to the organic load or affected by the presence of toxic compounds, as it directly reflects microbial activity at the surface of the colonized electrodes. Biosensors have been deployed at different sites in order to estimate either the organic load or BOD in real time (eg, groundwater, sewage networks...) or detect toxic compounds and assess their impact on their environmental sink (eg, industrial processes and wastewater treatment plants...). Through real case studies, the presentation will address the principle, information provided and advantages (in situ, autonomy, robustness, representativeness, sensitivity) of such devices and how they can provide unique information to act as a decision support tool (eg, targeted sampling, process optimization, process dysfunction identification, bioremediation treatment efficiency...). Work in progress regarding a metrological station that uses a combination of different monitoring devices developed to manage aquatic environments in real time will also be presented.

Diagnosis of pollutes sites using LIBS

Laurie Pontreau

IVEA, FR

Metallic pollutants, once called "heavy metals" and now referred to as Metallic Trace Elements (MTE), are the cause of respiratory, digestive, nervous or cutaneous disorders and sometimes even carcinogens. Since analyses of the health and environmental risks has been conducted, ICPE (Installations Classées Pour l'Environnement) have to follow regulations (national, European ...) which fix limit values for emissions into air, water, sludge ... The public action also aims to establish the inventory of old industrial sites and the census of polluted sites and soils. In order to monitor and rehabilitate historically polluted sites, having tools which measure MTE in soils and provide qualitative and quantitative information to carry out their diagnosis seems essential. An on-site measuring instrument greatly reduces the time required to obtain results and promotes a quick decision to implement decontamination. Issues are therefore environmental, human (impact on health), economic and technological. Diagnoses of polluted soils are based on on-site measurements of ETM concentrations by two multi-element techniques: portable X-ray fluorescence (pXRF) and laser-induced plasma spectroscopy (LIBS). The pXRF benefits from more than 20 years of development and application to the study of polluted soils, and its interests and limitations are now known. On the other hand, the development of LIBS in soil analysis is more recent and its potential, linked to its complementarity with pXRF, is widely recognized by the scientific community. Currently, the acquisition, interpretation and data management in the context of polluted sites and soils are a real problem. The scientific community is then very interested in measuring tools as well as supports for the interpretation of these data. Indeed, during a measurement campaign, the data obtained are punctual; and for a good assessment of soil pollution, all these data have to be represented spatially. Thus, the miniaturization of a multi-element technique such as the LIBS integrating a geostatistical tool aims to establish a semi-quantitative mapping of the pollutants in real time on site. Thanks to this map obtained in real time, the operator could tighten or expand the mesh of measurements in real time in order to refine the mapping and could obtain a smart sampling. The integration of such a processing tool into a field analyzer will guide the operations of diagnosing polluted sites as well as possible.

A novel approach to high-resolution mapping of dioxin contamination in extended floodplain areas and its relevance for the assessment of impact on the river basin scale

Patrick Jacobs¹; Ronald Koomans²

¹ Tauw GmbH; ² Medusa Explorations BV, DE

This study was conducted in the floodplain of the Spittelwasser creek in Saxony-Anhalt, Germany, which is a part of the Elbe river basin. It is highly contaminated through waste water formerly discharged from the near-by Bitterfeld-Wolfen industrial mega site over many decades. In the Spittelwasser creek and the subsequent Mulde and Elbe rivers polychlorinated dibenzodioxins and furans (PCDD/F) play a prominent role, impairing sediment and surface water quality still today. Due to their specific affinity to solid particle surfaces, transport and fate of the PCDD/F are primarily a sediment issue involving riverine sediment deposits as well as the extended flood plain areas. Accordingly and due to the historical time frame of industrial source processes today's contaminant distribution shows a complex spatial pattern.

Floodplains are a sink to particulate matter during flood events and therefore also to particle bound contaminants as PCDD/F. Identifying highly contaminated areas within the floodplains and the quantification the respective contaminant inventory is relevant for both the assessment of potential direct risks and for the assessment of recontamination mechanism and pathways to the relevant surface water bodies. However, conventional investigation strategies (sampling and lab analyses) are usually not practical when aiming to detect small scale variations or contamination hotspots. Therefore, an alternative innovative investigation technique was applied in the Spittelwasser floodplain. This indirect technique uses the Medusa MS-4000 field gamma spectrometer developed for indirectly determining texture, grain size and chemical composition of the top layer of soils or sediments. Following pre-defined grid lines in the field the quad-mounted gamma spectrometer measures the natural element-specific gamma radiation of the soil substrate originating from isotopes of potassium (⁴⁰K), uranium (²³⁸U) and thorium (²³²Th) along with the very low concentrations of caesium (¹³⁷Cs), from man-made fall-out since the early 1960ies. Previous studies have shown that various minerals or types of soil can be distinguished by their different isotopic compositions, their so-called 'radiometric fingerprint'. In many cases, significant relationships were also found between one or more of the radionuclides (the proxy) and one of the textural or chemical properties of the sample. This relation has been used successfully to translate maps of the measured radionuclides into maps of sediment/soil texture and/or pollution levels.

In this study, we successfully applied this approach to PCDD/F and other organic compounds in floodplain soils, for the first time. Detailed results from pilot testing of the technology will be shown which underpin the superiority of this approach compared to the interpolation of conventional analytical data when aiming to resolve small scale contamination patterns. Furthermore full-scale results will be shown and the calculated PCDD/F inventories will be correlated with the PCDD/F loads of the subsequent surface water bodies during normal and flood discharge to assess the recontamination potential from the flood plain areas investigated.

Using dynamic flux chambers to estimate the natural attenuation rates in the subsurface at contaminated sites

Renato Baciocchi¹; Roberto Pecoraro²; Iason Verginelli¹

¹ University of Rome Tor Vergata; ² versalis, IT

The occurrence of aerobic biodegradation in the subsurface by ubiquitous soil microbes has been shown to reduce and in some cases eliminate the impacts of petroleum hydrocarbon vapours on indoor and outdoor air quality. Unfortunately, biodegradation is typically not included in the simplified non-reactive models used in risk assessment guidelines and tools, which account only for the diffusion of contaminants from the source zone. To evaluate the significance of aerobic biodegradation, field investigations are usually carried out by employing multi-level soil-gas nested probes to evaluate the vertical profiles of vapours and oxygen in the subsurface and hence to evaluate the attenuation factors in terms of reduction of soil-gas concentrations. In this work, natural attenuation rates occurring in the subsurface were estimated in a versalis site located in Sarroch (Sardinia, Italy), using dynamic flux chambers, characterized by a continuous flow of an inert gas. The site is characterised by the presence in the subsurface (mainly in groundwater) of BTEX and light petroleum hydrocarbons. The flux of volatile organic compounds (VOCs) from the subsurface was estimated using 14 "dynamic" chambers, by measuring with a canister the concentration of vapours collected over a period of approximately 6 hours. Before starting the measurement, the achievement of steady-state conditions inside the chamber was assured by purging at least 3 to 4 chamber volumes of an inert gas. The measurements in the 14 sampling points were repeated in 3 seasonal campaigns. The fluxes measured in the different campaigns were quite similar, leading always to acceptable risks from vapour inhalation and showing that in the investigated site the seasonal effects on VOCs emission were quite limited. The measured fluxes were compared with those predicted using a non-reactive model, starting from the source concentrations, showing that, in line with other recent studies, this model can overestimate the expected outdoor concentration of petroleum hydrocarbons in some cases up to 4 orders of magnitude. On the other hand, by coupling the measured data with the fluxes estimated with the diffusive non-reactive model, it was possible to perform a mass balance to evaluate the natural attenuation loss rates of petroleum hydrocarbons during the migration from the source to ground level. Specifically, the loss rate of petroleum hydrocarbons was estimated as the difference between the diffusive flux estimated with the non-reactive model from the contamination present in the source underlying the flux chamber and the flux effectively measured at the surface. Based on this comparison, the estimated BTEX loss rates were up to 0.5 kg/year/m². These rates are in line with the values reported in the recent literature for natural source zone depletion and are not far from the rates reported for some active remediation options. In short, the method presented in this work can represent an easy-to-use and cost-effective option that can provide a fast and reliable line of evidence of natural attenuation rates expected at contaminated sites.

ThS 1c.1: Monitoring microbial degradation processes

Microbial molecular and isotopic biomarkers of chloroethene (PCE, TCE, DCE, CV) biodegradation to evaluate natural attenuation contaminated plumes: which added value?

*Jennifer Hellal*¹; *Stéphane Vuilleumier*²; *Jérémy Denonfoux*³; *Louis Hermon*²; *Gwenaël Imfeld*⁴; *Stéphanie Ferreira*³; *Catherine Joulian*¹

¹ BRGM; ² Université de Strasbourg; ³ GenoScreen; ⁴ University of Strasbourg/ENGEEES, CNRS, FR

The extensive use of aliphatic chlorinated hydrocarbons (e.g. tetrachloroethene (PCE) and its degradation products) as solvents and their hydrophobic properties has resulted in their accumulation and persistence in aquifers worldwide, representing a serious risk for human health and the environment. The monitoring of polluted sites (and their natural attenuation) benefits from the classical physical-chemical assessment of the plume. In addition, the evaluation of the potential of chlorinated hydrocarbons' degradation relying on molecular biomarkers may be valuable for site diagnosis. In the framework of this research project (BioDispol: Applicability of microbial biomarkers for evaluating natural attenuation of polluted sites) financed by ADEME (French Environment and Energy Management Agency), we evaluate the relationship between PCE, TCE, DCE and CV degradation and specific functional and taxonomic bacterial genes to eventually develop the role of biomarkers in a coherent framework of monitored natural attenuation (MNA). Groundwater was sampled biannually for two years in 12 piezometers at a contaminated site in France. Four parallel analytical approaches were coupled: (i) ground water physical-chemical parameters, (ii) compound-specific isotope fractionation analysis (CSIA) of chlorinated hydrocarbons, (iii) the quantification of taxonomic and functional genes, and (iv) microbial profiling with next generation sequencing (Illumina MiSeq). In addition to this onsite monitoring, the possible degradation capacities of specific molecules were assessed in batch assays, indeed validating the possibility of biological attenuation. Altogether, our results highlight the value of biological characterization of polluted sites to guide remediation strategies and site management.

Hunting for microbes able to detoxify PCB contaminated marine sediments: experiences from a chronically contaminated site of national interest in Italy

Bruna Matturro; Simona Rossetti

IRSA-CNR, IT

Polychlorinated biphenyls (PCBs) pose environmental concerns due to their toxicity and wide distribution in several matrices including marine sediments. Anaerobic reductive dehalogenation (RD) is the only bioprocess known to reduce such compounds to harmless products or less toxic forms. Despite the process has been extensively investigated on PCB-spiked sediments, very little is known about the identity and metabolic potential of PCB-dechlorinating microorganisms in real contaminated sites. Here we report a detailed study dealing with the estimation of the bioremediation potential of heavy polluted marine sediments by evaluating the contaminant biodegradation kinetics together with the composition, dynamics and activity of indigenous microbial population.

In the present study, marine sediment taken from the Mar Piccolo, Gulf of Taranto (Italy, Site of National Interest) chronically affected by long-term heavy PCBs contamination was analysed. Microcosms were initially constructed with the marine sediment taken from the PCB contaminated site (~ 4 µg PCBs g⁻¹ dry sediment), under strictly anaerobic conditions and without addition of external electron donor. The decrease of hepta-, penta- and hexa-CBs and the formation of tri- and tetra-PCBs were observed. The concentrations of the most representative congeners detected in the original sediment, such as 245-245-CB and 2345-245-CB, and of the mixture 2356-34-CB+234-245-CB, decreased up to 47% after 70 days of anaerobic incubation. The successive addition of a fermentable organic substrate caused the further depletion (up to 70%) of the high-chlorinated PCBs. Several biomonitoring tools, including Next Generation Sequencing (NGS), were applied to evaluate the dynamics of the sediment core microbiome and the activity of *Dehalococcoides mccartyi* strains adapted at high salinity conditions. NGS revealed the involvement of organohalide respiring bacteria other than *D. mccartyi* mainly belonging to *Dehalococcoidia* class. Overall, the study showed the capability of autochthonous dechlorinating bacteria to reduce the contamination level of the marine sediment suggesting that bioremediation may be an option to be further evaluated and exploited.

Designing enhanced bioremediation strategies using microbial passive samplers and in situ microcosms

Jean-Michel Monier¹; Olivier Sibourg¹; Sébastien Cécillon²; Timothy M. Vogel; Sébastien Kaskassian

¹ ENOVEO; ² Ecole Centrale de Lyon, FR

Successful bioremediation of subsurface environments, such as contaminated soil or groundwater, depends on understanding the physicochemical and geochemical conditions as well as microbial degradation processes. Multi-parametric characterization and monitoring over time are essential in order to take into account the complexity of interactions that occur between the solid matrix, indigenous microorganisms and pollutants. One of the major challenges with subsurface systems is the development of sampling techniques for microbiological investigations. Reliable sampling is critical since the detection of microbes and/or their expression and the quantification of genes involved in degradation processes are often used to design and monitor remediation processes. Conventional (active) sampling usually relies on the collection of individual spot samples and may often lead to an underestimation of the abundance, diversity and variability of the microbial community.

The objective of our work was to develop and optimize tools for reliable on-site passive sampling of microbial communities in a non-destructive manner. Different matrices ranging from activated carbon to coarse sand were tested for enrichment of bacterial growth in monitoring wells. Samplers were deployed for over 30 days and the microbial communities enriched on the different matrices compared to the communities of the surrounding soil and interstitial water using molecular tools (e.g., genetic fingerprints, next generation sequencing). Results obtained showed that while EMPs can offer an excellent alternative to active sampling, the choice of the matrix selected for passively sampling subsurface microbial communities is critical and some materials should be avoided. Data obtained with the different matrices in different environments will be presented and the advantages and limitations of this approach for different applications will be discussed.

On-going research (Project MISS : Microcosm-based In Situ Studies), to develop reliable and cost-effective alternatives to pilot studies performed in the field or under laboratory conditions to design bioremediation strategies, will also be presented. The technology, based on a multi-parametric chemical and microbial passive sampling strategy, could be used by site managers to evaluate performances of different bioremediation strategies over time and in situ.

Direct monitoring of biological BTEX degradation using Next Generation Sequencing

Elsemiek Croese¹; Janneke Wittebol²; Sabine Doddema¹

¹ Microbial analysis; ² Bioclear, NL

Aromatic compounds under which Benzene, Toluene, Ethyl benzene and Xylenes (BTEX) are the main abundant organic ingredients in nature after carbohydrates. They are produced worldwide with an incredible amplitude of 35 million tonnes annually. With these high amounts it is inevitable that some amounts are spilled into the environment causing concerns due to their toxicity, water-solubility and mobility. Especially benzene causes concerns due to its known human carcinogenic potency and toluene can enhance carcinogenesis by other compounds. Therefore it is important to gain insight into BTEX biodegradation potential and stimulation. Using new molecular techniques it has become possible to deliver strong and direct evidence for actual BTEX biodegradation which was unattainable until recently.

Since BTEX compounds are often present in the anoxic zones of the environment, anaerobic bioremediation is an alluring method. The biological pathway studies of BTEX compounds under anaerobic conditions lead to the characterization of some toluene and ethyl benzene degrading genes. However all studies indicate that the anaerobic biodegradation of benzene is by far the most difficult aromatic component providing little information about the genes involved.

For this reason it can be challenging to demonstrate the actual occurring biodegradation of all BTEX compounds on polluted locations. It is therefore accepted to combine several lines of indirect evidence to determine the anaerobic BTEX degradation. For example by combining laboratory degradation batchtests with the monitoring of specific compounds and isotopic analysis on site. However, strong direct proof for the presence of BTEX degrading microorganisms on site is not commonly applied.

In this presentation we will present an example of a location with a long history of BTEX pollutant. On this location the BTEX compounds are biologically degraded under anaerobic conditions. The BTEX compounds were monitored over the last ten years combined with the molecular technique QPCR. Using QPCR genes were detected which are involved in the degradation route of toluene, ethyl benzene and the intermediate benzoyl coa. This provided the proof that these compounds are biodegraded.

However, the biodegradation of the most abundant component benzene was not feasible using QPCR. This is due to the fact that the functional genes involved in the degradation of benzene are too complex to detect using QPCR caused by their high variety. This major drawback can be overcome by the use of Next Generation Sequencing (NGS). Using this state of the art technique, based on RNA, information is obtained about actual occurring processes giving insight into the biological community and pathways and therefore provides strong evidence for BTEX biodegradation potential. High tech data processing techniques are used to visualize the enormous amount of biological data and to process and visualize it in an orderly way which is understandable to every user. This location shows that new techniques can be used to provide strong and direct evidence for actual biodegradation of BTEX which were unprocurable till recently.

Real-time view on reductive dechlorination by functional gene analysis

Kathrin Rachel Schmidt¹; Irene Kranzioch-Seipel; Claudia Stange; Andreas Tiehm

¹ TZW: DVGW-Technologiezentrum Wasser, DE

By now it is well accepted that biodegradation can be very helpful to remove chloroethenes from contaminated sites in a safe, efficient and sustainable way. But still there is the challenge to unequivocally prove that the chloroethene decrease observed is really due to microbial activities. This process understanding is an important prerequisite for the acceptance of monitored or enhanced natural attenuation approaches (MNA/ ENA).

Reductive dechlorination by the bacterial genera *Desulfitobacterium* spp., *Dehalobacter* spp., *Desulfuromonas* spp. and *Desulfomonile* spp. can transform perchloroethene (PCE) via trichloroethene (TCE) down to cis-1,2-dichloroethene (cDCE). Bacteria belonging to the genus *Dehalococcoides* even are able of entire reductive dechlorination via vinyl chloride (VC) down to the completely dechlorinated ethene molecule. *Dehalococcoides* bacteria dispose of several different dehalogenases (=dechlorinating enzymes/ bio-catalysts) performing the different reactions steps: PceA (PCE TCE), TceA (TCE ethene), VcrA (cDCE ethene) and BvcA (VC ethene).

PCR (polymerase chain reaction) is already well established to assess the potential of a certain site for uncomplete or complete reductive dechlorination via the fast and easy detection of the different microorganisms/ dehalogenases. Nowadays, we dispose of even more sophisticated methods allowing to assess the expression of the dechlorinating enzymes in real-time. The trick is to analyse not only the genetic information stored within the bacterial DNA, but to analyse which part of the genetic information is currently used to produce a specific bio-catalyst. The so called messenger-RNA (mRNA) is transporting this information from its storage place - the DNA - to the production place of the enzymes. The mRNA is a rather labile molecule needing gentle analysing methods.

Here, we show the successful application of mRNA analysis of the dechlorinating enzymes of *Dehalococcoides* spp. in comparison to well-established DNA analyses and the degradation behaviour of dechlorinating laboratory cultures. To investigate the expression of the dehalogenase genes *pceA*, *tceA*, *vcrA* and *bvcA*, a protocol for mRNA extraction followed by reverse transcription and quantitative PCR analysis was established.

During complete dechlorination, an increase in the gene copy numbers of *pceA*, *tceA* and *vcrA* was observed with DNA analyses. Furthermore, the actual expression of the genes *tceA* and *vcrA* was observed through the temporary formation of mRNA during the dechlorination of cDCE and VC. Thus, the mRNA results were exactly reflecting the current degradation activity of the cultures.

Overall, PCR analysis is a suitable field-tested method to obtain more insight into the dechlorination potential of a specific field site and the *Dehalococcoides* sp. community composition. In addition, mRNA analysis is developed to assess the real degradation activity.

ThS 1c.2: Monitoring contaminant effects on subsurface biology

Monitoring of sediments microbial communities impacted by hydrocarbons

Cristiana Cravo-Laureau¹; Cyril Noel; Christine Cagnon; Fanny Terrisse; Robert Duran

¹ University of Pau, FR

Coastal marine sediments constitute unique functional ecosystems constantly subjected to oxic/anoxic oscillations according to tide cycles, bioturbation activities by macrofauna and other mechanical processes. Due to their location they are exposed to pollution injuries such as oil spills. Microbial communities play critical roles in global biogeochemical cycles in marine sediments, particularly in response to the presence of hydrocarbons. Thus, understanding the response of these key microorganisms exposed to hydrocarbons under oxic/anoxic oscillations provide pivotal information for estimating the resilience capacities of the ecosystem.

Recently, we showed that the organization of hydrocarbon degrading bacterial communities was driven by sediment reworking activities (Stauffert et al., 2013). Indeed, three different microbial communities were obtained applying various reworking strategies but their overall degradation efficiency was similar highlighting the functional redundancy involved in hydrocarbons degradation. In order to further characterize the microbial assemblages, the three microbial communities were incubated in different oxygenation regimes (oxic, anoxic and oscillating conditions) in bioreactors. Then Bacteria and Archaea 16S rRNA transcript amplicons were analysed by high-throughput sequencing. Although PICRUSt functional analyzes revealed that the three Archaea communities were different, they were not affected by the oxygenation conditions imposed in the bioreactors. In contrast, Bacteria communities were structured according to the oxygenation conditions. Correlation analysis showed that Archaea/Bacteria interactions, particularly the methanogens/sulfate-reducing bacteria relationships, are of primary importance in the microbial communities assemblages in presence of hydrocarbons including the hydrocarbon degradation capacity. We thus suggest to carefully examine the Archaea/Bacteria interactions in microbial ecotoxicology studies to evaluate the impact of pollutants.

Stauffert M, Cravo-Laureau C, Jézéquel R, Barantal S, Cuny P, Gilbert F, et al. (2013). Impact of Oil on Bacterial Community Structure in Bioturbated Sediments. PLoS ONE 8: e65347.

Integrated whole-cell ecotoxicity assessment of urban wet-weather discharges on *Chlorella vulgaris*: interest of sub-cellular biomarkers for fast toxicity and pollution monitoring

*Antoine Gosset*¹; *Pauline BARBE*¹; *Rémy BAYARD*²; *Claude DURRIEU*¹

¹ LEHNA; ² DEEP - INSA LYON, FR

Urban wet weather discharges (UWWDs) are designed as all the water discharged by sewerage installations (mixture of treated wastewater and rainwater), by combined sewer overflows (CSO) (mixture of non-treated wastewater and rainwater), and stormwater outfalls (non treated rainwater), during rain events. These events can lead to a rejection of a high number of micropollutants in aquatic ecosystems, as pesticides, polycyclic aromatic hydrocarbons, heavy metals, poly-chloro-biphenyls, or pharmaceuticals, due to the currently low number and efficiency methods to treat them. Consequently, there is strong issue to monitor them and prevent any degradation of suburban aquatic ecosystems. Many pollutants detected in UWWDs can impact aquatic organisms, as microalgae. These micro-organisms represent very sensitive bio-indicators, at the base of aquatic food webs. Numerous publications highlight the sensitivity and rapidity of response of these organism's biomarkers to UWWDs pollutants as heavy metals and pesticides; more sensitives than classical bioassays as algal growth inhibition.

Then, the aim of the study was to develop and apply a set of biomarkers on *Chlorella vulgaris*, a very common algae in potentially impacted aquatic suburban ecosystems as rivers and lakes, on UWWDs samples from a high diversity of watershed. Thus, this study's aim is to the interest of using these biomarkers for the fast monitoring of UWWDs pollution and toxicity.

UWWDs samples were obtained in a high urbanized region of France, Lyon agglomeration. Multiple campaigns were performed to obtain 14 samples collected on auto-sampled samples. A set of 4 biomarkers was developed to the ecotoxicity assessment of UWWDs. Among them, membrane permeability (linked to cell viability), esterase, phosphatase and photosynthetic activity were assessed after short (2 and 24 hours) UWWDs exposure. In parallel, physico-chemical analyses were carried out analyzing classical parameter (pH, conductivity, nitrates, etc.), 8 inorganic pollutants (heavy metals) and 112 organics pollutants to correlate ecotoxic effects to the presence of pollutants.

Results showed a significant impact of UWWDs on algal metabolism. Among these algal biomarkers, photosynthetic activity disturbance was the more sensitive, with high inhibitions observed after 24 h (until 85.6% of inhibition). Phosphatase and esterase activities were subjected to inhibitions or stimulations. No toxicity was observed with membrane permeability. The results can be explained by the fact that photosynthesis activity is a less specific biomarker, which respond to many families of micropollutants while phosphatase and esterase activities are linked to specific families of pollutants (heavy metals and pesticides), present in low concentrations in UWWDs. Moreover, stimulation can be linked to the presence of large concentrations of stimulant nutrients (phosphates and nitrates). Consequently, biomarkers can be classed in terms of sensitivity for UWWDs as following: Photosynthetic activity>Phosphatase activity=Esterase activity>Membrane permeability. In conclusion, these fast-response biomarkers were validated to be used for UWWDs fast monitoring.

Combined effects of environmental concentrations of copper and arsenic on natural river sediment microbial communities

*Ayanleh Mahamoud Ahmed*¹; *Stéphane Pesce*²; *Aymeric Dabrin*²; *Bernard Motte*²; *Bernadette Volat*²; *Christophe Rosy*²; *Chloé Bonnineau*²; *Josiane Gahou*²; *Emilie Lyautey*³

¹ Irstea, UR MALY/CARRETEL (USMB - INRA); ² Irstea, UR MALY; ³ CARRETEL (USMB - INRA), FR

Sediments are an essential component of aquatic ecosystems in terms of biodiversity and of ecological functioning. They receive direct or indirect inputs from the water column or from the watershed including some toxic and persistent contaminants (e.g. trace metals and PCBs) which can accumulate over time and impact exposed organisms. Among benthic organisms, microbial communities are major players in various key ecological processes such as organic matter recycling, greenhouse gas production and biomass production contributing to benthic food webs. The study of ecotoxicological effects on microbial communities paves the way to assess the impacts of contaminants on both taxonomic and functional microbial biodiversity which support many ecosystem functions and ensure their stability and resilience. Accordingly, microbial ecotoxicology offers prospects to develop new ecosystem quality indicators. However, knowledge about the effects of accumulated contaminants on sediment microbial communities is scarce. In this context, the main aim of this work was to evaluate the structural and functional impact of chronic exposure to environmental concentrations of copper (Cu) and arsenic (As), alone or mixed together, on river sediment microbial communities. Natural uncontaminated surface sediments collected in a French River (Ain) were spiked with As and Cu at a nominal concentration of 40 mg/kg and then were exposed for 21 days in laboratory channels with overlying waters. The response of heterotrophic microbial communities to metals was evaluated both in terms of genetic structure (using ARISA analysis) and functional potential (using exo-enzymatic, metabolic and metagenomic analyses). A pollution induced community tolerance (PICT) approach was also performed to assess if the exposure led to an increase in the capacity of microbial communities to tolerate metals. Our results showed rapid (within 48 hours) and marked effects of Cu alone on the exposed communities. It led to a significant inhibition of microbial functions such as respiration and denitrification as well as beta-glucosidase, leucine aminopeptidase and phosphatase activities, and affected the proportion of functional genes involved in denitrification pathways. Chronic Cu exposure also induced an increase in community tolerance to Cu, as observed by PICT measurement using beta-glucosidase activity. In contrast, the effects of As were mostly undetectable. Under mixture exposure (Cu+As), the effects were similar or higher than those provoked by Cu alone, depending on the measured parameter. Altogether those findings reveal that metals accumulation in sediments can impact exposed microbial communities thus affecting their functional role in aquatic ecosystems. They also show that PICT approaches have the potential to be a powerful microbial indicator to assess in situ the ecological quality of metal-contaminated sediments. These results open new perspectives to assess the ecological quality of sediments and confirm the need for developing studies to better understand the ecotoxicological impact of contaminants on natural sediment communities.

Key words: Benthic communities, metals, ecotoxicology

Microbial Resources Management for bioremediation

Olivier Sibourg; Jean-Michel Monier¹; Céline Baguelin; Sandra Entresangles; Cédric Malandain

¹ ENOVEO, FR

Successful site remediation through microbial degradation requires a thorough understanding of the microbial mechanisms implicated in the biodegradation of the pollutant in question. Regardless of the nature of the pollutant or environmental matrix, the success of a bioremediation project hinges on the consideration of two essential components: the presence of a microbial community which can be stimulated in order to promote biodegradation activity and the bioavailability of the pollutant (often influenced by the chemical and physical characteristics of the site). Understanding microbial degradation processes is therefore a major contribution to the success of such projects.

ENOVEO's biotechnological solutions include the characterization of the microbial degradation potential of a site and the evolution of the activity of indigenous bacteria. On-going technological advancements in the fields of metagenomics, metatranscriptomics and metaproteomics continue to bring new perspectives to our understanding of microbial mechanisms. Our presentation will illustrate how different molecular biology tools can be utilized to characterize and manage microbial resources, from the development of the remedial action plan to site treatment and closure, to identify any potential difficulties associated with up-scaling and to enable the optimization of depollution strategies.

Microbial Dynamics and Biofilm Development in Contaminated Aquifers

Juan Mujica; Stephen Rolfe; Steven Thornton

The University of Sheffield, GB

The use of Monitored Natural Attenuation (MNA) as a tool to manage contaminant plumes has served to guide engineered technologies such as Pump and Treat (PAT). There is evidence that this type of intervention lead to a reduction of the pollutant concentration and increase in the supply of electron acceptors due mixing between the plume and background groundwater. The change in groundwater geochemistry has enhanced the biodegradation by the autochthonous microbial community. Nevertheless, it is not clear if this increase in contaminant mass removal due bacterial/archaeal groups is sustained once the PAT stops operations. Furthermore, the identification of the groups responsible for the increase in biodegradation rates and which of them might be active across different geochemistry conditions, represented by different pumping regimes, has not been explored. This research focuses on a site polluted with phenolic compounds and intervened with PAT systems with different operation regimes; where after a year of pumping one of the boreholes was switched off. Annual surveys using high-resolution Multi Level Samplers (MLS) next to the pumping borehole were made before and after the change of the pumping regime for a period of 3 years. Samples were also collected in a pumping borehole operated continuously. In the MLS close to the borehole where pumping was stopped Total Phenolic Content (TPC) increased in several locations compared to pre-pumping values, which suggests a source term effect at this location. Meanwhile, in the MLS under the influence of PAT, TPC values remained as low as found in previous surveys. The use of quantitative PCR (qPCR) for genes related to nitrate reduction metabolism (*nar* and *nap*) will establish the presence of these microorganisms and how their abundance relates to the geochemistry at different stages and locations in zones under the influence of the PAT. Moreover, qPCR with *dsr-A* gene (related with Sulphate Reducer Bacteria SRB) will determine the extent of SRB suppression by high TPC and how this suppression might be related to PAT. Finally, the use of Illumina Sequencing at certain depths will identify the microorganisms and the shift in the microbial community structure across interfaces created by mixing between polluted and background groundwater due to PAT. This research will be useful to understand which groups contribute to the biodegradation processes, the microbial succession taking place under different pumping regimes and to identify the geochemical controls behind the enhancement in biodegradation.

ThS 1c.3: Isotope Analysis based Monitoring

Assessment of chlorinated ethene biodegradation in an anoxic aquifer using a multiple-lines-of-evidence approach

Annika Beckmann; Anko Fischer; Andreas Jahnel; Petra Bombach

Isodetect GmbH, DE

Chlorinated ethenes such as tetrachloroethene (PCE) and trichloroethene (TCE) are toxic, persistent and ubiquitously distributed groundwater pollutants that pose a serious risk for human health and the environment. Bioremediation strategies for chlorinated ethenes are often based on reductive dechlorination of the chlorinated ethenes to ethene, a process which is carried out solely by members of the Dehalococcoides group. However, reductive dechlorination of PCE and TCE can be incomplete, resulting in accumulation of dichloroethene (DCE) and vinylchloride (VC). Since VC is more toxic and mobile than PCE and TCE, a robust monitoring and, if necessary, stimulation of VC dechlorination are essential steps in the planning and implementation of bioremediation strategies.

In the present study, we investigated the biodegradation of PCE and TCE in a chlorinated ethene-contaminated aquifer at a former power plant site using an integrated approach comprising compound-specific stable isotope analysis (CSIA), molecular biological analyses and laboratory microcosms in combination with ^{13}C -labelled chlorinated ethenes as tracer compounds.

CSIA is based on the principle that molecules with heavier isotopes in their reactive position(s) (e.g., ^{13}C) are generally slower degraded than those with lighter isotopes (e.g., ^{12}C). The result is a shift in the isotopic composition (e.g., $^{13}\text{C}/^{12}\text{C}$) as the remaining contaminant fractions becomes progressively enriched in heavier isotopes (e.g., ^{13}C) in the course of biodegradation. CSIA provides an appropriate tool to assess in situ degradation of individual environmental contaminants both qualitatively and quantitatively in contaminated aquifers. At the field site investigated, stable carbon isotope analysis provided evidence that complete dechlorination of PCE and TCE to ethene was occurring along the anoxic contaminant plume. Using the Rayleigh model cis-DCE and VC biotransformation accounted for 5 to 69 % and 8 to 47 % of the cis-DCE and VC concentration decrease, respectively. Remarkably, microorganisms of the Dehalococcoides group and specific dehalogenases were found only occasionally in low gene copy numbers in groundwater samples. It is likely that Dehalococcoides species inhabit the sediments and therefore, were not detected by analysis of groundwater samples.

A laboratory microcosm was additionally conducted to investigate the reductive dechlorination of TCE, cis-DCE and VC and a possible stimulation of cis-DCE and VC biodegradation by addition of oxygen. Groundwater and passive sampler (BACTRAP®)-grown attached cells were used as inoculum and incubated under in situ-like conditions, using ^{13}C -labelled chlorinated ethenes as tracers. Mineralisation was detected with high sensitivity and quantified by analysing the formation of ^{13}C - CO_2 (aerobic biodegradation) or ^{13}C -ethene (reductive dechlorination). Under anoxic conditions, TCE were converted to cis-DCE and VC, while oxygen addition resulted in biotransformation of cis-DCE to CO_2 . The results of the three approaches provide a solid base for future management decisions at the field site.

Compound specific isotope analysis used to identify the origin of VOCs in indoor environment - Internal sources versus sub-surface contamination

Trine Jepsen¹; Mariam Wahid; Ida Damgaard; Nina Tuxen; Thomas Larsen

¹ Orbicon A/S, DK

Introduction: Volatile organic compounds (VOCs) in the indoor environment could either originate from intrusion of vapor from sub-surface pollution or from internal sources as e.g. dry cleaning facilities, oil burners etc. Until now, it has been hard or even impossible to distinguish the origin of VOCs. Therefore, the authorities handling unacceptable impacts from soil vapor contamination to the indoor air allocate significant means to handle contamination in households.

The aim of this project is to examine, evaluate and develop the use of compound specific isotope analysis (CSIA) and fingerprinting for risk assessment of vapor intrusion to indoor air, including identification of the primary source to the indoor air pollution.

Method: Many elements e.g. carbon and chlorine is a mix of different isotope species differing in the number of neutrons in the atom. The isotopic ratios of specific pollutants may vary dependent on the source material or fate in the environment. CSIA measures the isotope ratios of carbon ($^{13}\text{C}/^{12}\text{C}$) and chlorine ($^{37}\text{Cl}/^{35}\text{Cl}$) for specific chemicals in this case PCE, TCE and benzene. Thus, CSIA can exploit this characteristic to decide the origin of the contaminant.

CSIA and fingerprinting of VOCs in air samples from the indoor environment and the sub-surface source area are compared. Larger differences are indicating VOCs in the indoor climate and the subsurface to have different origins thus the contamination of the indoor air may originate from an internal source.

The method is tested on four well-characterized sites varying in compound of pollution and occurrence of internal and subsurface sources.

Conclusion: CSIA and fingerprinting generates data for a fast and noninvasive approach for risk assessment regarding unacceptable vapor intrusion from subsurface contamination to indoor climate. Traditionally, risk assessment of vapor intrusion from soil combines investigation of soil and groundwater followed by soil vapor measurements leading to an evaluation of the influence of vapor intrusion to the indoor environment. The traditional risk assessment is based on a minimum or even no samples of the indoor air. CSIA, on the other hand, makes it possible to evaluate the influence of soil vapor intrusion from measurements of the indoor air. The risk assessment is conducted from indoor concentrations in combination with information on the origin of the measured VOCs.

Based on experience from 24 sampling points recommendations regarding sampling procedure are compiled. E.g.:

- It is important to use the right adsorption material for the samples.
- The flow should be low (0,1 l/min).
- The volume of analyte on the adsorption tube is very important resulting in air volumes, depending on the concentration of contaminants, from 0,001 to 96 liters.
- At each sampling point, 3-4 replicates should be collected with a deviation of no more than 30%.

Fieldwork is well completed. Results and final evaluations are finished in spring 2017.

Monochlorobenzene Contaminated Site Characterization by the use of ^{37}Cl , ^{13}C and ^2H - Compound-Specific Isotope Analysis (CSIA), Biological Molecular Techniques (BMTs) and Numerical Modeling

Massimo Marchesi¹; Ilaria Pietrini; Matteo Antelmi; Luca Alberti; Tatiana Stella; Andrea Franzetti; Danilo Antonelli; Francesca De Ferra; Ramon Aravena; Orfan Shouakar-Stash

¹ Politecnico di Milano, IT

Background/Objectives: Chlorinated solvents contaminated sites entail costly management costs and often create significant impacts to the environment. Innovative tools such Compound-Specific Isotope Analysis (CSIA), Molecular Biological Techniques (MBTs) and fate and transport models can provide unequivocal information for site characterization and assessment of natural attenuation processes, particularly biodegradation. This contribution explores the potential for the tri-element CSIA approach, MBTs and transport models to study a heavy monochlorobenzene (MCB) and benzene contamination at a mega-site where potential multiple sources are presents.

Approach/Activities: Microcosms experiments were developed in order to estimate enrichment factors for ^{13}C and ^{37}Cl , and to investigate specific biomarkers under different conditions (soil slurry, natural and stimulated, a- and anaerobic). Field investigations were performed including $\delta^{37}\text{Cl}$, $\delta^{13}\text{C}$ and $\delta^2\text{H}$ for MCB and Benzene and illumina sequencing and qPCR coupled to reactive transport modeling efforts.

RESULTS: A significant difference in the $\delta^{13}\text{C}/\delta^2\text{H}$, $\delta^{13}\text{C}/\delta^{37}\text{Cl}$, $\delta^{37}\text{Cl}/\delta^2\text{H}$ and $\delta^{13}\text{C}/\delta^{37}\text{Cl}/\delta^2\text{H}$ for MCB and $\delta^{13}\text{C}/\delta^2\text{H}$ for benzene - in the high concentration spots - allowed distinguishing two distinct sources and plumes (merged at some areas). By the use of MNWs a detailed vertical distribution of the contaminants through the aquifer was assessed.

Concerning natural attenuation processes, although the site is characterized by reducing conditions with high concentrations of CH_4 , MBTs results indicated the presence of mainly aerobic potential degraders within the indigenous community at the site and ruled out a significant presence of dehalococoides or dehalobacters. Microcosms experiments and soil slurry with in-situ cultures showed a unique $\delta^{13}\text{C}/\delta^{37}\text{Cl}$ trend with almost no enrichment for ^{13}C but a ^{37}Cl ϵ of -0.7‰ .

The dual $\delta^{13}\text{C}/\delta^{37}\text{Cl}$ data also seem to indicate aerobic biodegradation processes as the main natural attenuation mechanism. Finally, regarding benzene, the $\delta^{13}\text{C}/\delta^2\text{H}$ data showed that benzene present at the site is probably not linked to MCB dehalogenation processes but is rather a primary contaminant; these data also showed benzene is being attenuated by biodegradation. Since not varying as a consequence of biodegradation processes, $\delta^{13}\text{C}$ and $\delta^2\text{H}$ for MCB were used in combination with the transport models to estimate the contribution to the contamination from the two distinct sources. After estimating the mixing ratios among the plumes, $\delta^{37}\text{Cl}$ was successfully used as a tracer to assess the natural attenuation processes at the site.

These results demonstrated the potential of combining tri-element CSIA in combination with other tools, particularly important insights regarding MCB natural attenuation were obtained by applying tri $\delta^{13}\text{C}$, $\delta^{37}\text{Cl}$, and $\delta^2\text{H}$ CSIA analyses.

Stable isotope analysis and probabilistic modelling for the characterization of nitrate pollution in groundwater

Arno Rein; Anja Wunderlich; Florian Einsiedl

Technical University of Munich, DE

Nitrate concentrations in groundwater have increased in many aquifers over the past years and decades, posing a serious threat to drinking water resources. The analysis of stable isotopes is a well-established methodology for characterizing subsurface water flow and residence times as well as pollutant fate and biogeochemical processes. In different areas of the Franconian Alb, Germany, which are characterized by karst aquifers, we have determined groundwater age distributions by a combination of tritium measurement and modelling. For a time period of about 14 years, we have measured nitrate concentrations in groundwater and $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of dissolved nitrate. Aims of our study were to analyse temporal and spatial trends in nitrate concentration and isotopic composition, which may be related to changes in agricultural practice. By applying probabilistic modelling, we have investigated potential contributions of different nitrate sources and processes that could have led to the observations.

Results of measurements revealed an isotopic shift to heavier isotopes in dissolved nitrate. In order to explain the observations, hypothetical model studies were done involving Monte Carlo simulations. Different hypotheses for the observed isotopic signals were tested, including possible mixing of different nitrate sources within the catchment, the influence of transport processes in groundwater, as well as microbial denitrification (biodegradation and related isotopic enrichment). Findings of elevated nitrate concentrations accompanied by increased $\delta^{15}\text{N}$ values may suggest a source-driven shift away from ammonium-based fertilizers to manure derived from animal waste. Simulation results can support this assumption, where the mixing of input from different sources and hydrodynamic processes in the subsurface seem contributing to a higher extent (higher probability) to the observed shift of $\delta^{15}\text{N}$ values, as compared to microbial denitrification. Further modelling studies are currently under way, where first results indeed point towards a lower influence of biodegradation. In the karstic aquifer system, conduit water constitutes the main component of groundwater flow, characterized by mean transit times below 60 years and related low potentials for microbial denitrification. The latter, however, is assumed to predominate in the rock matrix, with higher residence times of water (>100 years) which contributes to groundwater flow only to a minor portion.

Evaluation of sources and sinks of hexachlorocyclohexane (hch) isomers within a contaminated aquifer using compound-specific stable carbon isotope analysis (CSIA)

Safdar Bashir; Kristina Hitzfeld; Matthias Gehre; Hans-Hermann Richnow; Anko Fischer¹

¹ Isodetect GmbH, DE

Hexachlorocyclohexane (HCH) isomers are pollutants of particular concern because of their widespread distribution in the environment, toxicity and persistence. Especially at sites of pesticide production, formulation and dumping, significant soil and groundwater pollutions of HCHs have been detected. For cost-efficient and highly productive remediation strategies of contaminated sites, it is necessary to investigate pollutant sources and sinks. In recent years, compound-specific stable isotope analysis (CSIA) has gained more and more attention as a tool for characterizing and assessing contaminant sources and in situ degradation of organic pollutants, respectively. The intention of this study was to verify the potential of CSIA for assessing sources and sinks of HCHs within a contaminated aquifer at a former pesticide formulation plant.

Analytical methods were established and verified for determining carbon isotope ratios ($^{13}\text{C}/^{12}\text{C}$) of HCHs using gas chromatography – stable isotope ratio mass spectrometry (GC-IRMS). Based on the carbon isotope ratios of HCHs, several source zones could be identified near former processing facilities, a storage depot and a waste dumping site. This finding was confirmed by the concentration patterns of the contaminants and historical information. The ^{13}C -enrichment in HCHs provided evidence for biodegradation of HCHs especially downstream of the contaminant sources. CSIA from monitoring campaigns in several years revealed temporal trends in HCH biodegradation. Thus, the impact and progress of natural attenuation processes could be evaluated within the investigated aquifer. Conservative calculations based on the Rayleigh equation approach yielded extends of HCH biodegradation ranging from 30 to 86 %. Moreover, time- and distance-dependent in situ first-order biodegradation rate constants were estimated.

In summary, our study highlights the applicability of CSIA for evaluating sources and sinks of HCHs within contaminated aquifers located at sites of pesticide production, formulation and dumping.

ThS 1d.1: Geophysical and geostatistical methods in site characterization

Application and limitations of DC induced polarization tomography for the detection of organic pollutants in soils with litho-chemical metallic components. A case study.

Bárbara Biosca; [Ana Artalejo](#); Fernando Barrio-Parra; Jesús Díaz-Curiel; Eduardo de Miguel; Rafael Medina-Ferro

Universidad Politécnica de Madrid - ETSI Minas y Energía, ES

One of the geophysical techniques currently being evaluated for the detection and characterization of non-aqueous phase liquids (NAPL) is prospection using non-spectral induced polarization tomography. The response in chargeability of this kind of pollutants allows its delimitation using this method. However one of the limitations for the application of this technique is the presence of lithologies that contain metallic salts which produce greater anomalies of chargeability than those due to this type of contaminants.

In the present study a case of those characteristics is presented. The studies were conducted in an area contaminated by fuel leaks from supply tanks within a train maintenance facility. Those leaks occurred while the tanks were used but since its dismantling the leak stopped. The geology of the area presented strong heterogeneities besides important limitations of access. In order to locate and characterize the contaminant plume measurements of resistivity and chargeability were carried out simultaneously, in addition some in-situ tests were performed. The delimitation of the plume was affected by the presence of clays rich in metallic components such as K, Mg, Ca, Fe, Mn and Al.

MICROSCALE GEOPHYSICS USED IN CONCEPTUAL MODELLING

Thomas Larsen¹; Majken Caroline Looms²; Nielsen Lars²; Anders Vest Christiansen³; Thue Bording³; Egon Nørremark³; Knud Erik Klint⁴; Nina Tuxen⁵; Henriette Kerrn-Jespersen⁵; Anders Edsen¹

¹ Orbicon A/S; ² University of Copenhagen; ³ Aarhus University; ⁴ GEUS; ⁵ Capital Region of Denmark, DK

Background: A large part of the northern hemisphere has quarternary deposits consisting of glacial clay till. The till often has a complex hydrogeological structure consisting of networks of fractures, sand stringers and sand lenses each contributing to a transport network where water, free phase and dissolved contaminants are transported from the surface and downwards. Understanding the nature and structure of these networks are crucial in developing conceptual models (CSMs) of the spreading of contaminants. The toolbox used for characterization of the geological and hydrogeological structures typically consists of different kinds of soil borings, direct imaging tools like EC and MIHPT and different hydraulic/pneumatic tests. On larger scale, different geophysical methods has been used intensively for many years for different mapping activities with success, but most superficial methods have fallen short using it at a local scale. Due to that, research recently has been directed toward using these methods in different configurations and with more sophisticated data acquisition and processing trying to improve and optimize data collection.

Aim & Method: In 2015 the Capital Region of Denmark initiated a small program where the objective was to identify potential methods that could track/delineate sand stringers/lenses of a thickness of 10 cm in a 10 m by 10 m by 10 m clay till volume. Late summer of 2015 it was decided to test three different cross hole geophysical methods, which had the potential to succeed followed up by an excavation of the 150 m² test area for visual inspection of the volume. The test was carried out in November/December 2015. The overall objective was to make a proof of concept for the methods, comparing the results and interpretations with the actual geology at the test site. Based on the results further testing of cross hole ground penetrating radar tomography (GPRT) took place October 2016.

Conclusions: The test field was located near the digging front in a gravel pit west of Copenhagen. In the pit the geology comprises in general of a till clay with sand layers/stringers embedded down to 5-10 m. Underlain by vast layers of sand and gravel. At the actual test location, the clay was 6-8 m thick. Three cross hole techniques was tested: Ground Penetrating Radar Tomography (GPRT), Seismic Waves Tomography and DCIP Tomography (DCIPT) on a 5-15 m scale. After geo-physical testing the pit front was digged in a layer/staircase manner in order to get measures of the actual configuration of the embedded sand layers (size & orientation) giving a more complete picture than well logs alone. GPRT and DCIPT measurements clearly correlated with the observations from the excavation and borings, the seismic methods could not differentiate between the different layers. The GPRT had the shortest distance between wells in the first setup and was further tested at a larger scale on another site. GPRT has the advantage of ease and economics compared to DCIPT. GPRT on the other hand, with the setup used, had shorter range than DCIPT and the amount and detail of info obtained also seems to be bigger with DCIPT.

Improvement of traditional investigations by prior geophysical measurements

Anette Specht¹, John Ryan Pedersen¹, Helle Blæsbjerg¹, Rolf Johnsen¹, Jesper Bjergsted Pedersen²

¹Central Denmark Region, ²Aarhus University, DK

Background

Geophysical investigation methods has frequently been utilised in Danish groundwater mapping. As contaminated sites often are situated in urban areas interference has ruled out the use of geophysical methods for this purpose. Also the resolution of the upper soil layers has been inadequate. Now improved and new geophysical methods are qualified for high resolution interpretation of the uppermost geology.

In this project we will test the geophysical contribution to the traditional concept for investigations of contaminated sites. The project is part of the Interreg Topsoil project working on improvement of climate resilience by demonstrating and testing solutions for managing the top soil layers. For more details see paper 678, topic 6b.

Purpose

Traditionally, contaminated sites are investigated by drillings, water samples and soil gas measurements. Sampling points are initially based on potential point sources collected in historical archives, by interviews etc. Based on the first results subsequent points are allocated in order to delineate hotspot and/or plume. This approach contains a substantial uncertainty especially in a heterogeneous geological setting, thus a solid risk assessment implies a large number of boreholes.

The objective is to clarify if expenses and/or time can be reduced by adding an areal dimension (3D geophysics) prior to the point approach. The final output should be recommendations and guidelines for a better integrated practice.

Method

A traditional investigation draft is outlined and then compared to a draft based geophysical interpretations. The aim is to analyze possible differences in the number and location of boreholes in a traditional investigation relative to an investigation with a prior geophysical mapping. To secure an equal or improved risk assessment with the 'new concept', field investigations covering both proposals will be carried out and all results taken into account.

Case

The trial is carried out on a former landfill and an agricultural contractor, where pollution with leachate and pesticides has been proved. The geological setting is primarily quaternary sediments like clay tills and melt water sands. First proposal for investigations has been carried out and put aside, and next step is geophysical investigations with GCM and TowTEM towed by an ATV. These methods can dissolve the top 7-10 meters and top 30 meters respectively – depending on geology. Measurements will be driven with a narrow line spacing (5-10 meters) to see if detailed geological models give an advantage on small scale investigations compared to the groundwater mapping which the geophysical methods have mostly been used for. Geophysical interpretation will be completed within the next six months, followed by 1) new proposals, 2) field campaign, 3) analysis, 4) recommendations and guidelines.

Presentation

At the conference geophysical methods used, first results and interpretations will be presented as well as a more detailed plan for the next steps.

Optimizing groundwater flow and contaminant migration assessment using 3D Electrical Resistivity Tomography

Sean Carson¹; Jean-Marc Ragot²

¹ AECOM Geneva; ² Geogeophy, CH

Characterizing groundwater contamination plumes in fractured rock aquifers is highly challenging because the majority of groundwater flow and contaminant migration is focused in narrow zones of preferential flow. Installing groundwater monitoring wells that intersect such narrow zones of preferential flow can often be hit-and-miss. Wells that do not hit fractured zones may turn out dry or if they happen to intersect a fracture, they may miss the contaminant migration pathway because they are not intersecting the right fracture.

A geophysical method called 3D electrical resistivity tomography was used to identify zones of preferential groundwater flow and potential contaminant migration. This technique was used to successfully implant groundwater monitoring wells and better characterize groundwater conditions where many previously drilled wells were dry.

The principle of 3D electrical resistivity imaging or “tomography” is similar to 2D electrical resistivity profiling, but differs in that electrical current is additionally applied between adjacent 2D profiles to obtain information between the profiles, thus creating a 3D view of the subsurface. Proprietary advanced data processing software using multiple inversion calculations coupled with subsurface knowledge from at least one boring for calibration enables the creation of high resolution images that reveal variations in ground resistivity and geological formations with depth.

Seven electrical resistivity 2D profiles were performed using direct and reverse pole-dipole from 62 to 115 m in length using 168 electrodes, 4 at a time to investigate to 20m depth. The 3D tomography was performed between 7 profile pairs with various array types in arbitrary position in the urban environment. A total of 11907 measurements were obtained and treated by the proprietary data processing software.

The results of the geophysical study revealed the sloping surface of the gneiss bedrock and a series of narrow channels or swales oriented at an angle to the slope. It was concluded that preferential flow of groundwater and contaminants may occur in the narrow channels or swales within the gneiss and so groundwater monitoring wells were installed in these zones. All of the new wells were productive and groundwater from the wells installed within the central channel was found to be impacted by contamination arising from the study site. Furthermore, groundwater from one of the distal wells installed within the central channel was found to be more impacted than groundwater from pre-existing wells installed more closely to the site, but not installed within the same channel structure, thus revealing that the contaminant plume had migrated in a discrete manner further than previously known.

The geophysical technique of 3D electrical resistivity imaging or “tomography” enabled a better understanding and visualization of the subsurface beneath a contaminated site to allow an optimal installation of groundwater monitoring wells and identify zones of preferential contaminant migration to better characterize the contaminant plume.

ThS 1d.2: Biological and geochemical indicators in site assessment and MNA

Assessment and monitoring of polluted soil using bio-indicators based on the most abundant multi-cellular organisms in soil

Cécile Villenave¹; Camille Chauvin; Anne Jimenez; Hélène Cérémonie

¹ ELISOL, FR

Context of biological analysis in contaminated land

In the context of polluted sites and soils, biological analyses have proved their interest in addition to classical physicochemical analysis (total metal contents and other contaminants). They provide informations on biological conditions of soil and can reveal soil dysfunctions linked to contaminant presence; they also allow to evaluate the efficiency of soil management or to define the conditions for use of degraded soil (ex: redevelopment of wasteland into an urban park). In the context of multiple contaminations, bioindicators can reveal the synergistic toxic effects of pollutants ("cocktail effect") on organisms living in soil, impacts not revealed by the individual quantification of each pollutant.

From public research to the proposal of a service for civil society: soil nematofauna as bio-indicator

The nematodes community (nematofauna) was first used to characterize soil quality in agriculture. Their use has then been extended to polluted soils in years 90/95. Applied to different polluted sites, this bioindicator has since proved its reliability, robustness and efficiency in many scientific studies (around 40 international publications on this subject and, in France, ADEME program "Bioindicators of soil quality").

Indeed, given the ubiquity of nematodes, their great functional diversity and sensitivity to their environmental conditions, the composition of this microscopic worms community reflects the biological status of any soil. Soil nematofauna is characterized by a standardized method (ISO 23611-4): nematodes are extracted from composite soil samples of about 300g. They are morphologically identified at the family or genus. The different parameters collected (around 40) are used to make the diagnosis of soil conditions. These parameters are (1) the abundances of the different taxa, (2) the abundances of the different functional groups, (3) nematological indices and taxonomic diversity.

Development of a database collecting existing data as useful tool for interpretation: ELIPTO ©

ELISOL environnement has developed a database centralizing data of nematode analyses, supplemented with those linked to the soil context and the environment: location, climate, physico-chemical analyses of the soil (classical analyses and pollutant concentrations), land use, agricultural practices, site history, etc...

This database can generate repositories of biological soil quality (based on nematofauna analyses) specific to the soil use (eg agricultural land, industrial sites, natural areas...) and integrating the impact of different cultures / soil practices. The use of these specific repositories allow to underline the relevance of the nematode analysis and to improve interpretation of nematofauna analysis (newly proposed in polluted sites) for a robust monitoring of soil quality .

ELIPTO© database is currently referencing data from 40 polluted situations (mainly by metals Cu, Pb, Zn ...) located in 16 different countries; results of the meta-analysis realized on these data will be presented.

Natural attenuation through integrated methodologies at a former manufactured gas plant

Johan van Leeuwen¹; Niels Hartog²; Annemieke Marsman¹; John. R Parsons³; Thomas Wagner³; Olaf Brock³; Foppe Smedes⁴; Rick Helmus³; Jan Gerritse¹

¹ Deltares; ² Utrecht University; ³ University of Amsterdam; ⁴ University of ma, NL

Background and objective

In natural attenuation, biodegradation of contaminants is often characterized by geochemical transformations and the detection of contaminant degrading microorganisms. Usually the plume extension is modeled and in some cases carbon stable isotope analyses are applied (CSIA). The field conditions were measured and samples were taken at a former manufactured gas plant where Pintsch gas has been produced by the Dutch railways from 1910 to 1954. During production the leftover tars were discarded on site in dug out lagoons. As a result an estimated 6000 tons of tar remain in the water saturated subsurface. The majority of the tar is situated at an aquitard around twelve meters below ground surface. The water soluble components have been transported by groundwater flow and have created an extensive downstream plume area with a footprint of approximately 15.000 square meters.

The objective was to gain better insight in the occurrence of anaerobic biodegradation within the source zone, the high concentration and low concentration plume and to assess if there are stagnant plume conditions.

Materials and Methods

Pure phase tar samples were obtained from the pool zone and partition tests were applied to identify the maximum dissolution of the individual components. Then monitoring wells along a groundwater flow path were selected for sampling and analysis of mobile tar component concentrations. Concentrations of mobile tar components were conventionally sampled using a peristaltic pump and innovative using passive samplers. We used a passive sampling technique to determine bioavailability of water dissolvable tar compounds and included partition tests and analysis on metabolites formed by microorganisms. This was done to learn more about the bio-availability of the water soluble compounds. Both samples were analyzed using GC-MS. Cations, anions and fatty acids were analyzed on a LC-MS as the geochemical compounds. Microorganisms involved in biodegradation were identified and quantified using qPCR. Signature metabolites for anaerobic degradation of different compounds were analyzed using LC-qTOF-MS. For CSIA both hydrogen and carbon fractionation was measured to study the extent of degradation of specific compounds in situ. To delineate geochemical conditions, field parameters like pH, EC, redox, oxygen, temperature were measured using hand held devices during groundwater sampling. Conservative transport and transport including biodegradation were both modeled using the data obtained from the site.

Results and Lessons Learned

In this presentation we will guide you through the applied sampling and analyzing techniques, and what we can learn from this integrated methodology. Anaerobic biodegradation and the stability of the plume in the different zones will be discussed and flow condition results, sampling and analyzing techniques will be illustrated.

Towards geochemical quality indicators of urban soils. Example of the "Ile de Nantes"(France).

Baptiste Sauvaget¹; Cécile Le Guern²; Chantal de Fouquet³

¹ BRGM/Mines ParisTech PSL; ² BRGM; ³ Mines ParisTech PSL, FR

Optimized management of excavated soil in urban areas involve setting up channels for reuse of unpolluted or slightly polluted soil, to limit landfill, widely practiced at present in France. In this frame, the French guide on the management of excavated materials proposes to ensure the compatibility of these materials with the geochemical background of the soils of the receiving site. But the definition of urban geochemical background and its representation issues are still under consideration. Indeed, if we consider that the geochemical background matches the usually encountered geochemistry in a given area, then its application to highly heterogeneous urban areas raise the question of the definition of "local diffuse pollution".

Basing our reflection on a real site, we confront the usual statistical approaches for calculating the geochemical background to spatial approaches. The case study site is a central quarter of the agglomeration of Nantes (France). This former industrial quarter under redevelopment generates a large volume of excavated soil (about 100 000 tones per year are expected between 2015 and 2025). The data used come from pollution diagnostics, which provide a significant amount of analysis on the entire area (about 1850 samples analyzed identified).

Initially, conventional methods of calculating the values of geochemical background are compared: upper whisker, 90th and 95th percentile and "Median Absolute Deviation". These calculations do not take into account the geographical position of data. Furthermore, the result of each calculation is reduced to a single value, while a range or a distribution could be preferable in practice, particularly for the guidance of excavated soils . These calculations are applied taking into account the soil typology developed by the BRGM and including three types of made grounds (questionable, various, and natural like) according to their intrinsic potential of pollution. If they show variations in geochemistry consistent with our knowledge of this typology of soil, the results strongly depend on the method of calculation. Furthermore, treatment of high values, at this stage, is simplistic, as values above a predefined threshold are deleted.

In a second step, a spatial approach is examined to determine urban geochemical background . This geostatistical mapping by kriging analysis uses land use descriptors as well as geology. The kriging analysis can separate the different scales of spatial variability, which can be used to define geochemical backgrounds .

Comparison of the two approaches shows the importance of mapping for the development of geochemical quality indicators of urban soils. These latter can support the management of excavated soil.

Natural attenuation of petroleum contamination in forest ecosystems: role of pedological and biological (microorganisms, flora and fauna) characteristics – the CONPET project

Coralie Biache¹; Stéphanie Ouvrard; Pierre Leglize; Apolline Auclerc; Thierry Beguiristain; Jean-François Masfaraud; Catherine Lorgeoux; Raymond Michels; Delphine Cattelain; David Billet; Noële Enjelvin; Aurélie Cébron; Alain Rakoto; Pierre Faure

¹ LIEC - CNRS/Université de Lorraine, FR

The CONPET project focuses on natural attenuation of petroleum contamination in forest soil. In order to understand the process within this original ecosystem, petroleum-derived compounds were analyzed in parallel to abiotic physicochemical parameters and biological indicators.

Scientists from complementary disciplines gathered around a unique site (forest of Haguenau, Pechelbronn, France) contaminated by petroleum seepages inherited from a tertiary source rock exhibiting spatial contamination gradients from the seepages to more distant areas. This studied site was one of the first petroleum exploitation in Europe and more than 5000 drillings were done since the 16th century, leading to numerous petroleum seepages for hundreds of years.

The main objectives of the study are i) to evaluate hydrocarbon contamination and its natural attenuation, and ii) to investigate soil organism adaptation to the contamination and their involvement in hydrocarbon transformation.

Two seepages (GUN and ETV) presenting different pedological characteristics were studied. Soil (0-20 cm and 20-40 cm depths, vertical gradient) and litter (when present) were sampled at five points along a 15 m-section (lateral gradient) from the seepage points. Hydrocarbon contents and molecular fingerprints were determined (GC-FID and GC-MS, respectively). Microbial activities (aerobic and anaerobic carbon mineralization, enzymatic activities related to C, N and P cycles) were measured on surface samples. Metagenomic DNAs were extracted to estimate bacterial and fungal abundance (qPCR) and diversity (Illumina sequencing). Root and shoot were sampled from the plant *Carex brizoides* in order to evaluate the level of antioxidant defense and lipoperoxidation. Mesoinvertebrates (mainly 0.2-2 mm microarthropods) and macroinvertebrates (> 2 mm) were studied through the sampling of litter and soil blocks.

On both sites, results were roughly similar. Hydrocarbon indexes showed lateral and vertical gradients of contamination. Molecular fingerprints indicated that petroleum was unaltered at the seepage and that degradation products appeared with increasing distance from the seepage. Similarly, microbial mineralization activities and enzymatic activities related to C and N cycles were higher at the closest points to the petroleum source and decreased toward the less contaminated area. In *Carex brizoides*, petroleum contamination caused little to significant oxidative stress on the two sites. While oligochaete, litter invertebrate and oribatida density tended to increase with the distance from the seepage in ETV site, this tendency was not observed in GUN site, where only litter invertebrate diversity increased.

These results indicated that natural attenuation occurred at both sites as evidenced by hydrocarbon molecular analysis. The resulting contamination gradient affected microbial densities and activities, fauna density or diversity in surface soil and litter, and induced stress response in plants. Statistical analysis will allow integrating the whole set of data in order to evidence links between chemical fingerprints and biological characteristics.

Marine phages as tracers for colloidal subsurface transport

Lukas Y Wick¹; Nawras Ghanem; Bärbel Kiesel; Dr. René Kallies; Hauke Harms; Antonis Chatzinotas

¹ Helmholtz Centre for Environmental Research - UFZ, DE

Although previous work examined the transport of viruses in the terrestrial systems only very few studies exist on the use of marine phages (i.e. non-terrestrial viruses infecting marine host bacteria) as tracers for reactive colloidal subsurface transport. Marine phages and their bacterial hosts are naturally absent in the terrestrial subsurface and, like most phages, can be produced easily at high concentrations and detected at an enormous sensitivity as low as one or two phages mL⁻¹ of recovered water. They hence are prone to be applied for the identification of paths of water flow and reactive transport (filtration) of colloidal particles. Here we systematically quantified and compared for the first time the effects of size, morphology and physico-chemical surface properties of six marine phages and two coli phages (MS2, T4) during transport in sand-filled percolated columns. Phage-sand interactions were described by colloidal filtration theory and the extended Derjaguin-Landau-Verwey-Overbeek approach (XDLVO), respectively. The phages studied belonged to four different families and comprised four phages never used in transport studies (i.e. PSA-HM1, PSA-HP1, PSA-HS2 and H3/49). Phage transport was influenced by size, morphology and hydrophobicity in an approximate order of size > hydrophobicity ≥ morphology. Two phages PSA-HP1, PSA-HS2 (Podoviridae and Siphoviridae) exhibited similar mass recovery as commonly used coli phage MS2. The differing properties of the marine phages may be used to mimic reactive transport of indigenous viruses or anthropogenic nanomaterials of differing characteristics and, hence, contribute to better risk analysis of potential sites of interest. Our results underpin the potential of marine phages as tracers for reactive transport of colloidal particles.

ThS 1d.3: Integrated methods in assessment and monitoring I

Characterisation and monitoring of in situ remediation of chlorinated hydrocarbon contamination using an interdisciplinary approach (MIRACHL)

Charlotte Sparrenbom¹; Torleif Dahlin¹; Håkan Rosqvist²; Henry Holmstrand³; Catherine Paul¹; Matteo Rossi¹

¹ Lund University; ² Lund University/Tyréns AB; ³ Stockholm University, SE

To meet future challenges in urban development with sustainable planning of cities, more housing is built via densification. This is done by expanding housing into often contaminated industrial sites. Growing concerns are the 2000 sites in Sweden contaminated with carcinogenic chlorinated hydrocarbons (dry-cleaners and industrial solvents).

The main remediation technique in Sweden is the costly and micro-ecologically damaging excavation and landfilling, i.e. moving the pollutants from one site to another. This strategy leads to large transports and exposure of dangerous compounds. SEPA recommends the use of in-situ methods, because an increased use thereof will lead to large savings for clean-up, and contribute to EU Water Directive requirements and to reach our national environmental objectives. A major challenge for in-situ remediation is to monitor the underground processes and verify its effectiveness. In this project, we work with an integrated monitoring by combining 4D (time-lapse) geophysical measurements using the Direct Current resistivity and time-domain Induced Polarization (DCIP) method, with smart biogeochemical analyses and Compound Specific Isotope Analyses (CSIA) to better understand and follow in-situ remediation processes.

Earlier investigations suggest that degradation of chlorinated hydrocarbons takes place in zones next to the free phase plume. In order to verify what the detected DCIP anomalies are due to, the groundwater may be sampled for physiochemical characterisation and verification of microbiological activity of bacterial indicator species (Physical and BioGeochemical Characterisation, PBGC). We will implement two types of groundwater monitoring; in-situ measurements of redox conditions via an oxidation-reduction potential/pH/temperature/electrical conductivity loggers as well as classical groundwater sampling and analysis of the contaminants, degradation products and general characterisation of groundwater constituents. Detection and enumeration of indicator species, such as *Dehalococcoides* sp, can be done by molecular methods such as quantitative polymerase chain reaction using species specific primers (e.g. Hargreaves et al. 2013 and Hedman et al. 2013).

The continuous DCIP observations during the remediation will together with the smart sampling and analyses help follow the development underground. Today, the monitoring of the remediation action and confirmation on "good enough" is very uncertain, due to the current investigation techniques with point source monitoring. With our combined approach, we aim to retrieve a comprehensive coverage of changes underground through time, possibly reduce uncertainties and costs for monitoring the in-situ remediation and deliver a more pedagogic image of the action underground for presentation and discussion with stakeholders.

References:

Hargreaves, S.K. et al. Reaction-and sample-specific inhibition affect standardization of

qPCR assays of soil bacterial communities. *Soil Biology and Biochemistry* 59 (2013): 89-97.

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Evaluation of aromatic hydrocarbon biodegradation by combined application of in situ and laboratory microcosms and metabolite analysis

Petra Bombach¹; Anko Fischer; Anett Thomas; Annika Beckmann

¹ Isodetect GmbH, DE

Decisions to implement bioremediation techniques for the clean-up of contaminated field sites require a comprehensive characterisation of the site-specific biodegradation processes. In the present study, the intrinsic biodegradation of phenol, alkylphenols, polycyclic aromatic hydrocarbons (PAH), dibutyl ether, tetrahydropyran as well as benzene, toluene, ethylbenzene and xylenes (BTEX) was investigated in an aquifer with high levels of aromatic hydrocarbon contamination at a former coal refinement site.

A laboratory microcosm study was conducted to assess the potential for biodegradation of mono- and polyaromatic hydrocarbons under in situ anoxic conditions as well as under oxic conditions using groundwater and sediments from the site. Biodegradation was detected by analyses of decreasing contaminant concentrations. Under anoxic conditions, biodegradation was only observed for phenol and methylphenols. Addition of oxygen resulted in the stimulation of biodegradation processes with a rapid decline of phenol, alkylphenol, PAH, dibutyl ether and BTEX concentrations. No evidence for tetrahydropyran degradation could be provided both under oxic and anoxic conditions within four months of incubation. To demonstrate the intrinsic biodegradation of hydrocarbons, in situ microcosms in combination with amino acid-stable isotope probing (BACTRAP[®]) were employed. Phenol was selected as key compound of interest due to its high abundance within the aquifer. In situ microcosms were loaded with ¹³C-phenol and deployed for 12 weeks in groundwater wells located in the centre, plume or fringe of the phenol plume to enrich indigenous groundwater microorganisms. Significant ¹³C-incorporation into microbial amino acids extracted from the in situ microcosms was found, providing clear evidence of phenol biodegradation at the field site. Evidence for the in situ turnover of PAH, BTEX and phenol were provided additionally by the detection of specific intermediates formed during biodegradation. 2-Naphthoic acid, toluic acids and hydroxy benzoic acid, intermediates of the naphthalene, BTEX and/or phenol biodegradation, were detected solely in groundwater samples collected from the contaminant source zone. In wells with lower BTEX concentrations, concentrations of metabolites may be below detection limits. In contrast, methyl naphthoic acid, a putative metabolite in the anaerobic degradation of methyl naphthalene, was found solely at the fringe of the contaminant plume. The integrative approach based on hydrogeochemical and microbiological indicators provides a strong basis for evaluating the in situ biogeochemical processes at contaminated field sites.

PFAS in the Netherlands, a problem? The results of a nationwide monitoring program at sites with a contamination potential

Hans Slenders¹; Tessa Pancras; Martijn van Houten; Corinne Koot; Arne Alphenaar; Aiko Hensums; Anton Roeloffzen

¹ Arcadis Netherlands, NL

SETTING

Worldwide PFAS receive increasing attention as a result of their PBT characteristics and presence in surface waters and drinking water pumping stations. The presence of PFAS in the environment are expected to be ubiquitous as a result of their widespread use. In the Netherlands however PFAS is not (yet?) considered to be a contaminant of real concern. Except for the presence in soil, groundwater and air at a production facility, the presence and resulting risks for human health have not been proven elsewhere. This is mainly because they have not been looked for. Given the serious cases in Sweden, Australia, Germany and US, it must be assumed that there are similar situations in the Netherlands. Moreover it is expected that a more diffuse contamination might be present.

The Expertise Centre, with main members Witteveen+Bos, TTE and Arcadis have initiated a nationwide monitoring program at sites with an elevated risk on PFAS. In parallel they are working on a scope of action, with guidelines, technical documents and the gathering of data from other sources such as provincial networks, drinking water station monitoring programs. This abstract however only focusses on the monitoring program, field data and evaluation. Another abstract (Van Houten et al.) focusses on the scope of action and guidance's.

CONSORTIUM AND METHODOLOGY

Started with two symposia on the topic, the Expertise Centre took the initiative to gather site owners (Defence, Municipalities, Provinces, water boards, and regional authorities) and raise a budget for random checks at their sites. From this budget, and based upon the knowledge from the CONCAWE document and German Guidelines, a list of priority sites and sampling guidelines were developed. A wide range of activities and sites were selected (landfills, chrome plating workshops, fire training areas, fire incidents, regional monitoring networks etc.). The site owners cooperated in gathering site info and building conceptual models of the sites. The group of site owners regularly met to discuss procedures, developments and policy.

The sampling guideline contained directions to avoid the use of PFAS containing equipment and correct sample containers. Care was taken to select uniform analyses and detection limits. On those samples where PFAS were detected an additional Total Oxidisable Precursor analyses was performed in order to detect the hidden part of the PFAS iceberg. (the PFAS components that do not show in regular, standardized analyses). All in all 25 sites have been visited, sampled and analyzed. The results are reflected against available threshold values in the Netherlands and Europa (The EQS from the WFD).

RESULTS

The monitoring campaign currently is at the top of execution. The first results are available. After 25% of the campaign, no concentrations in excess of threshold values have been detected that need corrective action. By 2017 the program will be completed and the results evaluated.

MULTISCALEXPER: multiscale empirical treatability of the pollutants combined or not with multiscale numerical modeling: advantages, disadvantages, redundancies and failures on each scale and approach type.

Ioannis Ignatiadis¹; Stéfan Colombano¹; Hossein Davarzani¹; Stéphanie Betelu¹; Romain Rodrigues¹; Fabienne Battaglia-Brunet²; Julie LIONS¹; Samuel COUSSY¹

¹ BRGM; ² BRG, FR

To understand, evaluate and finely predict the spatiotemporal pollutants evolution in environments, under natural attenuation or remediation (by bio- or chemical treatment), it is necessary to resort with: i) geophysical, physico-chemical and biological measurements on site, ii) laboratory treatability experiments, and iii) numerical models.

In practice, that results in the use of parameters and/or empirical models for modeling on the scale of an actual site. This use permits to reproduce the controlled tests in laboratory or on site, which are used then as validation tests. However, their use for predictive calculations is problematic for the tests, where it is impossible to sweep the whole of conditions and couplings met in the system of interest. Within the framework of a predictive model, the improvement or invalidation of the empirical parameters/models must thus be done on the basis of comprehension of the subjacent mechanisms and their mutual interactions. With this purpose, it is necessary to have recourse to mechanistic and multi-scale approaches, which makes it possible to choose in a reasoned way the dominating mechanisms and their simplified exemplification.

MULTISCALEXPER aims to develop multi-scale experimentation actions, make use of numerical modeling on all the levels (from dimensioning to results interpretation). They will be carried out using numerical tools and multi-scale pilots. More particularly, it is a question of defining a dimensioning methodology for multi-scale experiments, based on numerical approaches. This project aims at reinforcing the depollution techniques on: i) the small scales in order to be able to interact with academic laboratories, working at increasingly smaller scale, and especially ii) the great scales in order to be able to interact with depollution firms, directed in the reverse way of increasingly large scale as fast as possible.

The first deliverable of the project was the critical analysis of about 15 BRGM collaborative projects, carried out in the depollution domain both of organic and inorganic pollutants. The projects were evaluated on the basis of a grid of techno-economic criteria and compared to the scale imitated, according to two approaches: 1) multi-scale experimentation (from a molecular scale to that of an actual site), in batch, column, plurimetric pilot, in situ demonstration, partial or total depollution of a site and 2) multi-scale numerical modeling.

The advantages, disadvantages, redundancies and failures concerning each approach and scale were highlighted. It results very rich issues from it, showing that only scientific and technical knowledge were not enough to solve complex problems. In a way much more pragmatic, it is shown that it is necessary to innovate in approaches and scales. In particular, in porous media, the feasibility of an integrated approach on a precise depollution subject depends on the pollutant behavior characterization and treatability on a large scale. The work, in different media and contexts, will have to be organized to cover all the stages allowing pollutants treatability by controlled, reasoned and pragmatic implementation of the methods and scales.

Application of the top-cut model for estimating chlorinated solvent contamination in soils: a methodological comparison.

Mariangela Donati¹; Aurélie Malvoisin¹; Gaël Plassart¹; Chantal de Fouquet²

¹ Envisol; ² Mines ParisTech PSL, FR

Key words: Top-cut model, kriging, soil contamination, long-tailed distribution.

The long-tailed distribution of organic pollutants (hydrocarbons, chlorinated solvents) in soils raises specific problems in estimating and mapping the concentrations. Some high values strongly impact the experimental variogram and extend the spots of pollution on the estimation maps.

Non-linear geostatistical models, such as the anamorphosed Gaussian model, have been proposed at the end of the 70. But these well-founded methods are rarely used by environmental consultants, mainly because of time constraints and because the hypotheses of the available models are not always satisfied.

An empirical method widely used by environmental consultants consists in truncating the high values to gain robustness in the variogram analysis. The truncation value is arbitrary, even if it has a great influence on the estimated concentrations of the polluted areas. Proposed to handle heavy-tailed distributions of ore deposit grades, the top-cut model justifies the use of truncated values and it corrects the underestimation of the mean caused by truncation [1].

With the decomposition of the variable into three components (the truncated value, a weighted indicator above top-cut value and a residual) this model makes the variographic study more robust and guides choosing the truncation value. The top-cut model has been tested with success on a hydrocarbon contaminated soil.

In the case of a chlorinated solvent contamination, a detailed comparison between estimation methods is performed: kriging with direct or indirect variogram fitting, estimation within the top-cut model, with respectively structured or pure nugget residual. Different techniques of cross-validation are considered and the results are compared taking into account the influence of a limited number of high concentrations on the quality of the estimation.

The results show that the top-cut model with nugget residual is robust, even if the hypotheses of the model are not perfectly satisfied. Conclusions are provided to implement the model in engineering consulting offices.

The results have been obtained in the framework of the Contrasol Project, under public funding of ADEME.

[1] Rivoirard J., Demange Cl., Freulon X., Lécureuil A., Bellot N. 2013. A top-cut model for deposits with heavy-tailed grade distribution. *Math. Geosciences*, 45(8) 967-982.

ThS 1d.4: Integrated methods in assesment and monitoring II

Fate and Transport of PFAS at an Agricultural Site Contaminated With Blended Compost

Thomas Held¹; Michael Reinhard¹; Rudolf-Karl Teichmann²; Andreas Schmid²; Reiner Söhlmann³; Manfred Flittner³; Gabriel Striegel; Ulrich Lang⁴; Armin Durach⁴; Thomas Gudera⁵

¹ Arcadis Germany GmbH; ² Stadt Baden-Baden; ³ Landratsamt Rastatt; ⁴ Ingenieurgesellschaft Kobus und Partner; ⁵ Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, DE

The largest site in Germany contaminated with PFAS (per- and poly-fluorinated alkylic substances) is located in the southern part of the country. Approximately ten years ago, a soil fertilizer contaminated with PFAS, was applied to agricultural land to a depth of 30 cm, resulting in PFAS contamination over an area of 3.7 km². In the fertilizer polyalkylphosphates (PAPs) and some perfluorinated compounds could have been detected. Commercial there is no analysis available for the detection of PAPs and therefore an alternative investigation method had to be employed. Soil and groundwater containing high concentrations of perfluoroalkyl carboxylic and sulfonic acids (mean value: 250 µg/kg), suggested that the original contamination had already undergone biotransformation to form persistent perfluoroalkyl acids (PFAAs). The partly biotransformable polyfluorinated compounds are called precursors. Hence, the so-called TOP (total oxidizable precursor) analysis was used to investigate the soil. During TOP analysis the sample is initially analyzed without treatment, then oxidized chemically to transform all precursors to persistent PFAAs and analyzed again. The concentration increase is then used to quantify the precursors. The results showed that substantial amounts of precursors (approximately 50 % of total PFAS) were present in the soil, but the groundwater was nearly free of precursors.

The industrial sludge derived PFAS contamination was overlain by a second PFAS contamination event originating from the use of aqueous firefighting foams (AFFF). The two sources were found to have different PFAS distributions. Precursors were found in groundwater at significant concentrations (approximately 20 % of total PFAS). It is hypothesized that hydrocarbon surfactants also occurring in AFFF created a strongly reducing biogeochemical environment, conserving the aerobically transformable precursors, whereas in the remainder of the area, oxidizing conditions allowed a fast and nearly complete biotransformation of the precursors to PFAAs immediately after transport into groundwater.

Remediation of PFAS contaminated soil would be required if PFAS accumulation in groundwater was found to exceed the intervention values set by regulators. However, at the beginning of the project the rate and timeframe for PFAS transportation from soil to groundwater was not known and in addition, the rate for precursors biotransformation to persistent PFAAs was not known. Hence, a study was initiated to determine site specific sorption coefficients. These sorption coefficients were used in a contaminant transport model to calculate the extent of the plume and to predict the influence future soil remediation measures would have. An additional study should determine the rate of the microbial production of PFAAs from precursor contaminated soil.

Environmental assessments on schools located on or near former industrial facilities: feedback on the use of attenuation factors for prediction of indoor air quality

Virginie Derycke¹; Hubert Leprond¹; Mathilde Scamps¹; Clément Zornig¹; Dominic Gilbert²

¹ BRGM; ² Ministère de l'Environnement, de l'Energie et de la Mer, FR

As part of 2nd and 3rd French National Environment and Health Action Plan, soil environmental assessments were carried at national level on schools built on or near past industrial facilities. It aims at evaluating if the soil, drinking water and/or air quality has been altered by those former activities. Environmental assessment included selection and evaluation of relevant exposure pathways using evidence-based information (industrial activities description, site history, school facilities, nature of potential contamination and analysis of relevant compounds and media). The French Ministry of Environment has entrusted the French Geological Survey (BRGM) with the task of delegated contracting authority to undertake organization of the environmental assessments and to ensure the homogeneity of the action and costs control at national level.

The present work focuses on the evaluation of school's indoor air quality that may be altered due to vapor intrusion and is based on data from 35 school sites spread across 9 regions allowing calculation of 599 dilution factors all compounds included. It is a feedback on the use of dilution factors (indoor air/soil gas) for the prediction of indoor air concentration for risk assessment using the following three phases protocol: (i) determination of the presence of potential volatile compounds according to reported past industrial activities, (ii) analysis of soil gas multiplied by a relevant dilution factor to estimate indoor air quality, (iii) sampling of indoor air if estimated air quality is above indoor air guidelines (toxicity reference values). Dilution factor are used in phase 2 to warrant further analysis in the indoor air. Dilution factors are chosen according to the school facilities and the media analyzed (soil gas or subslab gas). Their choice is based mainly on US EPA's feedback on vapor intrusion (US EPA, 2015) and models from Johnson-Ettinger (1991). However, differences in climate between US and France as well as differences in facility uses (air conditioning) or construction type (residential versus schools) may bring differences in vapor dilution and therefore may induce different values of dilution factors. Feedback of dilution factors included design, elaboration and implementation of a specific database and statistical treatment of data. The database allows input of building characteristic and soil gas sampling and analysis parameters such as temperature, slab thickness and quality, compounds concentration as well as data pairing (indoor air/soil gas) for calculation of dilution factor. The present work provides a statistical analysis of the data stored in this database. Data below quantification limit as soil or subslab were kept in the database but removed from the data treatment since they did not account for any vapor intrusion pathway. Data analysis focuses on 9 compounds (petroleum hydrocarbons and chlorinated solvents) and the calculation of 599 dilution factors all compounds included. Statistical analysis is still currently carried out and further results and conclusion will be included.

Conceptualization of residual contamination using depth discrete monitoring of dynamic PCE concentration changes during and after remedial pumping and pumping test

Mette M Broholm¹; Annika Fjordbøge¹; Klaus Mosthaf¹; Philip J. Binning¹; Bentje Brauns¹; Theodora Tsitseli¹; Poul L. Bjerg¹; Henriette Kerrn-Jespersen²

¹ Technical University of Denmark; ² Capital Region of Denmark, DK

PCE contamination in a fractured limestone aquifer at a former dry cleaning facility in Hedehusene, Denmark, has undergone pump and treat (P&T) remediation with re-infiltration for nearly 10 years after partial source removal in the overburden. A plume of PCE had migrated > 200 m down gradient prior to initiation of P&T remediation at the site. The pumping and re-infiltration has diverted the groundwater flow, and hence the transport of PCE, in the fractured limestone aquifer adding to the complexity. The distribution of PCE remaining in the limestone aquifer source and plume area was not well understood challenging evaluation of the remedial design.

The objective of the investigations was to obtain an understanding of flow and transport processes in fractured limestone and generate a conceptual model for the residual contamination in the limestone aquifer at the site.

High resolution PCE distribution in the aquifer and dynamic PCE concentration changes during discontinued remedial activity and during a pumping test were determined. Due to instability of boreholes in the upper crushed and highly fractured zones of the limestone, limestone cores suffered significant core-loss, and most boreholes at the site were equipped with relatively long screens and sand-packs. Passive, semi-passive and active groundwater sampling methods were tested and applied in addition to core sub-sampling to obtain high resolution PCE data. Samples were collected from several wells at the site and in the plume during ongoing P&T with re-infiltration, during discontinuance of the remediation, and during a pumping test (with multiple tracer injections). The high resolution PCE data were combined with a 3D site specific fracture model calibrated based on a multiple tracer injection test to create a conceptual model for the PCE source area and plume.

The highest PCE concentrations were observed in the upper crushed Copenhagen limestone and the highly fractured Copenhagen limestone, with lower and decreasing concentration with depth in the underlying Bryozoa limestone. Significant concentration increases were observed when remedial pumping and re-infiltration was discontinued (in one case from < 1 to > 250 µg/L PCE). The concentration changes in the near source area were very dynamic with a fast increase followed by a decrease and a second increase in concentrations in the fractured Copenhagen limestone. The dynamic changes observed are most likely due to fast fracture flow and back diffusion from the limestone matrix in areas with higher residual contamination. The crushed limestone responded more slowly due to its lower hydraulic conductivity compared to the fractured zone. Concentrations were lower and responded only weakly to pumping in the Bryozoa limestone. The remedial pumping and re-infiltration at the site has circulated water through some large fractures resulting in partial clean-up of a small area. The P&T system has had little effect on contamination in other zones and has resulted in the spreading of contamination outside the treated zone. The new conceptual understanding can be used to optimize remediation.

Methods and tools for the characterization of subsurface contamination source

Juliette Chastanet; Jean-Marie Côme

GINGER BURGEAP, FR

The French regulation on contamination soils highlights the necessity to remove contamination source zone whenever it is technically and financially acceptable. However it can be very complex to delineate a source and / or to produce quantified argument for source management to the authorities. Our work focuses on zone contaminated with organic compounds as these are the main contaminant encountered on French contaminated sites. In soils, these compounds distributes in four phases: a non-aqueous phase liquid or NAPL (mobile or not), a dissolved phase, a gaseous phase and a sorbed phase on the surface of the solid grains. Hence, the assessment of these can be tackle with different ways by sampling one or more phases. Among other methodology (UPDS report 2014, BRGM report 2016), the MACAOH source zone characterization methodology (Côme et al, 2006) recommends two methods, one based on water sampling and the other on soil sampling.

The water sampling method consists in interpreting dissolved contaminant concentration compared to equilibrium concentration and includes spatial interpolation and cartography. For this approach, an appropriate way to sample the water is multilevel as the NAPL tends to accumulate in specific areas in soil. Among multilevel tools, a new device has been recently developed in the framework of an ongoing R&D project; it is a passive multilevel sampler that shows satisfying results in measuring dissolved contaminants. Note that the method can be applied to a source zone that is only present in the saturated zone but it could be easily transposed to vadoze zone with soil gas sampling (Traverse et al, 2013). It enables the estimation of source zone volume but does not allow for quantification of the NAPL volume.

With the soil sampling methods, the soil concentrations are interpreted as NAPL saturations, which can require a computation tool such as OREOS. This software allows computing the distribution of contaminants in the 4 phases of the soil from soil concentrations. It then detects the presence (or not) of NAPL in soil samples and compute NAPL saturation as well as soil concentration threshold above which NAPL is present. The results can then benefit from spatial interpolation and cartography for source zone quantification. With this approach, soil sampling method must be adapted according to the characteristics of the contaminants. Whereas the MACAOH protocol has showed its efficiency with volatile contaminants, a new protocol is tested in the ongoing so-called SOSIE R&D project to tackle soil with high level of contamination (mobile NAPL) and in order to limit the loss of contamination during sampling. The soil sampling method enables the assessment of the source zone volume, the NAPL volume, and its spatial distribution.

These methods will be applied on several industrial contaminated sites from sampling techniques to volume and mass assessment of the source zone. We will demonstrate how the source characterization with advanced tools provides quantified arguments for contamination source management.

Detailed characterisation on non-aqueous phase liquid migration pathways in a complex coastal setting

George Flower; Jonathan Raven

Arcadis UK, GB

Severe winter storms of 2013/14 removed around 0.5m of sand from Portslade Beach in south England, with spring low tides exposing new localised rock outcrops. Neat, dark brown tar/oil was observed seeping from the fissures and gaps in the rock. The exact nature and origin of the non-aqueous phase liquid (NAPL) was not known, but the seepages caused staining and a heavy sheen. This, together with a powerful 'creosote-like' odour, was severely impacting the amenity value of the beach and local residents. Part of Shoreham Port was previously occupied by Portslade Gasworks. Operational between the 1870s and 1970s, the land and groundwater beneath was known to be variously and widely contaminated by a range of substances including coal tars and other pollutants. A credible source therefore existed, but the pathway and migration mechanisms producing the unique seepages of NAPL were unclear. The potential risks to beach users (contact with contamination) and local residents (vapour inhalation and odour) had been assessed by Public Health England (PHE), and Brighton and Hove City Council (BHCC) respectively.

All existing data and borehole information was combined, culminating in a detailed preliminary Conceptual Site Model (CSM) depicting the inner harbour through to the intertidal zone beach. The CSM identified uncertainties, data gaps and potential pollutant linkages. These directly fed into the design of the investigation, helping set the aims and data objectives that had to be secured. The ground investigation was designed with the specific aim of identifying the migration routes of the NAPL. Traditional site investigation techniques were modified to enhance the return on investment, while also minimising the potential for exacerbation of NAPL mobility. These included: the use of seismic refraction surveying along the low tide area of the beach to identify the sub-surface geological structure, a ground penetrating radar (GPR) survey in the former gasworks to locate potential intact or non-intact point sources, the installation of nested monitoring standpoints with automatic water level loggers, and detailed forensic testing of NAPL samples.

The unique methodology developed to investigate this complex site setting will be described, and the results summarised, identifying the benefits the investigation approach brought in collection of data which enabled robust decision-making, the cost effectiveness of the design and the techniques adopted to minimise risks associated with undertaking works in a dynamic coastal environment.

ThS 1e.1: Groundwater-soil-sediment-surface water interaction I

Characterization of how contaminants arise in a dredged marine sediment and analysis of the effect of natural weathering

Vincent Chatain¹; Julien Couvidat¹; Mostafa Benzaazoua²; Hassan Bouzahzah³

¹ Université de Lyon - INSA Lyon; ² Université de Lyon, Université Jean Monnet; ³ University of Quebec in Abitibi-Temiscamingue (UQAT), FR

Several million tons of sediment are dredged each year from the main ports in France. They are contaminated to different degrees but their management is strictly controlled. When removed from water, these sediments are very reactive, therefore their geochemical behavior must be understood in order to avoid dispersion of contaminated lixiviates in the surrounding soils. To do this, a thorough understanding of how of the contaminants occur in the sedimentary matrices would enable a suitable and adapted treatment to be envisaged, or even a valorization of all or part of the materials. To do this, it is necessary to evaluate the principal physico-chemical parameters, and also make advanced mineralogical analyses. In fact, these sediments are highly contaminated by metals, notably copper (1445 and 835 mg/kg, in the raw and naturally-weathered sediments, respectively), lead (760 and 1260 mg/kg, respectively), zinc (2085 and 2550 mg/kg, respectively), as well as by organic contaminants (PAH, PCB) and organometallics (organo-tins). A high concentration of sulfides was also observed both in the raw sediment kept under water (3.4 %MS of pyrite, and the presence of different copper sulfides), and in the sediment which had been naturally weathered in the open air (2% MS pyrite), and in particular framboïdal pyrite was present in the two materials.

The presence of reactive mineral species in the naturally-weathered sediment can be explained by the deposit of a protective layer, composed of sulfide and sulfate oxidation products and iron oxides, thus preventing oxygen from diffusing through to the sulfide surface. In addition, the presence of aggregates rich in aluminosilicates enveloping the minerals could also explain why these sulfides are still present in the naturally-weathered sediment. As organic matter is one of the principal constituents of the sediments (5.8 and 6.3% MS COT (% mass of sediment, total organic carbon), in the raw and weathered sediment, respectively), the aggregates are probably partially made up of stable and resistant humic material. It therefore appears that the weathering and the bioremediation treatment have led to a significant decrease in PAHs and organo-tins, but not in PCBs. The evolution of the granulometric structure and the distribution of the metallic contaminants could therefore enable us to envisage a treatment by sieving, and a possible valorization of the dredged sediments in civil engineering.

Factors governing sediment quality (PAH) in rivers

Peter Grathwohl¹; Marc Schwientek¹; Hermann Rügner¹; Michael Rode²; Ulrike Scherer³

¹ University of Tübingen; ² Helmholtz Centre for Environmental Research UFZ; ³ Karlsruher Institut für Technologie (KIT), DE

Transport of persistent hydrophobic pollutants such as PAHs or PCBs in rivers is coupled to transport of suspended particles. Concentrations of pollutants on suspended solids may be calculated based on a linear correlation of total concentrations of pollutants versus turbidity and/or total suspended solids in water samples collected e.g. during high discharge events. Results from catchments in South-West (upper Neckar River and tributaries) and Eastern Germany (Bode River and tributaries) revealed that correlations are robust and catchment specific. Long term measurements from sub catchments of the upper Neckar River also showed that pollutants on suspended solids are more or less time invariant at least in smaller catchments. The degree of contamination of these suspended particles was shown to depend on the mixture of "polluted" urban and "clean" background particles. The contamination of riverine sediments and suspended matter with hydrophobic pollutants is thus typically associated with urban land use. It is, however, rarely related to the sediment supply of the watershed. In this study it is shown for a suite of catchments with contrasting land use and geology and ranging in size from 100 to >3000 km² that the contamination of suspended particles with polycyclic aromatic hydrocarbons (PAH) may be predicted based on the ratio of inhabitants residing within the catchment and the catchment's long-term sediment yield. As data on sediment loads are rare and the implementation of appropriate monitoring programs is expensive and time consuming modelling of sediment loads based on the universal soil loss equation is proposed. Although this method lacks a physical basis, it has been shown that it is feasible at larger scales and leads to reasonable results at low costs. This is further demonstrated in this study by comparison with data for sediment loads measured in selected tributaries of the River Neckar catchment using long-term on-line turbidity measurements. In principle, the method allows for the assessment of pollutant concentrations in river bed sediments for catchments with comparable technical standards and standards of living, or – where a pronounced deviation from the predicted behavior is observed – gives hints to additional processes or pollutant sources which might have been overseen but have to be considered.

Identification of PFAS Precursor Transformation Down-Gradient of Source Zones. Discuss Relevant Geochemical Conditions at an Airforce Base in Australia

*Dora Chiang*¹; *Rachael Casson*²

¹ AECOM; ² AECOM Australia, AU

Knowledge regarding the complexity and mechanisms of fate and transport of Per- and Poly-Fluoro-alkyl Substances (PFAS) in the environment is evolving rapidly. Recent research has focussed on bench scale trials (mostly flow through columns) under controlled conditions. Presently, there is scant information evaluating the correlation between the findings of bench scale trials and 'real world' conditions.

To bridge the gap in understanding, a study has been conducted at an aviation facility (Study Area) to identify environmental conditions at and near a water retention dam that may induce the transformation (hydrolysis / oxidation) of PFAS precursors, resulting in elevated concentrations of PFAS down gradient of the primary source.

The Study Area forms part of a larger investigation area (50 km²) across the entire aviation facility and neighbouring land and is located on the east coast of Australia. The Study Area is located on highly permeable sandy soils; a shallow groundwater table with complex migration pathways; dynamic interaction between rainfall, surface water and groundwater; and runoff draining through extensively modified networks to two separate marine environments, containing wetlands and commercial fishing.

The surface water and groundwater is extensively used for residential and agricultural purposes.

PFAS contamination has been identified in soil, sediment, surface water, pore water, groundwater, concrete and biota (plants, aquatic species and birds). The PFAS plume is ~ 20 – 25 km².

Soil, groundwater, surface water and sediment were collected in winter from a transect and were analysed for 28 – 31 different PFAS using a high resolution Quadruple Time of Flight Mass Spectrometry (Q-TOF / MS) and low resolution Liquid Chromatography (LC – MS/MS). The same samples were tested using the Total Oxidisable PFAS (TOP) Assay; cations / anions; Total Organic Carbon (TOC); and Dissolved Organic Carbon (DOC). Geochemical parameters including pH, temperature, oxidation-reduction potential, dissolved oxygen and conductivity, were measured for groundwater and surface water.

Results indicated that:

- 27 PFAS were identified in soil, 19 PFAS were identified in the groundwater, 10 in the sediment and 12 PFAS in the surface water.
- As expected, the greatest oxidised PFAS mass generated were the Perfluoroalkyl carboxylic acids (PFCAs) - the highest concentrations were detected in the soil and sediment at the primary source area. Post TOP, PFCA increases were tens of thousands of %.
- Oxidisable precursor mass was also identified in groundwater and surface water, although to a much lower degree.

This presentation will outline the correlations between geochemical parameters and potential PFAS transformation and the implications for migration. Particular focus will be given to the dynamic interaction between surface water and groundwater for PFAS transformation. This information can be used to increase the accuracy and calibration of conceptual site models and hydrogeological modelling.

Understanding PFAS transformation potential also permits future professionals to select the most appropriate management /remediation strategy for a site.

Assessment of groundwater contamination impacting stream ecosystems

Poul L. Bjerg¹; Anne T. Sonne¹; Jes J. Rasmussen²; Sebastian Höss³; Vinni Rønde¹; Walter Traunspurger⁴; Ursula S. McKnight¹

¹ Technical University of Denmark, DK; ² Aarhus University, DK; ³ Ecosa/University of Bielefeld, DE; ⁴ University of Bielefeld, DE

Streams are significantly impacted by a large number of micropollutants and their transformation products (e.g. pharmaceuticals, chlorinated solvents, pesticides/biocides, nutrients, heavy metals), leading to a severe degradation of essential ecological functions and services. The large diversity of compounds and their sources makes the quantification of their occurrence and toxicity a challenging task. Conventionally, chemical impacts to ecosystems are assessed one compound/group of compounds or one source type at a time. We presume this will give us a good indication of the impact of a particular stressor. Our hypothesis, however, is that this will underestimate the combined impact caused by chemical cocktail effects, and interactions between stressors. Moreover, a stream system impacted by multiple stressors has a high chronic stress level, so even small perturbations on top of changes in water flow or additional chemical stressors may be detrimental to the stream health.

To address this issue, we identified contaminant sources and chemical stressors along a 16-km groundwater-fed stream corridor (Grindsted, Denmark) to quantify the contaminant discharges, and potentially link the chemical impact and stream water quality. Potential pollution sources include two contaminated sites, aquaculture, wastewater discharges, and diffuse sources from agriculture and urban areas. Data for xenobiotic organic groundwater contaminants, pesticides, heavy metals, general water chemistry, physical conditions and stream flow from three campaigns in 2012 and 2014 were assessed. Ecological status was determined by monitoring meiobenthic (e.g. nematodes) and macrobenthic invertebrate communities.

The results show a substantial impact on Grindsted stream from multiple sources of many origins. The groundwater plume from the Grindsted factory site caused elevated concentrations of chlorinated ethenes, benzene and pharmaceuticals in both the hyporheic zone and the stream water persisting for several km downstream of the discharge area. Heavy metal concentrations were found around or above the threshold values for barium, copper, lead, nickel and zinc in the stream water, hyporheic zone and streambed sediment. The calculated TU was generally similar along the stream, but for arsenic and nickel higher values were observed where the groundwater plume discharges into the stream. Thus, the overall chemical stress in the main discharge area is much higher than upstream, while it gradually decreases downstream.

The ecological results indicate a change in community composition for both meio- and macrobenthic fauna, pointing towards the presence of a local impact resulting from the discharging contaminated groundwater. Ecological impacts could be related to xenobiotic compounds coming from groundwater, as well as to the presence of trace metals of diffuse and/or biogenic origin in the same area, but linkage to one specific factor was not possible. This work highlights the importance of a holistic assessment of stream water quality to identify and quantify the main contaminant sources and resulting chemical stream stressors leading to potential ecological impacts.

Tackling sediment pollution in Flanders: identification of (potential) hotspots of sediment pollution linked with (former) risk activities

Carlo van den Berg¹; Goedele Vanacker²; Karen Van Geert³; Ward De Cooman

¹ Arcadis Netherlands; ² OVAM - Flemish Waste Agency; ³ Arcadis Belgium, BE

Sediments, an important resource, needs protection and targeted management. The OVAM took action to tackle the legacy sediment contamination and to prevent new contamination. To support the soil experts in decision making, they commissioned a study to identify and allocate potential sources of severe water contamination (hotspots).

Approach: The selection of hotspots is based on previously conducted research, recent and actual emission figures and expert judgement.

- A 1985 survey of hundreds of Dutch companies, discharging wastewater directly to the surface water resulted in a striking outcome that a vast majority of industrial discharges came from a limited number of companies
- IMJV-database: provides easily accessible key environmental data from industrial facilities in Flanders, about the amounts of pollutant releases to air, water, land and in waste water (91 listed key pollutants)
- Key-soil-expertise in history of industrial techniques/processes, complemented the selection with obsolete, but relevant, historical activities.

This revealed (former) industrial activities with potential hotspots for sediment contamination.

Knowledge to method

1: Vlarebo: Risk activities, facilities with a relatively high risk for soil contamination, are documented/standardized. Vlarebo equivalents of industrial activities were selected as the most potential hotspots for sediment contamination.

2: Ground Information Register (GIR): contains all information on soil quality and risk activities (Vlarebo) performed on a parcel of land. The register was completed with information from (very) old environmental permits, which proved very valuable.

3: Finding criteria: With the GIR 4 key factors were constructed:

- Cadastral plots: identify and locate hotspots
- Vlarebo: identify (former) industrial sectors: gas plants, tanneries, paper mills, wood preservation, textile dyeing, etc.
- Start date of the environmental permits, provides insight in historical development.
- The number of Vlarebo and environmental permits - related to a cadastral plot - gives an indication on the extent of the activities/expansion of the company.

Method: With the available data/criteria, prioritizing hotspots is possible in multiple ways: intrinsic (gas factory always above a paper mill), historical (brownfields), size (large industrial sites). We opted for an 8 score classification. This range of categories makes it easy to point out top priorities (2-3%/±300 sites) and provides the ability for policy/decision makers to consider aspects like work stock, budget and planning

Exchange and applications

All this results in a geographical data file, that can easily be linked with other databases. The hotspots were integrated in the sediment monitoring network and FEA dredging database, containing the results of the ecological characterization of sediments.

Through the exchange of information, the FEA network can be optimized, and in case of future dredging, (unexpected) contaminants can be taken into account. Vice versa, our method can be verified and calibrated, using practical FEA data.

The database with the risk activities possibly causing sediment pollution will be available in Dutch/English.

ThS 1e.2: Groundwater-soil-sediment-surface water interaction II

Metal trace elements and sodium chloride transfer dynamics in road retention basin

Lucie Barbier¹; Rémi Suaire¹; Béatrice Béchet²; Ivana Durickovic¹; Marie-Odile Simonnot³

¹ Cerema; ² IFSTTAR; ³ Université de Lorraine, FR

Metal trace elements (MTEs) (e.g. Cd, Cu, Ni, Zn) are present in road environment, because of pavement and vehicle degradation. Besides this chronic pollution, an additional seasonal pollution is due to the spreading of until 2000 kt per year of deicing salts (mainly chloride sodium) in France.

Runoff water transports this pollution load into retention basins before rejection into the environment. The adverse effects of NaCl on the environment have been highlighted. Indeed, many studies pointed out the role of deicing salt in altering water chemistry in the natural environment and its influence on the mobility of MTEs in roadside soils. In parallel, many studies have shown MTE mobility within retention basins. However, few authors focused on the NaCl impact in retention basins. Yet, some studies have shown its influence on retention structures, including its impact on the water stratification and the increase of toxicity due to its presence (Norroström 2005 Appl. Geochem. 20, 1907-19). Suaire (2015, thesis) also showed the influence of NaCl on the physico-chemical parameters in retention basins and the speciation of MTE. So, it is possible to consider effects of NaCl on the behavior of the basin, where its presence could affect the mobility of MTEs bound to sediments. The effectiveness of retention basins during winter periods could be debatable.

The present objective is to bring better understanding of the role of NaCl on the dynamics of pollutant transfer in a detention basin and to determine the predominant mechanisms involved. The effect of deicing salts on the functioning and efficiency of basins is studied based on the dynamics of transfer of MTE to the water-sediment and sedimentation mechanisms interface. As a matter of fact, its retention and further processes are influenced by physico-chemical interactions and also by hydrodynamics.

In order to assess the influence of the basin design, two basins of different designs have been monitored for two years. This work includes water and sediment characterization, investigation of sediment settling, and the role of physico-chemical interactions on pollutant dynamics (mainly conductivity).

The first results focus on the chemical characterization of water and sediments of both basins. The aim is to determine the quality of the environment and establish geochemical balances. Differences have been recorded between both basins including variations in granulometry, sediment composition and distribution, due to hydrodynamics and background. In parallel, the evolution of the entering and exiting flows is monitored. Conductivity measure enables us to characterize NaCl flow: the highest chloride concentration reached 1,5 g/L, yet studies highlighted NaCl impact on MTE mobilization for close concentrations.

In the course of the work, we will focus on NaCl effect on chemical balance and speciation of MTE. We will base upon first flush and sudden dilution that have the highest impact on basins. We expect to have the increase in metals concentration in the dissolved fraction (due to chlorine complexes and ion exchange) and in the particulate fraction (due to the aggregates remobilization).

3D numerical modelling of resuspension and remobilization of sediments in a stormwater detention basin

Xiaoxiao ZHU; Gislain Lipeme-Kouyi; Céline Becouze-Lareure; Sylvie Barraud; Jean-Luc BERTRAND-KRAJEWSKI

DEEP - INSA LYON, FR

Stormwater detention basins are key elements in sustainable urban stormwater management, aiming to both i) reduce flood risks, and ii) remove particulate pollutants by means of settling. However, settled particles may be resuspended depending on hydrodynamic conditions and transported elsewhere within the basin or towards the outlet.

Mechanisms involved in particles resuspension and remobilization are still not well known in actual detention basins. Computational fluid dynamics (CFD) offers an alternative to investigate the hydrodynamic characteristics and the solid transport mechanisms in detention basins. It is less expensive and more flexible than in situ measurements of all key parameters related to resuspension (turbulence, velocity field, shear stresses).

Investigations have been carried out about the evolution of microbiological, physico-chemical and ecotoxicological characteristics of accumulated sediments in the Django Reinhardt Basin (DRB) in Chassieu, France. During storm events, the resuspension and the remobilization of accumulated sediments with attached pollutants may explain the variability of physical, chemical, biological and ecotoxicological characteristics of sediments as well as low settling efficiency in detention basins. Although previous CFD modelling (Torres, 2008 and Yan et al., 2014) allowed analyzing hydrodynamic behavior and sediment distribution in the DRB, the resuspension and remobilization phenomena have not been well investigated. This research aims to simulate trajectories of settled sediments after their resuspension and remobilization in the basin and explain the variability of the particle characteristics.

The CFD approach is applied for hydrodynamics and solid transport modelling. The basic equations are the mass conservation and the momentum conservation (i.e. Navier-Stokes equations). The flow is simulated for steady state conditions and the turbulence is modeled by the Re-Normalization Group (RNG) k-epsilon model. The sediment transport is simulated based on the hydrodynamic model outputs and with the Lagrange approach (Discrete Phase Model). The boundary condition based on the bed turbulent kinetic energy (BTKE) developed by Yan et al. (2014) is applied.

Several simulations with different inflows, including the mean flow rate 0.35 m³/s in the DRB, have been performed. The numerical simulations allow to understand and quantify the resuspension behavior of settled sediments for different inflows by means of the percentages of resuspended sediments and those which escape from the basin. Results show that the sediments which contain the finer particles, have the more tendency to resuspend and be transported towards the outlet. This model could eventually help to indicate the preferential zones for sediment cleansing and to improve the design of detention basins, aiming to increase the removal efficiency.

Drainage of roadwater in a groundwater friendly way.

Britt Boye Thrane¹; Hans Peter Birk Hansen²; Troels Kjærgaard Bjerre³; Dorte Harrekilde¹

¹ Ramboll; ² Municipality of Odense, ³ VCS Denmark, DK

In order to protect the groundwater resource vest of the city of Odense the Municipality has decided to investigate if the water catchment area at Bolbro Well-field can be threatened by an accident caused by transportation of hazardous materials on the main road passing the catchment area. Bolbro Well-field delivers 20% of the water supply to the City of Odense. Groundwater protection is therefore high priority and € 20 mill. have already been used on establishing forest in the area.

Over a distance of 1 km the road water is lead to a small brook named the "Stegstedbrook" which passes very close to the abstractions wells of the Bolbro Well-field. The main road is appointed by the police to be the mandatory road for chemical transports.

An analysis of the drainage system in the area has been carried out and the risk of polluting the Bolbro Well-field has been evaluated. The analysis will give the Municipality of Odense and the water company VCS Denmark a strong decision making tool to manage and remediate a possible pollution.

It has not been possible to obtain information about which dangerous materials there are transported on the road. Gasoline and chlorinated solvents have therefore been chosen to be used as model substances since they behave very differently in the soil and groundwater environment.

The risk for an accident with leakage of hazardous materials is calculated to be 1/565 years.

The mapping of the main road's drainage system and the surrounding area showed that a spillage will be collected by the road drains and lead to either a drainage system which runs south or to the part of the Stegsted brook which is piped on a distance of 750 meters before it turns in to an open brook which passes very close to the abstraction wells belonging to the well field.

All available information about the geology and the hydrogeology was collected and a conceptual model was established. The aquifer is only covered by 5-15 meters of clay and is therefore very poorly protected against pollution from the surface. A pumping test in the area shows very good hydraulic contact to other parts of the catchment area meaning that an even larger part of the aquifer potentially is threatened if an accident happens.

The risk assessment shows that a spillage with chemicals on the main road will cause fast transportation of free phase product to the area around the abstraction wells at Bolbro Well-field.

It is estimated that a spillage with 30 m³ chemicals from a lorry in a worst case scenario will contaminate between 14.500-31.300 m³ of soil. Different remediation methods towards the model substances oil/gasoline and chlorinated solvents have been evaluated and it is estimated that it will take from 0,5 to more than 100 years to remediate a potential contamination depending of the size of the spillage, the actual chemical/chemicals and the extent of pollution.

The cost of the remediation due to the appointed methods is estimated to be between 3,5-14 mio. €. Changes in the drainage conditions have also been examined and solutions for optimized drainage of the road water have been proposed. The cost of these changes has been estimated to be below 1 mio. €.

From soil to sediments in French river basins

Rosalie Vandromme¹; Olivier Cerdan¹; Grangeon Thomas¹; Anthony Foucher²; Louis Manière²; Sébastien Salvador-Blanes²; Evrard Olivier³

¹ BRGM; ² Université François Rabelais; ³ CEA-CNRS-UVSQ, FR

In France, since the beginning of 20th century, rural landscapes have been completely modified by human activities. These practices have resulted in profound sedimentary and morphological alterations (channel bed incision, deposition of fine sediment, bank erosion, etc.), detrimental to the achievement of good water status.

Several research efforts have already investigated either global budgets at the river basin or continental scale or local detailed budget at the plot to the field scale. However, very few studies have tried to analyse the connectivity between fluxes and storages and to draw the links between temporal and spatial scales. In this broad context, the purpose of this study is to examine source-to-sink dynamic of the sediment cycle for the Loire River Basin. This project is broken down into two steps: the first step's aim is to understand poorly studied processes such as sediment production by agricultural drainage or bank erosion by catchment monitoring. The second step is to elaborate a distributed model of sediment connectivity from hillslopes to basin outlet.

For the first step, two catchment sites are studied, using historical data or monitoring: the linear of two small streams ("La Ligoire") and the Louroux lake catchment. Most of those two catchments are intensively cultivated and have been extensively submitted to subsurface drainage using drain tiles. The objectives of this part are threefold: quantify incision and deposition processes since the channelization of the streams, quantify in-channel deposition rates of fine sediments, and explain the spatial distribution of these deposits. For the second step, the modeling approach is based on the use of indicators to describe hillslope processes, potential downstream retention, attempting to link river basin characteristics to a prediction of sediment exports in rivers. It provides insight in the identification of the most influent sediment redistribution processes on the total sediment fluxes and on the differences between various basin typologies.

The Ligoire study shows an important stream incision and the influence of water obstacles on sediment distribution. The Louroux monitoring permits to differentiate between the different sources of sediment and highlight the importance of surface erosion during flood events and of bank erosion during low flows. The increased export of the sediment is primarily due to the very high human-made connectivity of these landscapes that was originally created to evacuate the excess water during the humid seasons.

The analysis of particulate sediment fluxes datasets at different spatial and temporal scales permits to identify some of the dominant processes, and also to distinguish natural from anthropogenic influences. Concerning upland physical soil surface erosion rates, we find that the average travel distance of eroded particles may be limited, implying a strong decrease in physical erosion rates when moving from the local scale to the river basin scale. The results also highlight the predominant role of surface connectivity to characterize the fraction of sediment exported out of river drainage areas by physical soil surface erosion.

Impact of hydraulic conditions on micropollutants mobility in the Carelle brownfield soil (France)

Martin Seidl¹; Julien Le Roux²; Rémi Mazerolles²; Olivier Fouché³

¹ LEESU ENPC Université Paris-Est; ² LEESU Université Paris-Est Créteil; ³ CNAM Paris, FR

Generally, brownfield sites exist in city's industrial sections, on locations with abandoned factories and buildings, acting often as waste disposal. Their restoration has gained prominence due to their potential to satisfy urban expansion and need of green areas. Typical contaminants found on brownfield include hydrocarbons, solvents and heavy metals.

Our study site is a 10ha brownfield situated on the Seine river bank, 20 km south of Paris, which should be restored as green space for local inhabitants. The site has 2 types of contamination, a 50-year-old demolition disposal zone and a recent zone where electric equipment was burned. The main objective of our study was to evaluate the mobility of present pollution (heavy metals, PAH / PCB) in the soil. Due to site locating in flooding zone, the research was focuses on the (vertical) pollutant mobility due to (1) groundwater upwelling followed by saturated infiltration and to (2) rainfall and subsequent non-saturated percolation.

As the setup of lysimeters was technically not possible on-site, representative soil profiles were reconstituted for both polluted zones: 3 vertical soil profiles, sampled from each zone, were mixed by layers of 10 cm and reconstituted in columns (d = 160 mm) in the laboratory. The "rain" columns were daily drop irrigated with 100 mm artificial rain water. The "flood" columns were first upwards saturated and then kept saturated, and then daily percolated with 2L of filtered river water. All effluents were weighted and analyzed after filtration for conductivity, dissolved organic carbon, 3D fluorescence, dissolved heavy metals (AAS) and PAH/ PCB (GC-MS). The soil heavy metals contents were analyzed by X-ray. Sampling and analyses were performed following GLP and APHA /AFNOR standards.

The results confirmed that both zones are highly contaminated, exceeding the French environmental standards. As expected, the burning zone exhibits high levels of PAH, but also very high levels of copper and lead (g/kg), even higher than in the demolition zone. The burning zone is only polluted in the upper 30 cm, and has natural sediments (silt) in the underground. The demolition zone is mostly of anthropic origin (sand, bricks...) even below 50 cm. All parameters measured in the eluent decreased with time. The pH, conductivity and DOC were more influenced by the soil type than by the hydraulic regime.

The total PAH content was in average 30 ng/l and did not significantly differ between the different zones and types of hydrology. Though the superficial metal content was twice as high in the burning zone than in the demolition zone, most metals showed higher levels in the latter (e.g., Cu and Zn were < 10 ppb in the burning zone eluent and 300 ppb and 80 ppb, respectively, in the demolition zone eluent).

Crossed statistical analysis of the results shows that the type of soil contamination is the main factor influencing pollutants release and that temporary flooding conditions produce lower impacts on the groundwater quality than an equivalent volume of rain. Details on specific parameters contributing to the apparent mobility of pollutants across different substrates will be presented.

ThS 2a.1: Human health risk assessment

Geostatistical mapping of health risks to improve decision making when regenerating contaminated sites (CARTORISK project)

Claire Fauchoux¹; H el ene Demougeot-Renard²; V eronique Croze³; Sylvie Traverse⁴

¹ Geovariances; ² eOde; ³ Element-Terre; ⁴ GINGER BURGEAP, FR

Redevelopment of industrial sites is a complex task which requires looking for the best compromise between several development alternatives. Reduction of health risks associated with site pollution must be balanced against remediation costs for various exposure scenarios depending on the construction projects and related uses. This analysis is particularly difficult in the highly uncertain context encountered in most of industrial sites. Site contamination is indeed always imperfectly known, due to the high complexity of spatial pollution distribution in soil or transfer media and the limited number of data collected during the investigation stage.

Mapping health risks linked to each redevelopment scenario while accounting for the spatial variability of soil contamination together with an estimation of related uncertainty can help decision making. It can also be used to estimate costs of remediation required to reduce risks.

Such a mapping can be obtained by coupling geostatistical models using soil, groundwater and soil gas results with pathways models and health risks computations. If this coupling does not raise any theoretical problem, its application should be examined in detail. Some challenging issues are expected both in the technical development of the methodology (e.g. accounting for models with various dimensions) and with the integration of the spatial risk models during the redevelopment operations and decision making process (e.g. how to bring practical benefits to the actors as city planners or real estate companies for industrial sites redevelopment?).

Cartorisk is a two-year project funded by Ademe (French Environment and Energy Management Agency) and conducted by four partners: eOde, Geovariances, Element-Terre and Ginger-Burgeap. The project has 3 main goals: 1) develop a general methodology for risk spatialization, 2) test the method on two industrial sites showing contrasted contamination situations, exposure pathways and redevelopment scenarios, 3) define with a panel of experts how to integrate the method in their decision making process to maximize the overall benefit of the re-urbanization operations.

The methodology developed in the framework of Cartorisk will be presented and illustrated with the two real cases of post-industrial sites. Difficulties and remaining challenges to obtain an efficient and workable method will be discussed.

Transfer of PCB and PCDD/F from soil to the terrestrial ecosystem with potential risk assessment for Humans and for the ecosystems

Karen Perronnet¹; Emmanuelle Boulvert¹; Nicolas Manier¹; Nicolas Pucheux¹; Olivier Faure²; Benjamin Pauget³; Annette de Vaufleury³

¹ INERIS; ² University of Lyon; ³ University of Franche-Comté, FR

Persistent organic pollutants (POPs) such as dioxins/furans (PCDD/PCDF) and polychlorinated biphenyls (PCBs) have been widely studied in aquatic ecosystems and in animals intended for human consumption. Their high stability and accumulation into fat led to a number of well-documented incidents (contamination of milk and meat/fish). However, only few studies have focused on their transfer from soil to terrestrial organisms, as these pathways are usually considered as minor.

Two research projects (TROPHE and TROPE) were devoted to assess POPs' transfer toward first links of food webs (vegetables, fodder and soil invertebrates) in order to further assess health human risks and terrestrial ecosystems risks. Based on two main experimental studies conducted in laboratories to evaluate bioconcentration factors, risk assessment was performed using multi-media exposure models: on one hand, Modul'ERS developed by INERIS to assess transfer of contaminants from the environment through the local food chain to human exposure and risk, and on the other hand, TerraSysTM for ecosystems risk, developed by Sanexen.

Four contaminated agricultural soils were sampled in the vicinity of a former industrial plant and thirtyfive compounds were analyzed (6 indicator PCB, 12 dioxin-like PCB, 7 dioxins and 10 furans). These soils were selected to present a wide range of concentrations (up to 246 ng I-TEQ.kg⁻¹ for Σ 17 PCDD/F+12 PCB-DL/up to 35,000 ng.kg⁻¹ for indicator PCB). They were tested under controlled conditions. In a first experiment, POPs were measured in leave-, fruit- and root-vegetables widely grown in French gardens (zucchini, lettuce, potato, carrot, green bean). In the second experiment using the same polluted soils, POPs were measured in soft tissues of two soil invertebrates (earthworms and snails). In addition, bioindicators and soil PCB bioaccessibility through *in vitro* test (Forhest) were also evaluated.

Results showed that POPs were both transferred into edible vegetables and soil invertebrates. Dioxins and furans showed lower transfer than PCB. Concentrations measured in green fodder collected in the field, and in edible vegetables cultivated in the laboratory exceeded in some cases the European threshold values for undesirable substances. Bioconcentration factors (BCF) for POPs were compared in the tested organisms. PCB transfer into vegetables depended on the number of chlorine substitutes and type of vegetables ($BCF_{zucchini} > BCF_{lettuce} > BCF_{root} > BCF_{bean}$). This trend was not observed for PCB with earthworms, whereas in snails, lower BCF were evidenced for highly chlorinated PCB.

Use of Modul'ERS multi-media model highlighted parameters with high sensitivity in human exposure through vegetables intake and soil ingestion. Due to lower PCDD/PCDF transfer into vegetables, child exposure was highly dominated by amount of ingested soil. Considering vegetables intake, human exposure globally depended on the number of chlorine substitutes with high PCDD/PCDF contribution in root vegetables, and with a variable PCB contribution according to the type of vegetables. Due to different toxicity values for POPs, health risks were not directly related to exposure with a major contribution of PCDD/PCDF despite of their low soil concentration and low transfer into edible vegetables.

Concerning risk assessment for ecosystems, the multi-media model TerraSysTM showed the high sensitivity of BCF values between soil and invertebrates. Use of maximal BCF values when a wide range was experimentally acquired helped not to underestimate POP transfer to the higher links in trophic chain. Use of a simple conceptual model was possible to foresee POP transfer into the ecosystem as far as two levels of predators were at least considered.

These studies help to identify common steps and tools between Human Health and ecosystems risk assessments as environmental studies need to be promoted and structured.

Acknowledgements : Authors acknowledge the French Environmental Agency (ADEME) for funding

A free (R-based) tool for Probabilistic Human Health Risk Assessment: Application to an Urban Garden scenario

Fernando Barrio-Parra¹; Alejandro Dominguez-Castillo; Miguel Izquierdo¹; Eduardo de Miguel¹; Rafael Medina-Ferro¹; Jesús Díaz-Curiel¹; Ana Artalejo¹

¹ Universidad Politécnica de Madrid, ES

Risk assessment is the process of modelling exposure to a toxicant and predicting health effects. Probabilistic Risk Assessment (PRA) allows to characterize variability and uncertainty in risk estimates, and may be particularly useful when point estimates of risk are unacceptably high, when environmental justice issues are raised or when exploring the impact of the probability distributions of the data in risk estimates. In this work we present a model developed in a R environment to study the variability of the exposure variables and to perform sensitivity and uncertainty analyses in human health risk assessments.

The model allows fitting of empirical data to 8 probability distribution functions (normal, log-normal, geometric, exponential, Poisson, Cauchy, Logistic and Weibull) through a single function that returns the results of the Kolmogorov-Smirnov and Anderson-Darling Tests and the Bayesian and Akaike Information Criteria. Another function returns graphical information to check the adjustment (histogram, Q-Q and P-P plots, and CDF). The calculation routine vectorises the random number generation so that the computational time of Monte Carlo simulations is reduced (particularly when compared with Excel implemented routines).

The model was applied to an urban gardens study case. The conceptual model considered the exposure to trace elements through accidental soil ingestion, dermal contact with soil, inhalation of resuspended soil particles and vegetable ingestion. The data employed to characterize the variability of exposure variables (exposure frequency, visit duration, body weight, vegetable intake rate) were collected through surveys (n=62). The concentration of As, Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn were determined in soil (n=24) and lettuce (n=23) by Atomic Absorption Spectroscopy. The results of the risk assessment revealed that vegetable intake was the exposure pathway with the highest contribution to risk, reaching values above the acceptable threshold for systemic cumulative risk for Cd, Co and Sb and resulting in an unacceptable carcinogenic risk from exposure to Pb. A sensitivity analysis showed that exposure frequency was the variable with the highest impact on the results for this scenario. The 95th percentile of risk distributions obtained through Monte Carlo simulations (10000 iterations) was lower than the deterministic risk estimates obtained in a Reasonable Maximum Exposure scenario (considering default USEPA exposure values). The uncertainty of risk results was assessed by building distributions (n=10000) of the 95th percentile of risk and estimating confidence interval for its mean.

PRA in general, and this freely available model in particular, improve the information leading to decision making in risk management. In the particular case of urban gardens, efforts to better characterize exposure need to concentrate in reducing the uncertainty associated with estimates of exposure frequency. Other sources of uncertainty which were not considered in this study, like gastrointestinal and inhalation bioaccessibilities of trace elements in soil, should be the object of future research efforts.

Indoor air problems caused by chlorinated solvents spreading through public sewage systems

Kaspar Rüegg; Boerge Hvidberg

Central Denmark Region, DK

Background: There has been a special focus on chlorinated solvents in indoor air in Denmark for many years. Investigations usually have focused on intrusion pathways from a local soil contamination to buildings in the vicinity.

On many sites we have found that contaminated groundwater from shallow aquifers is seeping into sewage systems. Once contaminated water is flowing in the large municipal sewers, vapor containing volatile compounds can move into any direction and pose a potential threat also for indoor air in housing far from the source.

Case studies:

The investigations were carried out at two locations with shallow aquifers, where sewage systems are situated below the groundwater table.

At both locations, indoor air problems were detected which could not be explained by local soil or groundwater contaminations. In both cases it was found, that the indoor air problems were caused by contaminated vapors originating from the public sewage. It was shown that preventing vapor from public sewage to enter the local sewage solved the indoor air problems.

In case one, a local rainwater sewage system at a contaminated hotspot acted as a drain thereby contaminating the public sewage. A successful solution has been found to avert indoor air problems in houses connected to the public sewer. Investigations are ongoing, as there is evidence that more houses than first anticipated, further away from the source are affected.

In case two, the source of the contamination in the public sewage is not yet determined but there are several known contaminations with chlorinated solvents in the vicinity. Investigations are ongoing to pinpoint the source and to determine the extent of contaminated vapor in the public sewage.

It will be exemplified how the contaminants enter the public sewage and how and how far they have moved. The used techniques to overcome the indoor air problems will briefly be reviewed and we will touch upon the legal aspects of such cases in Denmark.

Lessons learned:

Contaminations with volatile organic compounds (VOC's), for example chlorinated solvents, may be spread unexpectedly by public sewage systems. This can be the case, where the sewage systems are placed below the groundwater table. In large public sewage pipes, the VOC's may move in any direction by gas diffusion. This may cause indoor air problems far from the source, where there is no any apparent soil, groundwater or soil vapor contamination

Mercury contamination in the subsoil of a residential and rural area in the central part of Flanders (Belgium)

Ilse Van Keer¹; Kaat Touchant¹; Johan Patyn¹; Johan Gemoets¹; Johan Vos¹; Christa Cornelis; Danny Wilczek; Machteld De Wit²; Raf Engels²; Sabine Plingers²; Liesbeth Havet²; Jan Bronders¹; Jan Bronders

¹ VITO; ² OVAM - Flemish Waste Agency, BE

Based on several soil surveys conducted in the past in the framework of the reuse of excavated soil, increased mercury concentrations were reported for the top layer (upper 25 cm) of a residential and rural area in the central part of Flanders (Belgium). In general, the concentrations exceeding the soil remediation value for residential area in Flanders (4.8 mg/kg dry matter) range between 4,8 – 24 mg/kg dm. At one location, concentrations up to 100 mg / kg dry matter have been reported.

A (geo)statistical survey was conducted using a dataset of about 11.500 records. Statistical observations are characterized by a lognormal distribution. More than 90% of the measured values is less than 1 mg / kg dry matter. The observed concentrations and certainly the concentrations exceeding the reference value of 4.8 mg/kg dm show no spatial correlation, even when they are analyzed for each individual cluster. No spatial trend could be detected in the overall dataset.

Although a thorough deskstudy with respect to the source of the mercury pollution was carried out, we were not able to identify the activity / activities responsible for the enhanced mercury concentrations in the area of concern.

A generic human health risk assessment was performed to identify the locations where more elaborated soil research is necessary. Because most parcels with elevated mercury concentrations are situated in a residential area, a sampling campaign at two individual sites was carried out, including speciation of mercury and crop analyses.

Based on the research carried out it was concluded that:

- There are no indications for the presence of a regional pollution.
- There is no evidence of leaching of mercury in the groundwater.
- For a limited number of locations, the mercury pollution may be linked to activities which may result in increased mercury concentrations (e.g. former smith, scrap dealer)
- For plots located in delineated areas with enhanced mercury concentrations, special recommendations with respect to the consumption of crops harvested from kitchen gardens were formulated.
- Additional research has to be carried out at sites with concentrations exceeding the maximum permissible concentrations.

Subsequently the following measures were taken by the Flemish Authorities:

- The plots for which the concentrations observed exceeds the reference value for remediation are included in the Ground Information Register. Subsequently, specific user advice was added to the soil certificate. The owners have been informed by the OVAM.
- For three sites a descriptive soil research has been initiated.
- At one residential area, including a school environment, a soil investigation of private gardens is in preparation in relation to the human health risk assessment.

ThS 2b.1: Bioavailability assessment of PAHs and heavy metals

Measuring and modelling the dermal bioavailability of soil PAH

Darren Beriro¹; Mark Cave¹; Christopher Vane¹; Russell Thomas²; Christopher Taylor³

¹ British Geological Survey; ² WSP | PB; ³ National Grid Property Holdings, GB

This paper presents preliminary results of measuring and modelling the dermal bioavailability of polycyclic aromatic hydrocarbons (PAH) present in real-world soils. The work forms part of an industry funded programme to minimise uncertainties associated with the dermal pathway in human health risk assessments of post-industrial brownfields. The dermal extractions were made using a passive diffusion method and artificial skin. Soil used in the experiment were collected from former manufactured gas plants in the UK. Soils were applied to an artificial membrane as a mono-layer prior to extraction. The technical difficulties and how these were overcome are explained. A portable fluorimeter made using a 3D printer and parts from an electrical store was constructed for this project to optimise the dermal extractions and minimise expensive pre-cursor analytical work. Dermal bioavailable PAH were quantified using GC-MSMS. This paper places the work in the context of in vivo, in vitro and in silico methods from a wide variety of scientific disciplines including occupational and environmental exposure, medical, pharmaceutical and cosmetic research. The paper also describes how modelling approaches will be used to predict dermal bioavailability of soil PAH and determine the relevant process control mechanisms, including characterising the physico-chemical properties of the soil samples. Modelling methods described include chemometrics and quantitative structure activity relationships. The paper also identifies and explains a number of practical shortcomings of both measuring and modelling dermal bioavailability of PAH in soils which must be addressed if dermal tests are to be applied to laboratory analysis of contaminated soils for human health risk assessment.

Bioavailability and bioaccumulation of heavy metals, PAHs and PCBs in soils from industrialized urban areas

Cláudia Coelho¹; Susete Martins Dias; Myriam Hammada; Yves Perrodin; Jean-Philippe Bedell

¹ Université Lyon 1, UMR 5023, ENTPE, CNRS, FR

Soils from industrialized urban areas play an important role in the quality of life in the cities and are permanently subjected to changes in geochemical characteristics due to anthropogenic activities, becoming easily susceptible to contamination with potentially toxic elements such as heavy metals (HMs) and organic contaminants, namely polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

To correctly assess risks associated with contaminants presence it is important to know the total contents of the contaminants in the soil system and to understand the distribution and the availability of different forms of the contaminants present in soils.

The main objective of the present study was to assess the HMs, PAHs and PCBs bioavailability, potential bioaccumulation and exposure risks to ecosystems, through chemical extractions, bioaccumulation and ecotoxicological effects studies with plants and earthworms. These approaches help us to understand and quantify the potential accumulation and toxicity levels of these compounds in the soils, an environmental compartment strongly related to other compartments and biota. To this study, samples were collected in two distinct areas:

- Estarreja (North/Central-West of Portugal): soils from agricultural fields surrounding the Estarreja Industrial Complex and Estarreja city;
- Lyon (in East-central France): sediments from "casiers Girardon". During flood episodes, sediments of the river are deposited in the casiers.

A general physico-chemical characterization of the samples in order to evaluate the role of the soil properties in the OPs distribution, bioavailability and general behaviour was done. Levels of some heavy metals in soils were assessed, namely Mercury (0.2 – 100 mg kg⁻¹dw), Cadmium (0.50 – 4.0 mg kg⁻¹dw), Copper (7.0 – 760 mg kg⁻¹dw), Lead (8 – 1450 mg kg⁻¹dw) and Zinc (15 – 1500 mg kg⁻¹dw). PAHs contents in considered soil samples varies between 0.02 - 0.25 mg kg⁻¹.

Bioavailability of OPs was assessed in samples through chemical solid-phase soil extraction procedures that mimics the typical reactions that occurs in soil phase as well as the common plant-soil interactions.

Bioaccumulation and ecotoxicology tests (for risk assessment) were performed in order to measure the fraction of OPs that can be accumulated by plants as well as by soil organisms (earthworms) in the soil samples. Plant species typically found in the selected sites were exposed to contaminated soils, as AFNOR X31-201/202 and ISO 11269-2 procedures. Plants seed germination and growth and effects were evaluated. Tests were performed for each soil/sediment using one invertebrate specie (*Eisenia* sp.), according to standard protocol ISO/DIS 11 268-2 (2012) to infer about the effects in reproduction rates. Earthworm survival, body weight, cocoon production and hatching were also measured. After the exposure period, plants and earthworms were collected and the bioaccumulated fractions of contaminants determined.

This research work aims to contribute to the scientific knowledge about risk assessment and environmental quality in Rhône fluvial margins and in Estarreja area, regarding the HMs, PAHs and PCBs concentrations.

Using Leaching and Passive Sampling to Assess the Mobility and Bioavailability of PACs in Historically Contaminated Soils – Which Method is the Best to Use and for What?

Anja Enell¹; Staffan Lundstedt; Hans Peter Arp; Sarah Josefsson; Gerard Cornelissen; Ola Wik; Dan Berggren Kleja

¹ Swedish Geotechnical Institute, SE

Background: The importance of sorption of polycyclic aromatic compounds (PACs) and how to account for bioavailability when performing risk assessment has been debated for two decades. Despite this, regulatory guidelines for PAC contaminated soil often still do not account for bioavailability in general, and typically rely on screening values of total soil concentrations. Nevertheless, several different tools to assess bioavailability and mobility of these types of compounds have been developed and their practice in site-specific risk assessment projects is evolving. Different methods to quantify soil porewater concentrations of contaminants provide different types of information. Passive sampling measurements give freely dissolved porewater concentrations ($C_{pw,free}$), while leaching tests provide information on the mobile concentration ($C_{pw,leach}$), including contaminants associated to dissolved organic carbon (DOC) and particles/colloids in the porewater. This presentation describes a combination of these two measurements, performed to study the sorption and mobility of different PACs to DOC and particulate organic carbon (POC) in historically contaminated soils [1]. In total 16 polycyclic aromatic hydrocarbons (PAHs), 11 oxygenated-PAHs (oxy-PAHs) and 4 nitrogen containing heterocyclic PACs (N-PACs) were investigated. This is one of the first studies presenting DOC/water partitioning coefficients (KDOC) and POC/water partitioning coefficients (KPOC) for PACs, including oxy-PAHs and N-PACs, in historically contaminated soils.

Materials & Methods: 10 soil samples were collected from five different locations in Sweden and France: a former gasworks plant, a former wood tar production site, a coke oven plant, a wood preservation site and a coke oven and metallurgy site. Passive sampling was performed with polyoxymethylene (POM) [2]. Leaching was conducted with the Equilibrium Recirculation column test for HOCs (ER-H test) [1].

Results & Discussion: Observed $C_{pw,leach}$ was up to 5 orders of magnitude higher than $C_{pw,free}$ in systems where colloids and particles were present; implying large biases when $C_{pw,leach}$ is used to assess bioavailability or soil partitioning. Sorption to DOC and POC were important for the mobility of PACs with $\log KOW > 4$. Average KDOC correlated well with KOW and a universal relationship for all PACs was derived: $\log KDOC = 0.89 \times \log KOW + 1.03$ ($r^2 = 0.89$). This relationship could be a useful tool for estimations of KDOC's for PACs in the absence of measured $C_{pw,leach}$ values. The assessed KPOC were orders of magnitude larger than corresponding KDOC, indicating that high colloid concentrations could lead to relatively more rapid mobilization of PACs but at the same time lower relative bioavailability of this fraction. Accordingly, in soils susceptible to colloidal transport it is recommended to perform the POM and the ER-H tests in parallel. However, the presented KPOC values [1] could also be of use (if field concentrations of POC are known) in order to generate a rough estimate of the mobile concentrations.

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Ultrasound Probe Sonication and Microwave-Assisted Extraction for Rapidly Extractability Assessment of Metals from Polluted Mining Soils

Sara Garcia-Salgado; M. Angeles Quijano

Universidad Politécnica de Madrid, ES

The accumulation of trace and toxic elements in environmental samples causes a potential risk to human health. In soils, they are present under different chemical forms or types of binding, so the total metal content is a poor indicator of metal bioavailability, mobility or toxicity, since these properties basically depend on the chemical association of the different components of the soil. Therefore, the environmental impact of metalliferous soils is better assessed on the basis of the environmental accessibility of toxic elements [1].

Single and sequential extraction procedures are used for discrimination of different solid-phase associations of trace metals in soils or sediments [2, 3]. Several studies have focused on standardization of single and sequential extraction tests for soil and sediment samples, which pointed out the need for highly detailed procedures, in order to provide reproducible data for decision makers and governmental regulators [4].

In this work, ultrasonic probe sonication (UPS) and microwave-assisted extraction (MAE) were used for rapid single extraction of Cd, Cr, Cu, Ni, Pb and Zn from soils polluted by former mining activities (Mónica mine, Bustarviejo, NW Madrid, Spain), using 0.01 mol/L calcium chloride (CaCl₂), 0.43 mol/L acetic acid (CH₃COOH) and 0.05 mol/L ethylenediaminetetraacetic acid (EDTA) at pH 7 as extracting agents. The optimum extraction conditions by UPS consisted of an extraction time of 2 minutes for both CaCl₂ and EDTA extractions, and 15 minutes for CH₃COOH extraction, at 30% ultrasound amplitude, whereas in the case of MAE, they consisted of 5 minutes at 50 °C for both CaCl₂ and EDTA extractions, and 15 minutes at 120 °C for CH₃COOH extraction [5]. Extractable concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The proposed methods were compared with a reduced version of the corresponding single extraction procedures proposed by the Standards, Measurements and Testing Programme (SM&T).

The results obtained showed a great variability on extraction percentages, depending on the metal, the total concentration level and the soil sample, reaching high values in some areas. However, the correlation analysis showed that total concentration is the most relevant factor for element extractability in these soil samples. From the results obtained, the application of the accelerated extraction procedures, such as MAE and UPS, could be considered a useful approach to rapidly evaluate the extractability of the metals studied.

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Contribution of colloidal metals to apparent extract concentration in leaching tests for environmental risk assessment

Yukari Imoto¹; Tetsuo Yasutaka; Masayuki Someya; Kazuo Higashino

¹ National Institute of Advanced Industrial Science and Technology, JP

Keywords

leaching tests, toxic metals, colloidal form, dissolved form

Introduction

Assessing the leachability of toxic metals from soils is crucial to the evaluation of their environmental impact. A commonly used approach to assessing their leachability is the leaching test. In the test, a solid-liquid separation procedure is applied to remove excessive colloidal particles. However, it has been found that colloidal particles could not be completely removed from the extracts for some types of soil by the stipulated method and the total extract could potentially consist of dissolved and colloidal metals. To truly assess the risk of toxic metals, both forms of metal should be separately quantified. The purpose of this study is to provide an exploratory analysis of the contribution of colloidal metals to the apparent extract concentration of a leaching test.

Methods

Batch leaching tests were conducted using two metal-contaminated soils (Soil A and Soil B). The suspension was centrifuged at different centrifugal intensities covering the range of intensities specified in the standards. All centrifugates were filtered by vacuum filtration through a 0.45 µm membrane filter (MF) and the centrifugate at the maximum intensity was also filtered through a 0.10 µm MF. Arsenic and lead concentrations, and the turbidity of the filtrates were measured. From the results of the metal, we calculated the contribution of 0.10–0.45 µm colloidal metal to the total concentration of 0.45 µm filtrate.

Results and Discussions

The variation in the turbidity of the 0.45 µm filtrates largely depended on the centrifugal intensities: 0.55–150 NTU for Soil A and 0.04–1.2 NTU for Soil B. The 0.45 µm filtrates that underwent the highest centrifugal intensity of 3000 g for 6 h had the lowest turbidities for each soil type and appeared colorless and transparent to the naked eye. However, the turbidity of the 0.45 µm filtrate was significantly higher than that of the 0.10 µm filtrate at the same centrifugal intensity for both soils ($P < 0.05$, Student's *t* test). This result indicated that 0.10–0.45 µm colloids were present in the 0.45 µm filtrates in all solid-liquid separation conditions used in this study.

The contribution of 0.10–0.45 µm colloidal metal to the total metal concentration of 0.45 µm filtrates varied according to the centrifugal intensity, soil types, and metal species: 52–90% for arsenic of Soil A, 42–92% for lead of Soil A, 2–18% for arsenic of Soil B, and 8–80% for lead of Soil B. The contributions of colloidal lead to the total lead concentration for both soils were almost the same level despite the lower turbidity of the filtrates for Soil B. A possible reason for this could be that the lead concentration per turbidity for Soil B was higher than it was for Soil A.

ThS 2b.2: Bioavailability and bioindicators

Usefulness of bioindicators of soil and plant health in ecological risk assessment of contaminated soils: A case study of a phytostabilization process.

*Marina Le Guedard*¹; *Jean-Jacques Bessoule*¹; *Hélène Cérémonie*²; *Olivier Faure*³; *Gérald Fayolle*⁴; *Jean-François Nau*⁴; *Cécile Villenave*²; *Cécile Grand*⁵

¹ University of Bordeaux, ² Elisol-Environnement; ³ EMSE; ⁴ EODD; ⁵ ADEME; FR

For several years, the environmental risk of contaminated soils has mostly been addressed through physicochemical methods. Although these analyses are necessary for hazard characterization, they neither provide information about the ecological status and functioning of soils, nor on the risks resulting from contaminant transfers and their overall impacts on the ecosystem. Bioindicators are sensitive tools providing such informations and are thus required to assess the impact of contaminants on ecosystem health. Therefore, they have recently been integrated in ecological risks assessment through the TRIAD approach which combines three lines of evidence (chemistry, ecotoxicology and ecology). However, their usefulness in assessing ecological risks has been poorly demonstrated and, as a consequence, their use is still infrequent. In this context, a research program has been implemented (the APPOLINE program, funded by ADEME), with the main objectives of evaluating, based on experimental results, the usefulness of some bioindicators in ecological risk assessment. The bioindicators tested during this program were: a plant accumulation indicator to assess metal bioavailability (CMT Index: "Total Metal Charge") and two impact indicators using either nematodes (Nematofauna Index) or plants (Omega-3 Index) to evaluate soil and plant health, respectively.

Phytostabilization process is a soil treatment with the aims of reducing contaminant leaching and restoring soil health and functioning. Thus, one objective of this program was to evaluate the interest of these bioindicators, in addition to chemistry and bioassays, in the assessment of the efficiency of phytostabilization process. For that purpose, these bioindicators were investigated on an old metallurgical landfill where a phytostabilisation project was implemented since 2009. On this site, experimental plots were set up in order to compare the efficiency of different organic amendments: "Rameal Chipped Wood" (RCW), Composted Sewage Sludge (CSS) and mineral fertilizer (NPK). Plots were sown with a mixture of herbaceous species combining Poaceae and Fabaceae. Five years after the beginning of the treatments, physicochemical analyses showed that application of CSS led to the improvement of soil nutritional status in comparison with RCW and NPK. According to bioindicators studies, the two organic amendments reduced the metal transfers towards plants (except for Cr) and improved the soil biological activity as well as plant health. Moreover, especially the application of CSS improved plant development in terms of percentage of soil recovery and species diversity. Finally, ecotoxicological tests highlighted that organic amendments contributed to reduce the soil ecotoxicity for plants and nematodes.

The overall results showed that these three bioindicators may provide specific and complementary informations to physicochemical analyses and therefore they constitute valuable tools for assessing the efficiency of metal phytostabilization processes. They can be easily integrated in an approach such as TRIAD which covers chemical, ecotoxicological and ecological lines of evidences for assessing ecological risk.

Capacity of earthworm and land snail to reveal bioavailability of PCB and PCDD/F in contaminated soil

Nicolas Manier¹; Benjamin Pauget²; Karen Perronnet¹; Pascal Pandard¹; Annette de Vaufleury²

¹ INERIS; ² University of Franche-Comté, FR

Given their stability, lipophilicity and high persistence, PCB and PCDD/F represent a group of anthropogenic substances that can easily accumulate into the food web. While the transfer and accumulation of these substances are well documented for the aquatic food web, only few studies focused on their transfer from soil to terrestrial organisms.

The two projects TROPHÉ (INERIS) and TROPE (University of Bourgogne Franche-Comté) were undertaken to assess the PCB and PCDD/F transfer into terrestrial biota in order to further evaluate risks to terrestrial ecosystems. Thirty-five compounds were monitored (6 indicator PCB, 12 dioxin-like PCB, 7 dioxins and 10 furans) from four soils contaminated by a former industrial fire and showing a wide range of concentrations (up to 246 ng I-TEQ.kg⁻¹ for Σ 17 PCDD/F+12 PCB-DL and up to 35 000 ng.kg⁻¹ for indicator PCB).

The transfer of these compounds was then studied in two soft-bodied soil-dwelling invertebrate species: the oligochaete (*Eisenia fetida*) and the gastropod (*Cantareus aspersus*). Oligochaetes are one of the most important biotic components in the soil and frequently represent the most abundant species in terms of biomass. They are exposed to soil contaminants by digestive and cutaneous routes. Snails are characteristic of the soil surface and exposed directly to soil contaminants by the same routes as earthworms and also indirectly by ingestion of plants. Their ability to accumulate PCB, PCDD/F is unknown.

Worms and snails were exposed in controlled conditions to the soils up to 28 days. The concentrations of the 35 substances were measured after 14 and 28 days of exposure in worms and after 28 days in snails. Bioaccumulation factors (BAF) were calculated according to the concentrations recorded in each soil. The results clearly showed that PCB and PCDD/F were transferred into the worms and snails. A steady state was reached from 14 days of exposure of worms. For both organisms, PCB showed a higher transfer by comparison with PCDD/F as evident by higher concentrations and thus higher BAF (by factor 10) calculated. PCDF (especially 2,3,7,8 TCDF and 1,2,3,4,6,7,8, HpPCDF) were more accumulated than PCDD (OCDD was the most accumulated). Concerning the PCDD/F the lower BAF_{worms} were observed for the higher chlorinated compound. Such tendency was however not observed for PCB. Among iPCB, PCB₁₅₃₋₁₃₈₋₁₀₁₋₁₈₀ reached the highest concentrations. Overall, similar tendencies were observed for both species but with higher BAF in worms. This could be the result of a specific ability of accumulation and/or of the way of exposure of these soil invertebrates to contaminants.

Authors acknowledge the French Environmental Agency (ADEME) for funding the researches.

Climatic Influence on PAH Availability in Contrasting Industrial Technosols

Robin DAGOIS¹; Christophe Schwartz²; Samuel COUSSY³; Catherine Lorgeoux⁴; Stéphanie Ouvrard⁵; Pierre Faure⁶

¹ Laboratoire Sols et Environnement / Laboratoire Interdisciplinaire des Environnements Continentaux; ² Laboratoire Sols et Environnement; ³ Bureau de Recherches Géologiques et Minières; ⁴ UMR 7359, CNRS/Université de Lorraine/CREGU; ⁵ UMR 1120, INRA/Univ, FR

Predicting the long-term effect of climate on soil organic contamination is essential for natural attenuation assessment. Particularly, climate is suspected to be a major factor influencing the long-term fate of industrial soils. However, most of the studies are limited to monitoring the content and the availability of selected contaminants spiked in natural/agricultural soils under various temperature and humidity conditions. Indeed, freshly injected contaminants within soil matrixes greatly differ from historical industrial soil contamination (both in reactivity and content), which already underwent aging processes.

The aim of this study is to understand the evolution of a wide set of anthropogenic soils through pedogenesis processes induced by climatic aging factors. In a first step, PAH contaminated soils from former industrial sites were characterized and artificially aged through several individual climatic processes under controlled conditions defined by freeze-thaw (FTC) and wetting-drying cycles (WDC) and the number of days where the soil temperature rises above 28°C (HDS).

The global OM reactivity was assessed by measuring the dissolved organic carbon (DOC) content. This was followed by a measure of PAH availability performed by cold methylene chloride extraction and GC-MS quantification in initial and artificially aged soils.

Selected soils exhibit usual signatures of Technosol characteristics in term of total organic carbon (TOC), carbonates content and textural distribution. PAH content and distribution in the selected soils were representative of a large range of industrial contaminated soils.

After aging, DOC and PAH content followed several trends depending on the climatic aging events. FTC induced a general DOC and PAH decreases. HDS induced a sharp DOC and PAH increase and WDC caused both DOC increase and PAH decrease.

In a second step, a method using HYDRUS-1D was developed to predict pedoclimatic events over time as a function of atmospheric climatic conditions, soil properties, and depth. The pedoclimate was modelled for 10 year using datasets collected from 6 global weather stations (Nancy, Nantes and Marseille – France, Darwin – Australia, Denver – USA and Helsinki – Finland) to predict the occurrences of FTC and WDC cycles and temperature regime (HDS). The results show that FTC and HDS occurrences were correlated with the climatic regimes whereas the WDS cycles were mainly a function of the soils properties. The combination of the consequences of individual climatic processes (FTC, WDC and HDS) on PAH availability and the climatic sequences representative of the investigated climates revealed that the reactivity of DOC and PAH can decrease, i.e. natural attenuation, but in some case, the climate led to an increase in the PAH availability suggesting a possible natural amplification instead of a natural attenuation.

AHR-Mediated Effects and (Bio)Availability of Polycyclic Aromatic Compounds of Soil with Different Contamination Sources

Monika Lam; Maria Larsson; Magnus Engwall

University of Örebro, SE

Polycyclic aromatic compounds (PACs) such as polycyclic aromatic hydrocarbons PAHs, oxy-, nitro-, and alkyl-substituted PAHs and heterocyclic compounds (NSO-PACs) are common contaminants in industrial areas, especially at old gasworks sites, gas stations and former wood impregnation facilities, and occur as complex mixtures. Risk assessment of contaminated soil sites with PAHs are based only on the measurements of the 16 parent PAHs prioritized by the US EPA. However the traditional monitoring methodology of using chemical analysis of a small number of organic pollutants to determine the degree of contamination in soil usually overlooks potential contaminants present in the samples. A mechanism-specific cell-based bioassay measures the overall toxic effect of all contaminants of a sample and can provide complementary information to the chemical analysis. In addition, risk assessment often rely on the total soil concentration and do not consider the bioavailability of compounds and thus overestimating the risk. The passive sampler polyoxymethylene (POM) is increasingly used to analyze the bioavailable fraction of organic compounds in soil and has shown promising properties for sorption of hydrophobic organic compound (HOCs), like PAHs and dioxins. This present study investigated ten different soil samples from four different locations in Sweden with different contamination sources by using POM76-stripes as a passive sampler. Soil and POM76-stripes were analyzed by chemical analysis (GC/LRMS) of 70 PACs including PAHs, alkylated PAHs, oxygenated PAHs, methylated dibenzothiophenes and azaarenes in combination with a mechanism-specific cell-based bioassay (H4IIE-luc). The H4IIE-luc assay detects all compounds that activate the Ah-receptor (AhR), like dioxins, PCBs and many PACs. Furthermore profiles of PAC-contamination of the soils were analyzed. In addition, freely dissolved pore water concentrations of PACs were measured with the help of POM76-stripes to estimate bioavailability of PACs. The measured biological effect (BIOTEQ) of the POM-fraction ranged from 10 to 59436 pg/g. BIOTEQ of soil was higher than the effect derived from the chemical analysis, thus the mass-balance analysis revealed that there are unexplained fraction in the sample. This means that most substances in contaminated areas are unknown, thereby pose a risk to humans and the environment that cannot be estimated by only analyzing the 16 EPA-PAHs. The use of the passive sampling method in combination with bioassay analysis will take the bioavailability of all toxicants into account in a comprehensive manner, and thereby not overestimating the risk for substances with low bioavailability and complement the chemical analysis for a comprehensive picture of the pollution situation.

RHIZOtest: an innovative tool for phytoavailability assessment and risk management in polluted soils

Laure Lemal¹; Marine Valmier¹; Matthieu Bravin²

¹ MetRHIZLab; ² Cirad, MetRHIZLab, FR

Keywords: risk assessment, phytoavailability, metals, decision support

Resulting from 25 years of research at Inra and Cirad in France, RHIZOtest is a plant-based test that was standardized at ISO to assess the phytoavailability of trace elements in polluted soils. Initially, mainly developed on moderately contaminated soils, the objective is now to apply the RHIZOtest as a tool to assess the phytoavailability in heavily Polluted Sites and Soils.

The RHIZOtest concretely measures the transfer of soil contaminants (mainly trace elements) to the plant, i.e. the phytoavailability. It takes into account the interactions between several contaminants, i.e. the mixture effect. By mimicking soil-plant interactions specific to each type of soil and plant species, the RHIZOtest reproduces natural processes to assess the actual risk. Finally, the RHIZOtest allows to reproduce, in few weeks in a laboratory, widely generalizable studies hardly achievable in the field for reasonable implementation time and cost.

Today operational for transfer analysis of trace elements in the agricultural context, the RHIZOtest deployed by the spin off MetRHIZLab, offers new perspectives for the risk assessment and management of polluted sites and soils, such as: (i) assessing risk of transfer according to use, (ii) proving the effectiveness of remediation techniques, (iii) optimizing a site, (iv) attending revegetation or (v) characterizing the state of contaminated soil to be recycled.

In order to test these new perspectives for the risk assessment and management of polluted sites and soils, a preliminary study was conducted on three soils from polluted sites. Soil 1 and 2 were collected in an ancient mine in southern France. Soil 1 and 2 are exhibiting high concentrations in Zn, Pb and Cd. Soil 3 is highly contaminated with As, Cd, Cr, Cu, Ni, Zn and even more Pb by atmospheric fallouts from a battery recycling plant. The three reference plant species, cabbage, fescue and tomato, were cultivated on these soils according to the ISO 16198 standard. Firstly, no difference of plant biomass was observed between the three soils. This shows that the RHIZOtest was able to assess phytoavailability of trace elements without any phytotoxic artefact. Secondly, the three plant species highlighted the same phytoavailability for each soil and each trace element. Thus, the RHIZOtest showed its capacity to give a robust measure of the phytoavailability of trace elements in heavily contaminated soils.

Based on this preliminary study, a R&D program is underway to confirm these results with soils exhibiting contrasted physical-chemical properties and contaminations. Soils will be selected among different types of polluted sites such as ancient mines and industrial wasteland managed with various techniques (washing, phytomanagement or bioremediation), to create a decision support method based on RHIZOtest.

Dedicated to design offices, laboratories and experts, the RHIZOtest is an innovative decision support tool that should enable soon to assess risks and to optimize the management of polluted sites and soils.

ThS 2b.3: Ecological Risk Assessment and Modelling

Ecological risk assessment – Case studies – Application of the Soil quality TRIAD approach

Nicolas Pucheux; Pascal Pandard; Sandrine Andres

INERIS, FR

Different categories of tools are suitable to perform a site specific ecological risk assessment. Most often, a pragmatic combination of these tools will allow a proper risk assessment. The International Standard ISO/FDIS 19204 “Soil quality – Procedure for site specific ecological risk assessment of soil contamination (Soil quality TRIAD approach)” describes in a general way the application of three combined lines of evidence (chemistry, ecotoxicology and ecology). The soil quality TRIAD approach is conceived as a tiered stepwise approach.

The risk assessment method described in ISO/FDIS 19204 on a soil contamination has been used on an open mine operated during 60 years and which the activities stopped about 100 years ago. The ground still contains high levels of metallic pollution (Pb, Cd, Zn).

In 2016, the soil quality TRIAD approach has been used on five contaminated areas of the old open mine selected for their different profiles with respect to bioavailability or vegetation cover.

The Tier one for the three lines of evidence has been applied on every selected locations. The combined use of chemical concentration in soil (Chemistry), plant screening test and earthworm avoidance test (Ecotoxicology) and simple vegetation survey (Ecology) were sufficient to conclude on a potential risk for some of the 5 stations. Individually, the different tools of the first tier of TRIAD were associated with high uncertainties, but used as a whole, they were indeed sufficient to assess the ecological state on some locations. Consequently, some of the expensive and time consuming data collected in these locations were not needed to conclude on an unacceptable risk. For these locations, the use of TRIAD method could have saved financial and time resources.

On other locations, uncertainties were still too great and the implementation of higher tier was needed. The lack of ecotoxicological data among the existing data had been noticed and recommended bioassays (Ecotoxicology approach of TRIAD) were scheduled at the end of 2016. With these complementary results, the TRIAD approach will be reapplied, and as a result, focus will be made on the methodology in order obtain practicable results according to the complexity of the study and, as a consequence, its uncertainties.

In situ long-term modeling of phenanthrene dynamics in an aged contaminated soil using the “VSOIL” platform

Stéphanie Ouvrard¹; Khaled Brimo²; François Lafolie³; Geoffroy Séré¹; Patricia Garnier³

¹ INRA - Université de Lorraine; ² ADEME; ³ INRA, FR

Industrial sites formerly associated with coal exploitation and gasworks are frequently highly contaminated by persistent organic pollutants. Among them, polycyclic aromatic hydrocarbons (PAH) are given great interest due to their carcinogenicity, bioaccumulation and persistence in the environment. In the context of remediation operations, site management and environmental risk assessment, an accurate knowledge of these compounds behaviour, biodegradation, transfer or accumulation in soil medium is necessary. For addressing these issues there is an increasing need of development of complex models integrating all the relevant processes occurring in a soil. Though some simulation models describe the dynamics of PAH in polluted soils, these models remain few and generally focus on only one or at most two of the major processes influencing PAH behaviour in soil (e.g. degradation process or sorption and aging or plant uptake and rhizosphere activity). These models have only been tested using experimental laboratory data and reliable kinetic data for PAH at the field scale remain very scarce.

Recently, we have developed kinetics modules for PAH that proved successful at simulating experimental incubation results of a contaminated industrial soil at the laboratory scale (Brimo et al., 2016, Environ. Pollut. 215, 27-37). The present work extends this approach to integrate the previously calibrated “PAH module” in a new coupled model adding transport and transformation processes in the framework of the INRA VSOIL modelling platform (<https://www6.inra.fr/vsoil/The-Project>) to be used at the field scale. This coupled-model is one-dimensional and is composed of five main modules: heat transport, water flow, solute transport, PAH sorption and PAH biodegradation. The climatic data are provided by specific modules and considered as boundary conditions. This study focused on soil processes without any plant effect and no modules associated to plant processes were implemented at this stage.

This model was calibrated and proved successful at simulating the fate of phenanthrene, taken as representative PAH, in an aged soil of a former coking plant under real conditions over a five-year field monitoring experiment. Simulation showed that i) degradation of PHE was characterized by two degradation phases, ii) PHE removal was governed by substrate transfer limitation from the strongly sorbed compartment into the weakly one and not by the microorganisms. This validated model was then used to predict phenanthrene behaviour over a forty-year period (2010-2039) under two climatic scenarios reflecting future climate changes proposed by IPCC (Intergovernmental Panel on Climate Change): A2 (the most intense scenario) and B1 (the most modest scenario). It clearly appeared that meteorological factors were important and should also be accounted for in each management strategy.

Internal problems in an incoming alternative drinking water source: Spatial and historical distributions, release potential, and ecological risks for nutrients and heavy metals in sediments in Lake Tongjiqiao, China

Qiushi Shen¹; Cheng Liu; Juhua Yu; Chengxin Fan

¹ Nanjing Institute of Geography & Limnology, Chinese Academy of Sciences, CN

Lake Tongjiqiao is a medium-small size reservoir (5 km²) designed for flood control and irrigation but was chosen as the alternative drinking water source for more than 210 thousand people in the nearby city in 2015. The lake was considered in good water quality for fish farming. However, cyanobacterial blooms were found in some regions in the lake in the last several years. Therefore, a systematic pollution investigation and research for the lake water environment should be conducted. In this study, we investigated the spatial distribution and historical accumulation characteristics of nutrients and selected heavy metals in the lake sediment. Internal diffusion fluxes of nitrogen and phosphorous in sediments from different lake regions were evaluated. Potential ecological risk assessment of eight toxic heavy metals including As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in sediments were also estimated.

Results showed that nutrient loadings in sediments were high in the whole lake but there were typical spatial heterogeneities in different lake regions. Surface sediments in the dam region and east lake were heavily polluted by nitrogen and phosphorous. Total nitrogen (TN), total phosphorous (TP), and loss on ignition (LOI) researched as high as 6915.3 mg/kg, 6390.7 mg/kg, and 20%, respectively. Whereas in the north and west lake, TN, TP, and LOI loadings were significantly lower. Nitrogen and phosphorus exhibited different release characteristics. Diffusion fluxes of ammonium nitrogen were almost high in the whole lake and sediments showed strong potential to release NH₄⁺-N to the overlying water. Diffusion fluxes of PO₄³⁻-P showed typical spatial heterogeneities. Sediments from the central lake showed release potential to the overlying water, whereas PO₄³⁻-P exhibited diffusion potential from overlying water to the sediment in north and west lake. Surface sediments in southwest lake and dam region exhibited slight pollution and accumulation of Hg, Cd, Pb, and As. Sediment Cr, Cu, Ni, and Zn contents were lower than local backgrounds in the whole lake. Results showed that the heavy metal contents decreased along with the sediment depth and researched local backgrounds at the depth of 10~15 cm. Potential ecological risk index (RI) assessment implied that surface sediment were in moderate to high ecological risk states. The RI decreased to moderate to low levels in most parts of the lake at the sediment depth of 15 cm. The findings of the presented study strongly indicated that in order to ensure the water quality and drinking water security, the internal sediment pollution treatment of Lake Tongjiqiao should be performed.

Occurrence and leachability of PACs in contaminated soils

Maria Larsson¹; Monika Lam; Patrick van Hees; Magnus Engwall

¹ University of Örebro, SE

The composition of hazardous chemicals at contaminated sites tends to be highly complex; for instance, at sites contaminated with polycyclic aromatic hydrocarbons (PAHs), thousands of PAHs, oxy-, nitro-, and alkyl-substituted PAHs and heterocyclic compounds (NSO-PACs) may be present, collectively referred to as polycyclic aromatic compounds (PACs). The chemical composition differ widely due to contamination sources and weathering processes in the environment.

Despite the high complexity in PAC-contaminated areas, current risk assessment is commonly based on chemical analysis of the 16 priority PAHs, originally selected by the U.S. EPA. Consequently, many chemicals are unknown and thereby the risk to humans and the environment. In addition, risk assessment is often based on the total concentrations of selected chemicals, which give no information on the availability and mobility of the chemicals in the soil. Many polar PACs may, besides being toxic, have a higher tendency to leach than less polar PACs.

SOILEFFECT is a 3-year project aiming to develop a reliable and relevant bioreporter-based technology for area survey and risk assessment of toxic chemicals in contaminated areas. Bioreporters are genetically engineered cell-based test systems made sensitive to toxicants acting via various types of mechanisms of toxicity. An analytical methodology including both chemical (GC-MS) and bioreporter (H4IIE-luc) analysis is used to analyze all samples throughout the project. The H4IIE-luc provides an integrated response of all chemicals activating the Ah-receptor, like many PACs.

One main aim within SOILEFFECT is to examine the availability and mobility of toxic chemicals in contaminated areas. To explore the mobility of PACs in soils, glass column leaching tests were performed on six soil samples collected in four different areas contaminated with PACs (abandoned gasworks sites, former wood impregnation facilities with creosote).

In this presentation we will show levels and profiles of 70 PACs in soils from various PAC-contaminated sites and discuss toxic and frequently occurring PACs. We will also show results from the column tests; leachable PACs, distribution of PACs between soil and water at the sites, and discuss how that can be interpreted in terms of leaching and risk. Bioreporter results from all samples, will be presented, as well as mass balance estimations, that is, correlation of predicted effects based on chemical analysis to the observed effects in the bioreporter.

Ecological risk assessment of Lake Bourget (France, Savoie) littoral sediment contaminated by heavy metals, PAHs and PCBs through chemical analyses, biomarkers, laboratory and in situ bioassays

Nathalie Lecrivain¹; Vincent Aurenche; Nathalie Cottin; Victor Frossard; Bernard Clement¹

¹ LEHNA, FR

In the early 1980's, the water level of Lake Bourget (France) was artificially regulated for hydroelectricity. This reduction in the amplitude of fluctuations negatively impacted the development of reed-beds. In autumn 2017, the water level will be lowered in order to stimulate the growth of the reed-beds. We assume that the modifications of the physical conditions of the shallow littoral zone (water depth, oxygen content and redox potential, temperature, ...) could change the mobility and bio-availability of contaminants at the water-sediment interface. As a matter of fact, whereas the sediment is generally a sink for contaminants entering the lake, it may act as a source in such changing conditions. The aim of the present work is to assess the basal contamination and ecotoxicity of the sediment of the littoral zone of Lake Bourget in order to study further this phenomenon.

For this purpose, we applied a Sediment Quality Triad approach (Chapman, 2000) on sediments from the shoreline of Lake Bourget (France) in order to evaluate their contamination and ecotoxicity. We first characterized the total content of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn), the 16 polycyclic aromatic hydrocarbons (PAHs) identified as priority pollutants by the USEPA and the 7 indicator Polychlorinated biphenyls (PCBs, congeners 28, 52, 101, 118, 138, 153 and 180) in the surface sediment of 10 sites all around the lake. We then conducted laboratory microcosm assays to assess the biological response of cultured species (*Lemna minor*, *Daphnia magna* and *Chironomus riparius*) exposed to these sediments in controlled conditions. Finally, we performed in situ investigations such as biomarker measurements - Acetylcholine-esterase and Glutathione S-Transferase - on the autochthonous macro-fauna (*Corbicula fluminea*, chironomids, gammarids and oligochaetes) and fitness tests on caged laboratory cladocerans (*Daphnia magna*).

The geographical repartition of the contaminants was mostly in accordance with the pollution sources identified on the watershed. The ecological risk assessment based on Quotient risk and Consensus-Based Sediment Quality Guidelines from MacDonald et al., (2000) showed that sediment from some littoral sites could have a toxic effect on the biota. Despite bio-accumulation of contaminants observed on the laboratory organisms exposed to these sediments and on the autochthonous organisms, no significant toxic effect was observed regarding survival, growth, reproduction, feeding rate endpoints. In addition, biomarker activities measured in the autochthonous benthic organisms did not significantly point out more stressful sites in particular.

Our result highlight the importance of studying the biological response of exposed organisms to assess an appropriate ecological risk of a complex mixture of pollutants. The next step will be devoted to the study of contaminants bioavailability and mobility under water level fluctuations, with the assumption that these changes lead to modifications of organisms' exposure and contaminant bioaccumulation.

ThS 2c.1: Risk assessment emerging pollutant and multi-compounds

Fate of emerging contaminants in retention basin sediments: four year monitoring results

Laure Wiest¹; Robert Baudot¹; Florent Lafay¹; Jean-Baptiste Aubin²; Sylvie Barraud²; Gislain Lipeme-Kouyi²; Emmanuelle Vulliet¹

¹ Institut des Sciences Analytiques de Lyon; ² INSA de Lyon, FR

Retention/detention basins are widely used to manage stormwater in cities: their effectiveness has already been proven to prevent flooding and trap micropollutants, by adsorption onto particles before they contaminate receiving waters. Nevertheless, to ensure optimal efficiency of these basins, accumulated sediments should be regularly removed, which raises the question of their further management. In order to choose the best solution, accurate data are needed about their physico-chemical characteristics, particularly on micropollutant concentrations and their associated risk. Although the fate of atmospheric pollutants like Polycyclic Aromatic Hydrocarbons (PAH) is well documented, many fewer studies are devoted to emerging contaminants such as surfactants and flame retardants.

Within the framework of the ANR project, called CABRES, this work consisted in a four year (2012-2016) monitoring of sediments from different sampling points of the Django Reinhardt detention-settling basin in Chassieu (France). Target substances including nine polybromodiphenylethers (PBDE 28, 47, 99, 100, 153, 154, et 209), seven alkylphenols and alkylphenol ethoxylates (para-ter-octylphenol (4-t-OP), 4-n-nonylphenol (4-NP), bisphenol A (BPA), nonylphenol and octylphenol mono and di-ethoxylates), belong to the Water Framework Directive list and/or were selected according to their bioaccumulation and high occurrence in the aquatic environment. Rigorous and sensitive analytical methods, based on gas and liquid chromatography coupled with mass spectrometry, were developed, validated and finally applied to 46 samples of sediments.

Thanks to limits of quantification comprised between 6 and 150 µg/kg, four PBDE and five alkylphenols and alkylphenol ethoxylates were detected and quantified. Although PBDE frequency of quantification was below 10%, three alkylphenols (4-t-OP, 4-NP, BPA) and the nonylphenol di-ethoxylate were quantified in more than 80% of the samples, at concentrations ranging from 7 to 4642 µg/kg. Thus, this study revealed a strong impregnation of sediments by alkylphenols, but also a spatial heterogeneity of contaminant concentrations through the basin. Finally, statistical treatments of these data with other parameters followed during the project, such as sediment grain size, organic content and PAH concentration, will contribute to a better understanding of key mechanisms related to sediments fate in dry stormwater retention/detention basin.

Tracking perchlorate contamination sources in France: an historical approach

Daniel Hube

BRGM, FR

Perchlorate (ClO_4^-) is a stable energetic oxyanion of chlorine forming high water-soluble salts. Chronic exposure to perchlorate disturbs thyroidic functions. During 2011- 2015, ClO_4^- has been detected in drinking water with concentrations above french recommended levels, in the northeast of France, along frontlines of World War I (WWI), and outside, in agricultural environment. For time, there are no scientific large scale researchs focusing on the real perchlorate sources in France and their relationships with the observed contamination. Moreover, the extent, the time and space fates of the contamination of groundwater have not been studied yet. This desktop study aims to highlight the origins and possible ClO_4^- sources in the specific historical frame of France. Detailed archivist researchs have been conducted in France, in London and in the USA. Furthermore, high explosives (HE) loading shells of Great War, discovered near Verdun have been sampled by the BRGM and analyzed for perchlorate, chlorate (ClO_3^-), nitrate, ammonium and NitroAromatic Compounds (NAC).

Two origins of perchlorate have been identified: natural ClO_4^- as impurity of chilean nitrates and (electro)synthetic perchlorate. Chilean nitrates had been massively imported in France before the WWII as fertilizers for intensive agriculture of beet and wheat and to supply the industry in nitrogen to produce nitric acid, synthetic fertilizers and NAC. ClO_4^- has thus polluted "conversion salpeter" (KNO_3), entering the composition of traditional black powder, ammonium nitrate and TNT of artillery shells, increasing dangerously the sensitivity to detonation when firing the projectiles. The presence of ClO_4^- impurities had been measured by the BRGM in sampled NAC HE as well in black powder by german chemists at the end of the XIXth century. Premature blastings of shells during firing due to ClO_4^- impurities were described by the gunners since 1880. During Trench War (1915-1917), enormous needs of HE for trench artillery and grenades motivated the development and large scale production of 4 types of synthetic (per)chlorated HE compositions, based on mixes of ClO_3^- or ClO_4^- energetic oxidizer with paraffinic fuels colored by methylen blue. 130 900 tons of (per)chlorate HE have been produced in France during WWI in France. The paraffin coating the salts may drastically hindered the dissolution rates of the explosives. The perchlorate could be introduced in the soil by old soil fertilizing, sparsed low-order detonation of projectiles, corrosion of the thin steel bodies of unexploded ordnances, or by massiv ammunition surpluses breaking-down operations during the interwar period.

Further researches are needed to define the kinetic dissolution of ClO_4^- in HE, to develop analytical and isotopic tools to fingerprint the origin of perchlorate. Specific methodologies are required too to define the sources, agricultural and/or military, of perchlorate in the specific case of France. Projects aiming these objectives are currently starting in the Vosges Mountain, in the region of Verdun, and in the Champagne area.

Transport models for risk assessment of natural and engineered nanoparticles in groundwater

Tiziana Tosco; Carlo Bianco; Rajandrea Sethi

Politecnico di Torino, IT

Nanosized particles of several materials, such as TiO₂, graphene, zero-valent iron, iron oxides, carbon nano-tubes, etc., are commonly used in industrial processes and for the manufacturing of commercial products. They can be released into the environment and, in particular, into groundwater throughout their entire life cycle, thus representing a potential risk for human health. Once released, nanoparticles can exhibit inherent toxicity, or play a role in enhancing the mobility of many contaminants, acting as a mobile solid phase which accelerates the transport of strongly sorbing contaminants (colloid-facilitated contaminant transport). It is therefore extremely important to develop approaches and tools suitable to predict the long-term fate of these emerging contaminants and the associated potential risk.

The quantification of the toxic and carcinogenic risk towards potential receptors requires the application of transport models for the evaluation of the nanoparticle concentration at the exposition point, C(poe). Nanoparticle transport in porous media is usually described by a modified advection-dispersion equation that takes into account the mass exchanges between liquid and solid phase due to physical and physico-chemical interactions. According to the degree of detail of the risk assessment procedure, C(poe) can be calculated via analytical formulations, Tier 2, or numerical tools, Tier 3.

In this work, NP-specific transport models are simplified and adapted to the analytical solutions commonly adopted in the conventional Tier 2 RBCA approach. The analytical solutions commonly used for the calculation of dissolved contaminant C(poe), are here extended to account for particle-porous-medium interaction. Moreover, the numerical tool MNM3D is proposed for the simulation of nanoparticle transport applied to Tier 3 risk assessment. MNM3D is a modified version of the well-known RT3D code, which implements numerical solutions to the NP transport equations porous media, accounting for the dependency of the attachment and detachment kinetic coefficients on transients in pore water ionic strength and velocity.

The analytical solutions and the numerical code MNM3D are here both applied to a synthetic case of release of silver nanoparticles and the results are compared. Finally the same release in a more complex hydrogeological scenario is simulated using the MNM3D code to highlight the effects of hydrochemical heterogeneities on the long term fate of nanoparticles in the environment.

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Groundwater Characterisation in Military Range Training Areas

Richard Martel

Institut national de la recherche scientifique, CA

Past decade of hydrogeological characterisation of range training areas (RTA) in Canadian military bases has shown that activities may be ranked based on their potential risks of groundwater (GW) contamination by ammunition residues. GW is a medium that integrates the behaviour of contaminants at the surface and the interaction/transformation of these dissolved contaminants within the vadose zone. Energetic materials (EM) in training areas may potentially migrate off range mostly via surface water (SW) and GW. Observation wells installed in those areas are tools for long term surveillance of GW quality and help to manage and sustain training. The challenge of water sampling in military training ranges is to avoid contamination bias of the samples with surface soil particles that may contain traces of metals perchlorate or EMs. A methodology for groundwater characterisation in RTAs is proposed and involves: (1) UXO (unexploded ordnance) detection, escort and drilling site preparation for security purposes, (2) borehole drilling, (3) well installation, (4) well development and purge, (5) hydraulic testing of wells (slug tests and water levels), (6) well sampling (Low flow – peristaltic pump or bladder pump and (7) lysimeters installation and sampling. The interpretation of geochemical data involves their comparison with existing water quality criteria and background values (for metals only), checking concentrations persistence between sampling campaigns and their relationship with neighbored observation wells. A Quality Assurance/ Quality Control program is trivial and includes field and trip blanks and duplicates. Examples of water characterisation works in RTAs at different scales illustrate that it is possible to perform such studies between training activities or during range clearance operations. These examples are: (1) the hydrogeological characterization of a small arms range backstop (copper, lead, antimony, zinc) and of a firing position of an anti-tank range (nitroglycerin and degradation products) with lysimeters and wells; (2) the aquifer delineation and groundwater flow direction in the entire training areas of an army base using LIDAR image, surface water elevation, water levels in wells, and water age.

1,4-dioxane found on TCA-polluted sites: a trigger towards a policy on contaminants of emerging concern

Griet Van Gestel¹; Roeland Van Muylder²; Nele Bal¹; Johan Ceenaeme¹

¹ OVAM; ² Witteveen+Bos, BE

For more than 20 years the Soil Decree is operative in Flanders, and proved to be a very successful legal instrument. Many contaminated sites are cleaned up, and a rigorous system of data collection and processing on soil and groundwater quality is set up. However, some improvements can be made. In the common practice of soil remediation, only the main components of soil polluting products are considered and analyzed. Yet, it is known that products like mineral oil, gasoline or chlorinated solvents contain additives, sometimes in high percentages.

1,4-dioxane was added to an industrially used chlorinated solvent, 1,1,1-trichloorethaan (TCA), to improve its functioning and stability, often in volume percentages larger than 1%. 1,4-dioxane is soluble in water, mobile, persistent and toxic for humans. Therefore, OVAM, the Public Waste Agency of Flanders, considered it necessary to launch an exploratory survey. The aim was to estimate the extent of the problem in Flanders, and to work out an approach towards a solution. The survey was carried out by Witteveen + Bos and MAVA.

The OVAM data base contains information on about 200 sites with TCA contamination in groundwater. 16 sites were selected, evenly distributed over Flanders, and 1,4-dioxane was analyzed in several wells on each site. On 13 out of the 16 sites, the concentration of 1,4-dioxane in groundwater was higher than the threshold value of 50 µg/l, based on risks for human health (drinking water). On several sites, concentrations of 1,4-dioxane exceeded 1000 µg/l. These results show that for sites contaminated with TCA, 1,4-dioxane should be analyzed and taken into account for risk assessment. Changes to regulations are envisaged.

1,4-dioxane is one of the many emerging contaminants that are not well covered by the common legal and practical approaches of soil and groundwater remediation. The policy of OVAM on this matter is to give priority to substances of highest 'overall' risk, and for which remediation or prevention is feasible. The scale of use of the substance, the way and extent to which it was spilled into the environment, the persistence, mobility and toxicity are taken into account to estimate the 'overall' risks.

In a previous survey, tributyl alcohol (TBA) was measured on sites where groundwater was contaminated with MTBE. Surveys on other substances will follow.

In the presentation, the policy of OVAM on emerging contaminants will be explained, and the need for transnational co-operation and exchange will be stressed. The challenges or matters of concern are great: risks for human health and ecosystems, risk for further spreading (e.g. by dredging of sediments), lack of guidance for local and regional authorities, problems with liability, ... Transnational co-operation will offer major opportunities to solve these problems in a more effective and efficient way.

ThS 2d.1: Risks related to surface & subsurface energy systems

Environmental implications of black shale weathering in the Grand Duchy of Luxembourg

Valérie Cappuyens; Pieter Geris; Rudy Swennen

KU Leuven, BE

The attention for black shale formations increased in recent years because of their potential for CO₂ storage. Another potential concern is their enrichment with potentially toxic elements (PETs), which may be of environmental concern upon weathering of the shales. A comprehensive study of the so-called Schistes à Carton, a black shale formation occurring in the south-west of the in the Grand Duchy of Luxembourg was performed. Three weathering profiles, drilled from the soil surface till the fresh bedrock were investigated in detail to understand (i) the changes in mineralogy as a function of depth in comparison to the mineralogy of the bedrock; (ii) the elemental distribution of major and trace elements within the weathering profiles; (iii) the availability of trace elements within the soil overlying the black shales.

Besides geochemical analysis (major and trace elements, organic and inorganic carbon content, pH), the mineralogy of the Schistes à Carton was investigated by microscopy and X-ray diffraction. The relation between the mineralogy and the distribution of (trace) elements was deduced from FEG-EPMA analyses. The leaching of trace elements was determined by the application of leaching tests (pHstat tests and pH depended leaching tests) and single extractions (with NH₄-EDTA, HOAc and CaCl₂).

The mineralogy of the Schistes à Carton bedrock consists mainly of illite and kaolinite, quartz, calcite and pyrite. At a depth of 4.25 m, the bedrock starts to be affected by chemical, oxidizing weathering processes as pyrite is altered to goethite and gypsum. Gypsum is only precipitated till a depth of around 1.50 m. The acidity generated by pyrite oxidation is neutralized by calcite dissolution, resulting in neutral to slightly alkaline pH conditions.

The elemental distribution and enrichment factors within the weathered shales and at the soil surface indicate an increase in concentration for As, Cd, Fe, Mo, Ni, Pb and Zn towards the surface, in comparison to the chemical composition of the bedrock (background level). Most of these elements are not leached from the shales in the prevailing pH conditions (7 - 7.5), except Ni and Mo. Most PETs are co-precipitated in goethite and adsorbed on clays, goethite and organic matter. The elevated concentrations of Pb and Zn are

thought to be (partly) related to the presence of an anthropogenic pollution source (nearby steel plant). The Mo concentrations within the weathered shales were significantly higher (up to 75 mg kg⁻¹) than worldwide background concentrations. The weathering of the Schistes à Carton implies only low environmental risks for the majority of the PTEs as they are co-precipitated in goethite and adsorbed on clays, goethite and organic matter upon weathering. The risk is medium for Ni and Mo as they are mobile at circumneutral pH conditions. This type of investigations is a useful basis for the further development of soil legislation in Luxembourg, and shows the importance of subsurface composition and its influence on soil geochemistry.

Risk assessment of organic pollutants in shale gas flowback and produced waters

Andrii Butkovskyi; Harry Bruning¹; Annemarie van Wezel²; Huub Rijnaarts¹

¹ Wageningen University; ² KWR, NL

The presence of highly toxic organic compounds in fracturing fluids used for natural gas production from shales has become a source of awareness both among the scientific community and general public. However, the existing literature on risk assessment of organic chemicals in water cycle related to shale gas production is limited to the chemicals listed in fracturing fluid compositions provided by well operators and not on empirical data. It also does not take into account structural changes of chemicals that occur downhole. The data on organic composition of flowback and produced water (FPW) from shale gas wells are scarce and unsystematised, and therefore environmental impact of FPW remains unclear.

Fracturing fluid can reach the environment as a result of accidental spills, whereas a significant fraction of FPW is regularly discharged to the environment as a waste stream. FPW is treated before discharge, but the treatment strategies are mostly focused on the removal of inorganic components, while organic chemicals often remain unaddressed. This study systematizes knowledge on the presence of organic compounds in shale gas FPW and introduces a risk assessment approach for prediction of potential hazards associated with release of these compounds to the environment.

Original empirical data on the presence of organic chemicals in FPW were extracted and structured from peer-reviewed papers and reports as a base for the risk assessment. The detected compounds include BTEX, PAHs, phthalates, saturated aliphatic and aromatic hydrocarbons, heterocyclic and halogenated compounds, linear surfactants and different classes of biocides.

The potential hazards of these compounds to the environment associated with the discharge of treated FPW to the surface waters was assessed for the Dommel river basin (the Netherlands). The Dommel basin lies completely within the area of a prospective shale gas production. The average discharge of FPW from shale gas field equal to 600 m³/d was estimated by extrapolation of historical data and assessing water management practices in the U.S. shale basins. This value was compared with the average flow at the river mouth at dry periods (3 m³/s) to obtain a dilution factor of 435.

Absence of organic pollutant removal during treatment was assumed. The environmental concentrations of organic chemicals reported in the reviewed literature were estimated using their maximal reported concentrations and the dilution factor. Predicted no effect concentrations (PNEC) were calculated from chronic and acute toxicity data using assessment factors of 10 to 1000. Risk quotients of 1,3,5-Trimethylbenzene, carbon disulfide, naphthalene, 2-methylnaphthalene, phenanthrene, bis(2-ethylhexyl)-phthalate, di-n-octyl phthalate and the transformation product of biocide dazomet (hexahydro-1,3,5-trimethyl-1,3,5-triazinane-2-thione) exceeded 1. These compounds were defined as "prioritized shale gas-related organic compounds".

The proposed risk assessment approach can be applied for estimation of potential hazards from FPW discharge and designing FPW treatment facilities that will be suitable for removal of potentially hazardous organic compounds.

Petroleum Vapour Intrusion - Practical learnings: background sources, remedial objectives, and corrective measures

Mattias Claesson¹; Maelle Cargouet¹; Richard Sumner¹; Bart Eklund²

¹ AECOM France; ² AECOM USA, FR

Vapour intrusion (VI) is the vapour-phase migration of volatile contaminants from a subsurface source into overlying buildings or other structures. VI cuts across multiple technical areas – from the subsurface transport of Light Non-Aqueous Phase Liquids (LNAPL) and vapours to building design and construction materials, ventilation and toxicology – and is therefore a complex issue to adequately assess and mitigate. The regulations and guidance addressing VI have evolved in recent years as our technical knowledge has grown. This paper presents practical learnings from a former refinery site where assessment and active mitigation of Petroleum VI are currently on-going.

An accidental release of refined petroleum hydrocarbons to the subsurface occurred in the 1980's. The release generated a LNAPL plume expanding beneath a residential area reported to exceed 100 hectares. The current LNAPL plume footprint has been reduced to the order of 15 hectares by active LNAPL recovery measures.

Project data show that VI is no longer occurring within the historic extents of the LNAPL plume. However a part of the plume footprint still remains below a residential area where VI is observed. LNAPL mobility, recoverability and persistence are therefore key aspects of the Conceptual Site Model (CSM) and of understanding VI at the site.

VI has been documented at numerous properties with benzene measured in indoor air at concentrations several orders of magnitude above regulatory thresholds. A routine indoor air monitoring programme is established and includes sampling at some 70 building locations. The occurrence of VI within the current plume footprint is spatially variable without evident correlation to features such as LNAPL thickness, soil gas quality, geology, and building type, etc., emphasising the complexity of the VI issue. It is plausible that the absence of clear correlation between VI and such features is predominantly related to the foundation construction and integrity as well as the building ventilation regime which are inherently different for each building in the area.

The presence of other (background) sources of volatile compounds has been demonstrated by the assessments at the site. Background sources include atmospheric emissions, other sub-surface sources, as well as domestic sources such as smoking, wood-fired stoves and household products. The importance of accurately considering background sources in setting remedial goals and in measuring effects of mitigation measures is emphasised.

VI mitigation measures have been deployed at several tens of properties and have included sealing of building basements and floors, enforced building ventilation, sub-slab extraction of soil gas, and temporary resident relocation. Amongst the engineering measures, sub-slab extraction systems have demonstrated the most consistent effect in mitigating VI. Also, the sub-slab systems can typically be installed with little to no civil works in indoor living areas, which reduces the disturbance for the residents.

Contaminated fiber banks – release and uptake of organic contaminants from an organic-rich sediment

Sarah Josefsson¹; Anna Apler; Lovisa Zillén; Ian Snowball; Lisa Vogel; Anna-Karin Dahlberg; Karin Wiberg

¹ The Geological Survey of Sweden (SGU), SE

During the 19th and 20th centuries, the forest industry, including the pulp & paper and board industries, discharged substantial volumes of wastewater into the aquatic environment in coastal and inland waters of Sweden. The wastewater contained wooden fibers and cellulose, and these releases were deposited mainly in shallow areas close to the industries in the form of fiber banks. In addition, process chemicals and other contaminants were also discharged. Inventories of fiber banks in the northern counties of Sweden have showed that the banks contain high levels of organic contaminants, e.g. PCBs and pesticides, and metals, e.g. mercury. They also have a high organic content, which on one hand can enhance contaminant sorption, on the other hand facilitate spreading due to gas ebullition from organic matter degradation. In the ongoing project TREASURE, the risk of spreading of contaminants from fiber banks to the surrounding environment through abiotic and biotic routes is investigated.

During the summers of 2014 and 2015, extensive field sampling was performed at three fiber bank areas located close to Kramfors, Sweden. Sampling was performed in gradients from fiber banks to fiber-rich sediments and on to cleaner, more minerogenic sediment further from the shore. Sediment samples were analysed for various organic pollutants, including PCBs, DDTs, HCHs and HCB. Bioavailable concentrations of contaminants were measured by shaking sediment with polyoxymethylene (POM) samplers. In addition, benthic biota was sampled to investigate bioaccumulation and biomagnification of the contaminants. Fluxes from the sediment were measured in situ using flux chambers with semipermeable membrane devices (SPMDs). The effect of resuspension on contaminant remobilization was investigated by sampling water close to the sediment surface during resuspension events.

Results from the analyses showed that contaminant levels were higher in fiber banks than in the adjacent fiber-rich sediment, even on an organic carbon basis (instead of on a dry weight basis). This indicates that the origin of the pollutants is similar as the origin of the fibers forming the fiber banks. The fiber bank sediment was anoxic and no benthic biota was found. In the fiber-rich sediment, polychaetes and crustaceans were found. Biota-sediment accumulation factors (BSAFs) showed that bioaccumulation of organic contaminants occurred and most likely also biomagnification, as BSAFs were higher in the crustaceans (predators) than in the polychaetes (deposit-feeders). The bioavailable concentration showed that sorption of organic contaminants, as expected, was higher in the fiber banks than in other sediment. Surprisingly, biota concentration were better correlated to total sediment concentrations than to bioavailable concentrations. Flux samples are currently processed in the laboratory. When all results are available, they will allow us to evaluate the risk of spreading of organic contaminants from contaminated fiber banks by different processes.

Significant differences between calculated and measured contaminant fluxes from sediments of industrial origin

Paul Frogner-Kockum¹; Mikhail Kononets²; Anna Apler³; Sarah Josefsson⁴; Gunnel Göransson¹; Lovisa Zillén⁵; Karin Wiberg⁶; Ian Snowball⁷

¹ Swedish Geotechnical Institute; ² Göteborg university; ³ Swedish Geological Survey; ⁴ The Geological Survey of Sweden (SGU)Swed; ⁵The Geological Survey of Sweden (SGU); ⁶ Swedish University of Agricultural Sciences; ⁷ Uppsala University, SE

Metal-fluxes across the sediment-water interface have previously been predicted in Sweden by diffusion flux models in risk-assessments of contaminated sediments. These models are based on gradients between pore water concentrations and/or overlying bottom water. However, large uncertainties exists using flux models, because overall fluxes (a sum of diffusion, advection and bioturbation) from sediments might be greater than diffusion alone. A difference between predicted and measured fluxes has earlier been observed by Pakhomova et al. (2007). They measured Fe and Mn which are redox-sensitive, adding additional uncertainty and making it challenging to assess differences between models and observations.

The objective of our study was therefore to compare flux-measurements with predicted fluxes of Mo, Ni and Co from "fibre-banks" and fibre-rich sediments. The "fibre-banks" and fibre-rich sediments are accumulations of heavily contaminated cellulose-rich sediments derived from pulp and paper factories at Sandviken and Väja, situated adjacent to the river Ångermanälven in Sweden. Fluxes of Mo from fibre-banks were in the range of 0.42- 0.66 $\mu\text{mol}/\text{m}^2/\text{day}$, while predicted fluxes were 0.02-0.1 $\mu\text{mol}/\text{m}^2/\text{day}$. Measured fluxes of Ni from fibre-banks were 3.9-8.5 $\mu\text{mol}/\text{m}^2/\text{day}$, while the predicted value was 0.03 $\mu\text{mol}/\text{m}^2/\text{day}$. In fibre-rich sediments, we determined Co fluxes of 0.46-2.6 $\mu\text{mol}/\text{m}^2/\text{day}$, while the predicted value was 0.01 $\mu\text{mol}/\text{m}^2/\text{day}$. These significant differences between calculated and measured contaminant fluxes demonstrate that risk assessments based solely on model predictions severely underestimate the real hazard. Such erroneous estimations will also have severe implications for the possibility to achieve the environmental goals of a non-toxic environment and a marine environment in balance.

ThS 3a.1: Advances in biological reductive dechlorination

Impact of Magnetite Nanoparticles on the Syntrophic Dechlorination of 1,2-Dichloroethane

Patrícia Leitão¹; Federico Aulenta²; Simona Rossetti²; Henri Nouws³; Anthony Danko¹

¹Universidade do Porto Faculdade de Engenharia, ²IRSA, ³ISEP; PT

The chlorinated aliphatic hydrocarbon (CAH) 1,2-Dichloroethane (1,2-DCA) is commonly used as a degreasing agent and as a precursor for the production of polyvinylchloride. As such, it is frequently detected in contaminated soil and groundwater due to improper handling, storage and disposal.

In anaerobic environments microorganisms exchange electron equivalents with different microbial community members and with compounds present in the soil and groundwater. These interactions may play an important role in natural biogeochemical cycles as well as in the bioremediation of sites contaminated with chlorinated solvents. CAHs, including 1,2-DCA, may be reduced chemically or biologically under anaerobic conditions. Microorganisms may serve as catalysts to carry out this transformation, via reductive dechlorination or dihaloelimination, into lesser or even non-chlorinated end products. Several microorganisms have been shown to carry out these reactions and include those from the genus *Dehalococcoides*, *Dehalobacter* and *Desulfitobacterium*.

Interspecies electron transfer (IET) may occur by several mechanisms: diffusion of redox compounds or direct contact between cells (via redox proteins or conductive appendages such as nanowires) and maybe facilitated by conductive nanoparticles possibly serving as electron conduit. Recent evidence has shown that magnetite and other conductive minerals serve as electrical conduits to facilitate electron transfer between species. Some studies have suggested that iron and manganese minerals may inhibit CAH dechlorination by serving as more suitable electron acceptors. Others demonstrated that magnetite stimulated trichloroethene reduction using acetate as an electron donor. Despite these results, it is still unknown whether similar results may be obtained with other CAHs.

Our study examined the effect of magnetite (Fe₃O₄) nanoparticles on the kinetics and the microbial population of a 1,2-dichloroethane (1,2-DCA) mixed dechlorinating culture. The addition of magnetite nanoparticles (170 mg/L as total Fe) was shown to enhance 1,2-DCA dechlorination kinetics up to 3.3-times, while decreasing the lag time by 0.8 times (23 days) when compared to unamended microcosms. The concentration of Archaea was higher in microcosms without magnetite, which suggested that syntrophic interactions were less efficient without the presence of these electron conduits. A remarkable finding was that dechlorination activity was correlated with the abundance of *Dehalococcoides mccartyi* spp., indicating a key role of this microorganism in the dechlorination process. Given the widespread abundance of conductive minerals in the environment, the results of this study may provide new insights into the fate of 1,2-DCA and suggest new tools for its remediation by linking biogeochemical mechanisms.

Characterization of a Dehalobacterium-containing enrichment culture fermenting high concentrations of dichloromethane under reducing conditions: microbial composition, isotope analysis and potential inhibitory effect of co-contaminants.

Alba Trueba-Santiso¹; Eloi Parladé¹; Mònica Rosell²; Marc Lliros¹; Siti Hatijah¹; Maira Martínez-Alonso¹; Nuria Gaju¹; Lucía Martín-González¹; Teresa Vicent¹; Ernest Marco-Urrea¹

¹ Universitat Autònoma de Barcelona; ² Universitat de Barcelona, ES

Dichloromethane (DCM) is one of the most frequently detected groundwater pollutants and its biodegradation under reducing conditions is solely reported for *Dehalobacterium formicoaceticum* and *Dehalobacter* species via a fermentative pathway. We present an enrichment culture, obtained from a membrane bioreactor operating in an industrial wastewater treatment plant, capable of transforming high concentrations of DCM and the brominated analogue dibromomethane (DBM) to acetate and formate. Comparative analysis of bacterial 16S rDNA-DGGE profiles from colonies derived from serial dilution-to-extinction vials showed that cultures degrading DCM contained a predominant band belonging to *Dehalobacterium*, but it was absent when DCM was not degraded. Analysis of the microbial composition of the consortia by Illumina MiSeq sequencing confirmed the presence of *Dehalobacterium* together with three additional phylotypes belonging to *Acetobacterium*, *Desulfovibrio*, and *Wolinella*, representing all four OTUs >99.9% of the retrieved sequences. The carbon isotopic fractionation (ϵ) determined for DCM degradation in this culture was $-27 \pm 2\text{‰}$. This value differs from the ϵ previously reported for the DCM-fermentative bacteria *Dehalobacter* ($-15.5 \pm 1.5\text{‰}$) but they are both significantly different from those reported for facultative methylotrophic organisms (ranging from -45 to -61‰), which allows to differentiate between hydrolytic transformation of DCM via glutathione-dependent dehalogenases and fermentation pathway in in situ applications. In addition, we studied the effect of the concentration of a wide array of frequently detected co-contaminants in groundwaters (i.e. chlorinated solvents, personal care products and pesticides) on the capability of *Dehalobacterium* to ferment DCM.

Molecular tools for assessment of thermally enhanced bioremediation of TCE – bench-scale testing

*Petra Najmanova*¹; *Jana Steinova*; *Marie Czinneva*²; *Jan Nemecek*³; *Vladislav Knytl*; *Martin Halecky*⁴

¹ DEKONTA, a.s.; ² Technical University in Liberec; ³ ENACON s.r.o.; ⁴ University of Chemistry and Technology Prague, CZ

The worldwide industrial use of chlorinated solvents has resulted in an extensive groundwater contamination by compounds such as the suspected human carcinogen trichloroethene (TCE). TCE can be biologically dechlorinated under anaerobic conditions to cis-dichloroethene, vinyl chloride and finally to ethane. The temperature dependence (in range 10 – 30 °C) of TCE dechlorination was observed within lab experiments in contaminated groundwater and soil for nine weeks. Total concentration of chlorinated ethenes (TCE dominant) was

26, 895 µg/L. Biotic reduction was significantly supported by whey addition as an organic substrate for indigenous bacteria. The degradation process was monitored using numerous techniques, including physical-chemical analyses or molecular biological analyses. The abundance changes of organohalide-respiring bacteria were studied using quantitative PCR. Functional genes *vcrA* and *bvcA* as well as 16S rRNA specific for *Dehalococcoides* spp., *Dehalobacter* spp., and *Desulfitobacterium* spp. were amplified. Moreover, sulphate reducing bacteria and denitrifying bacteria were monitored by amplifying functional genes *apsA* and *nirK*, respectively.

The temperature increase and whey addition had positive effect on TCE dechlorination at the temperatures 17 and 22 °C. The chlorine number (average number of chlorine atoms per ethene) dropped after 9 weeks from 2.5 to 0.1 at 22 °C, to 1.1 at 17 °C and to 1.7 at 12 °C. The result indicates, that complete reductive dechlorination at 22 °C was achieved. The results of chemical analyses were in congruence with vinyl chloride reductase genes (*bvcA* and *vcrA*) and *Dehalococcoides* spp. rapid increase after 9 weeks at 17 and 22 °C. *Dehalobacter* spp. and *Desulfitobacterium* spp. increase was observed earlier (after 6 weeks) with the maximum at 22 °C.

The results of this study demonstrate the feasibility and high efficiency of the thermally enhanced biotic dechlorination of chlorinated ethenes. The temperature 22 °C had the greatest positive impact that was confirmed by the wide scope of chemical and molecular analyses. Only small temperature increase can significantly accelerate the process of biological reductive dechlorination, which seems to have high potential in remediation of sites contaminated with chlorinated solvents. Based on the positive results of laboratory bench-scale tests performed a field test was carried out (presented in a separate paper).

Tools and concepts for quantifying in situ degradation rates of chlorinated solvents

Katerina Tsitonaki¹; Liselotte Clausen²; Rasmus Jakobsen³; Christian Nyrop Albers³; Anders Johansen⁴; Mette M Broholm⁵; Ida Damgaard⁶; Henriette Kern-Jespersen⁶; Nina Tuxen⁶; Adrian Schiefler⁶

¹ Orbicon A/S; ² Krüger A/S; ³ GEUS; ⁴ Aarhus University; ⁵ DTU Environment; ⁶ Capital Region of Denmark, DK

Background

Chlorinated solvents from dry-cleaning and degreasing activities are the most common groundwater contaminants in Denmark, detected in approximately 10 % of drinking water wells. In Denmark, it is the state authorities, like Capital Region, which are responsible for assessing the risks and manage the many sites polluted with chlorinated solvent. Hence, Monitored Natural Attenuation (MNA) as a remediation strategy would probably reduce costs of site management. The usability of MNA would improve greatly, if reliable in-situ degradation rates for chlorinated compounds could be established.

Aim

The Capital Region has therefore initiated a project aiming to develop and improve field tools to measure degradation rates in situ with a higher level of precision and reliability.

Methodology

The first phase of the project included a review of the literature, in order to map the available tools. Based on the results of the literature review we test a method concept that includes a combination of several cutting-edge analytical and biomolecular technologies in order to quantify degradation rates for chlorinated compounds. The project includes an array of established methodologies: a) 2D- Compound Specific Isotope Analysis of carbon and chlorine isotopes of TCE, cis-DCE and VC, b) QuantArray-Chlor, which allows for the simultaneous quantification of a multitude of key microbes (Dehalococcoides, Dehalobacter, Dehalogenimonas, Desulfitobacterium) and functional genes responsible for biodegradation, c) Next generation sequencing for examining the microbial community composition. Finally, the project includes a new method of degradation quantification under development by GEUS where ¹⁴C-cis-DCE is injected into core samples from the sites and the resulting ¹⁴C-VC, ¹⁴C-ethene, ¹⁴C-ethane and ¹⁴C-CO₂ are quantified. The above tools combined with standard chemical and geochemical analysis and knowledge of the transport times between sampling points can be used to calculate degradation rates.

Results and conclusion

The array of tools will be applied at three test sites. The first test site is undergoing stimulated reductive dechlorination, and serves therefore as a reference site for testing the concept and detection limits of the applied tools. Activities at this site are taking place in November–December 2016. We plan to apply the same tool package at two more test sites, on which the aim is to quantify rates of natural degradation rates during the first half of 2017.

The presentation will present concepts and preliminary results from the performed tests including the quantified degradation rates for chlorinated solvents as well as a feasibility assessment and evaluation of the tool package.

Remediating 1,2-Dichloropropane Contaminated Groundwater in Low-Permeability Media using Micro-scale ZVI and Organic Carbon Amendment

Alberto Leombruni, Mike Mueller

PeroxyChem, AT

Background: In situ chemical reduction (ISCR) combined with bioremediation via enhanced reductive dechlorination (ERD) are effective and widely applied remediation methods for chlorinated solvent-contaminated groundwater. In situ groundwater remediation is often accomplished by injecting liquid or particulate reactive amendments to stimulate biological and/or abiotic degradation mechanisms. This approach is challenging to apply in low permeability media, due to the difficulty in distributing amendments in the targeted treatment zone. For example, EHC ISCR reagent is a combination of solid organic carbon and zero valent iron (ZVI) used for the treatment of groundwater and saturated soil impacted by persistent halogenated compounds, including chlorinated solvents, pesticides and organic explosives. The EHC formula is the culmination of years of research and successful field use around the globe. EHC is comprised of a synergistic mixture of micro-scale ZVI and controlled-release organic carbon, stimulating both abiotic and biotic dechlorination mechanisms. Aim: Following a truck accident on one of the main motorways in the North of Italy, about 3.000 Liters of 1,2-Dichloropropane were released into the ground, causing an immediate contamination of soils and groundwater. As an emergency response remedial action, approximately 900 m³ of shallow soils were excavated and disposed into landfill. Secondly, the contaminated aquifer has been physically delimited emplacing metal sheet piles to a depth of 6 meter below ground level (bgl) to limit further contaminant migration. Lastly, a total of 55.000 kg of EHC was injected into a triangular grid of 42 injection points between 1 m - 6 m bgl. A subsurface recirculation system has also been maintained over the EHC treatment period, designed to enhance diffusion of the amendments in the aquifer. The target goal for the grid set forth in the Clean-up Plan developed for the site was to obtain a removal efficiency of at least 90% reduction in 1,2-Dichloropropane compared to baseline concentrations at compliance points located in the treatment area. Conclusion: 1,2-Dichloropropane removal rates peaked approximately 15 months after commencement of the remediation activities, at > 89 percent removal. Two years after the application, these rates increased slightly to approximately 96 percent removal, and have remained at that level for nine months continuously supporting treatment of groundwater. A significant increase in Dissolved Iron and Total Organic Carbon (TOC), coupled with low redox (ORP) conditions were measured in the treatment area during the first 1 to 2 years. The EHC reactive zone constitutes a "green remedial solution", having produced a low carbon footprint during application, use of few energy requirements, and with minimal maintenance costs limited to groundwater monitoring over the life of the treatment. Site closure was accomplished in 2015. The authors will present an overview of the technology, its field application processes, lessons learned, and economics of the project.

ThS 3a.2: Pilot and Field Scale biological reductive dechlorination

Assessment of the bioremediation potential of groundwater contaminated with chlorinated solvents and enhanced reductive dechlorination pilot test at an industrial site in Barcelona (Spain)

Natàlia Blázquez-Pallí¹; Marçal Bosch²; Joan Varias²; Mònica Rosell³; Albert Soler i Gil³; Teresa Vicent¹; Ernest Marco-Urrea¹

¹ Universitat Autònoma de Barcelona; ² Litoclean; ³ Universitat de Barcelona, ES

The aim of this project was to assess the bioremediation potential of an aquifer located in an industrial site in Barcelona (Spain) contaminated with perchloroethylene (PCE) and its breakdown products (trichloroethylene (TCE), cis- and trans-dichloroethylene (DCE) and vinyl chloride, VC). Based on these results, a strategy to enhance reductive dechlorination was selected and implemented to clean up the groundwater through a pilot test. Prior to the design and implementation of the in situ pilot test, two sampling campaigns (May and October 2016, 14 monitoring wells in total) were carried out to characterise the geochemical and hydrogeological conditions of the groundwater, and to assess natural attenuation of chlorinated ethenes from (i) their carbon isotopic composition ($\delta^{13}\text{C}$) along the contaminated groundwater plume and from (ii) laboratory microcosm studies with groundwater (containing fine sediments) collected from the bottom of 4 different monitoring wells. Significant differences in the $\delta^{13}\text{C}$ of PCE, TCE, and cis-DCE (greater than 2‰) across the different wells, and closed isotopic balances among these compounds, indicated biological reductive dechlorination processes taking place in the field. Laboratory microcosms were prepared to evaluate whether native bacteria could completely dechlorinate the chlorinated ethenes present in the groundwater samples, and how different fermentable organic substrates (sodium lactate, a mixture of methanol and ethanol, and a commercial fermentable product) could enhance this biodegradation. Results showed that biostimulated microcosms transformed chlorinated ethenes to ethene at a noticeable higher rate in comparison to the controls containing solely groundwater. In particular, ethene production proceeded faster in the microcosms amended with lactate, which was fermented, primarily, to acetate and hydrogen. Finally, PCR with primers targeting *Dehalococcoides mccartyi* 16S rRNA gene and reductive dehalogenase genes implicated in VC reductive dechlorination will be used to identify and confirm the presence of *Dehalococcoides mccartyi* species in groundwater, as suggested by the presence of ethene. Following the above-mentioned results, sodium lactate was selected as organic fermentable substrate to perform in situ biostimulation. The pilot test started on the 25th October 2016 with the injection of 1.7 m³ of an aqueous solution of sodium lactate at around 120 g/L, containing sodic fluorescein as a conservative tracer, through one of the most contaminated monitoring wells. The indicators selected for monitoring the success of this test, determined periodically from up and down-flow monitoring wells, are (i) the change in the redox conditions of the groundwater; (ii) the consumption of lactate and generation of acetate, and (iii) the concentration and $\delta^{13}\text{C}$ evolution of chlorinated ethenes with time. Fluorescein is used to determine the arrival of the biostimulation at different places of the aquifer, in order to monitor chemical and isotopic characterization. The results obtained during the monitoring of the biostimulation process will be presented in this conference.

Thermally Enhanced In Situ Bioremediation of Groundwater Contaminated with Chlorinated Solvents – A Field Test

*Jan Nemecek*¹; *Jana Steinova*²; *Tomas Pluhar*²; *Petra Najmanova*³; *Vladislav Knytl*³; *Kamil Nesetril*²; *Miroslav Černík*²

¹ ENACON s.r.o.; ² Technical University in Liberec; ³ DEKONTA, a.s., CZ

In situ bioremediation using reductive dechlorination is a widely accepted and commercially applied technology for treatment of groundwater contaminated with chlorinated solvents. Compared to physical or chemical technologies however, it is a relatively slow approach. As elevated temperature has a positive kinetic effect on microbial metabolism, thermal enhancement may prove a viable means of accelerating in situ bioremediation.

Results of laboratory bench-scale tests performed during the first phase of this study (presented in a separate paper) indicated that the optimal temperature range for reductive dechlorination by indigenous dechlorinating microorganisms is from 22 to 25°C.

We tested a thermally enhanced in situ bioremediation technology at a pilot site where the total concentration of chlorinated ethenes (cVOC) ranged from 249 to 14,539 µg/l. The aquifer at this site is situated in shallow sandy saprolite underlined by irregularly fractured granite. A circulation system comprising pumping and injection wells was used to heat the aquifer. A layout of the circulation system was designed using mathematical modelling of heat transfer. The temperature of the extracted water was raised to 35-45°C with a solar and electricity heaters then injected back into the aquifer, the temperature being adjusted in order to maintain a temperature in the aquifer ranging from 20 to 25°C. Fermentable substrate (whey) was injected in three batches into the injection well. The test was monitored using hydrochemical and molecular biological tools (e.g. quantitative polymerase chain reaction).

Addition of a substrate and increasing the temperature resulted in a rapid increase in total biomass, sulphate reducing bacteria (functional gene *apsA*), and reductive dechlorinators (especially *Dehalococcoides* sp. and vinyl chloride reductase genes *vcrA* and *bvcA*), along with a strong increase in cVOC dechlorination. After just one month, total cVOC concentration had decreased by 54% - 94% in effectively influenced wells. At the same time, chlorine number (average number of chlorine atoms per ethene in the groundwater sample) decreased from an initial 1.1-1.6 to 0.1-0.8, indicating significant reductive dechlorination. In a reference well where reductive dechlorination was enhanced with substrate only, the degradation process was significantly slower.

In sum, results of the pilot tests indicate that thermally enhanced in situ bioremediation is a promising remedial approach for treatment of chlorinated ethenes.

Bioremediation of chloroethylenes using a groundwater recirculation system (BEAT)

Gerard Borggreve¹; Albert Smits¹; Dennis Scheper; Luuk Wallinga²; Maurice Henssen³; Dick Specht³; Adri Nipshagen³

¹ NTP Enviro; ² RUD Drenthe; ³ Bioclear, NL

Due to historic activities numerous sites are polluted with chloroethylenes. Many of these sites are located in densely build and populated areas which imposes specific requirements to the remediation technique that can be used.

Technique

From more than ten years of experience with an in situ groundwater and biomass recirculation system called the BEAT-concept (Biological Enhanced Augmentation Technique), it can be concluded that this is a valuable technique to remediate groundwater contaminated with chloroethylenes. With the BEAT-concept, the reductive dechlorination is stimulated by mixing DHC (cultured DHC in an anaerobic bioreactor), carbon source (like lactate or acetate) and nutrients in situ with contaminated groundwater. The success of the BEAT-concept is highly dependent on the distribution of the amendments within the targeted treatment zone. Smart location choice of extraction wells and infiltration wells is essential. The phase in which active groundwater extraction and infiltration takes place, is called the active phase of the bioremediation, in which the soil pore volume of the treated area needs to be flushed 1.5 times. When the targeted treatment zone is provided with sufficient carbon-source and biomass, the bioreactor is removed, and the passive phase starts. In the passive phase the chloroethylenes are further degraded to ethene and ethane. A successful BEAT-concept remediation results in total concentration of chloroethylenes of 10 µg/l or lower. The total amount of pollution is reduced by 97 to 99.9%, within a passive phase period of (median) 100 - 250 days.

Casus

The remediation site Holwerd is located on the outskirts of the town of Coevorden in The Netherlands. The groundwater is polluted with high concentrations of chloroethylenes (perchloroethylene and trichloroethylene). Commissioned by the provincial government, NTP Enviro and Bioclear have made a design for the remediation of the polluted groundwater, based upon biological anaerobic dechlorination processes. Essential for the planning of the project was the construction of a shopping mall, and the strong agreement that the stores were to be opened before Christmas 2014.

Development and remediation go hand in hand.

The remediation and monitoring systems were installed underground before construction of the floor of the mall. The remediation started in August 2014 with the extraction of contaminated groundwater, the addition of a carbon source and dechlorinating biomass (*Dehalococcoides* sp (DHC)) and infiltration of the water and additives.

The results

After two years the targeted treatment zone up to a depth of 10 m-gl is provided with 28,000 kg of carbon source and 103 cells DHC/ml by recirculating 75,000 m³ of contaminated groundwater. To date all the perchloroethylene (130,000 µg/l) and trichloroethylene (15,000 µg/l) has been fully degraded to dichloroethylene and vinylchloride. The redox conditions are methanogenic, and there is still sufficient carbon source to maintain further degradation to ethene and ethane.

During the remediation and monitoring, the site is used as a shopping and parking center without any inconvenience from both sides.

Source Zone In Situ Biostimulation and Bioaugmentation of Elevated Concentrations of Chlorinated Ethenes in Groundwater

Mark Mejac¹; Laurie LaPat-Polasko¹; Sherrick Baffert; Linda Conlan²

1 Ramboll Environ; ² AMECFW, US

Introduction: The purpose of the in situ bioremediation system was to evaluate the effectiveness of biostimulation in combination with bioaugmentation to promote biodegradation of chlorinated solvents in source area groundwater. Elevated levels (>30 milligrams per liter) of tetrachloroethene (PCE), trichloroethene (TCE), and cis-1,2-dichloroethene (cis-1,2-DCE) were detected in site groundwater. The natural attenuation evaluation indicated that reductive dechlorination was occurring in several of the on-site monitor wells.

Bench-scale testing indicated that a variety of carbon substrates were effective at reducing the oxidation reduction potential (ORP) to levels that were conducive to reductive dechlorination. However, the indigenous microbial population was not able to successfully degrade PCE to ethene. When a microbial consortium including *Dehalococcoides* was added to the microcosms, complete reductive dechlorination was observed within several weeks.

Approach: A pair of recirculation wells was installed to inject the carbon sources and microbial consortium into the groundwater. Lactate was injected to promote highly reduced conditions. Once the ORP was less -150 mV, the *Dehalococcoides* consortium (KB-1) was injected into the groundwater. Approximately 8 months post the bioaugmentation event, the slow release carbon substrate EOS Pro[®] and CoBupH-Mg were injected to provide a long-term carbon substrate and buffering agent, respectively. The groundwater was monitored on a monthly basis. In addition, the groundwater was also monitored compound specific isotope analyses (CSIA).

Results: Within four months after the bioaugmentation event, there was more than a two order of magnitude decrease in PCE and TCE in downgradient monitor wells. However, about five months post the bioaugmentation event, there was a significant increase in the PCE and TCE concentrations in another downgradient well, which then decreased by more than three orders of magnitude post the slow release carbon substrate injection. Consistent with the chlorinated ethene and ethene data, there was a significant increase in the *Dehalococcoides* population in the groundwater. The CSIA data also demonstrated that active biodegradation of PCE, TCE and cis-1,2-DCE was occurring in the source area. This presentation will discuss how the amendments impacted the chlorinated solvent concentrations, microbial community and chemistry of the groundwater in the area around the recirculation wells over a two year period. It will also review the various injection approaches applied at the site and their effectiveness to distribute amendments.

Treatment of a large industrial site impacted with chlorinated solvents using a combination of electron-donor substrates

Marcello Carboni; Paola Gorla

REGENESIS Remediation Solutions, Europe, IE

This presentation describes the in situ remediation of a 60,000m² disused industrial site located in Northern Italy. The site was contaminated with primarily TCE and its by-products, with a complex distribution and concentrations ranging from DNAPL to very low groundwater concentrations in a highly heterogeneous geology.

The complex hydrogeology includes a semi-confined aquifer of silty-sand lenses; with the confining silt layer having been pierced by construction works in the source area. In addition, the site is bounded by a tidal river and groundwater depth and flow direction are periodically affected.

Remediation comprised of excavations in the source areas, with pump and treat (P&T) used to hydraulically contain the impacted groundwater onsite. Regenesi completed the treatment of the residual groundwater contamination using enhanced reductive dechlorination (ERD) to treat 10,000m² via approx. 500 injection points to 12mBGL, in 6 months.

Prior to application the site was split into different areas based on hydrogeological conditions and contaminant distribution. A treatment plan was tailored to the requirements of each area by varying the injection depth, spacing, dosage and co-application of up to 4 products. Pilot studies were completed onsite to prove the approach and gain further information to provide the most accurate design for the main works.

Full-scale treatment was started at the site boundary along the river using the injection of high viscosity products in a barrier formation, to control risk of offsite migration close to the hyporheic zone. The barrier also had to cope with extra groundwater flow (contaminant flux) from the ongoing P&T system (required by regulator).

A high volume substrate with the ability to widely distribute in the subsurface was injected in a grid pattern across multiple source and plume areas. This allowed the injection grid to be widened to 6m by 6m, minimising the number of injection locations, saving time and money.

Results (12 months to date; 20 in June'17) show that precise tailoring of the treatment to match site conditions has resulted in firstly the rapid establishment of the ideal conditions for ERD and secondly, accelerated biological degradation of the contamination. Reductions from very high concentrations are taking place with full reductive dechlorination occurring, without egress of breakdown products from the treatment zone. In less impacted areas concentrations are now close to target levels.

Italian legislation requires stringent targets at property boundaries (for some solvents <1µg/L). Achieving these through biodegradation alone will be challenging in the low concentration boundary areas, as microbial populations there will be starved of a food source. Therefore an additional ERD enhancement will be implemented through in situ adsorption using a Liquid Activated Carbon for which a pilot test is currently being carried out onsite (Results expected to be available in June'17).

This case study shows how thoughtful design of electron donor substrates can be used to provide cost effective treatment of large-scale chlorinated solvent sites, remediating high concentrations to achieve low targets.

ThS 3a.3: Bioremediation of contaminants of emerging concern

Biodegradation Potential Assessment on a Site Contaminated by a Mixture of BTEX, MCB, and Pharmaceuticals – Case Study

Ondřej Lhotský¹; Tomáš Cajthaml²; Torgeir Rodsand³

¹ Dekonta, a.s. + Charles University; ² Charles University, CZ; ³ ALS Laboratory Group Norway AS, NO

The pilot site is located in the premises of an old chemical and pharmaceutical plant where chemical production started in 1934. The entire site is significantly contaminated mainly by organic solvents (BTEX, monochlorobenzene – MCB) but also by pharmaceuticals.

During previous remediation works, phase liquids were removed and concentrations of contaminants decreased but the residual contamination is still high and it still poses a significant risk.

Biodegradation seems to be a feasible method for remediation of the residual contamination, as the main contaminants (BTEX, MCB) are readily biodegradable under aerobic conditions. Therefore, a pilot test to assess the biodegradation potential of these contaminants in situ has been performed.

The most contaminated spot in the factory was chosen for the pilot test and investigated in detail. Detailed MIP investigation took place together with core sampling of the soil prior to the pilot test. The MIP results well correlated with the core sampling. The shallow (starts about 3.5 m bgl) aquifer on the site is about 4 m thick and consists mainly of very permeable gravels with loam on the top of it and clays in the bottom. Both MIP and core sampling showed that the top (loam) and mainly the bottom (clay) layers of the aquifer were highly contaminated and acted as long term sources of groundwater contamination.

After the site investigation a pump and treat system was installed on site and operation started. It was based on groundwater aeration and further treatment by the so-called “photooxidation”. Hydrogen peroxide was added into the treated water and irradiated by UV light to create high reactive hydroxyl radicals capable of destroying even highly persistent organic contaminants like pharmaceuticals. Treated water with residual hydrogen peroxide (up to 200 mg/l), having an elevated temperature (approx. 20 degr. C), was infiltrated back to the underground.

Furthermore, 4 different oxygen sources (Oxygel, ORC Advanced, Ixper 75C, and 5% hydrogen peroxide) were injected via direct push mainly into the top and the bottom layers of the aquifer during summer 2016. Each of the oxygen sources was injected into 2 boreholes in an amount that should be capable of providing 17 kg of releasable oxygen.

The locality was monitored intensively throughout the pilot test using conventional and passive sampling methods both for analysis of chemical compounds (all the contaminants, intermediates, cations, anions, etc.) and microbiological populations (cultivation tests, PLFA, qPCR).

The results obtained so far show significant decrease in the concentrations of the target contaminants and provide an evidence of ongoing biological degradation.

Another MIP and core sampling investigation will take place in the spring of 2017. Therefore, we should have detailed information on how our pilot test changed both the quality of the groundwater and the soil, what were the processes that were driving these changes and what were the impacts of different actions we took. Overall, we should obtain the evidence whether biodegradation is a feasible clean up solution for the site and propose the optimal way of bioremediation enhancement.

Removing micropollutants from groundwater resources used for drinking water production with bioremediation

Nora Sutton; Alette Langenhoff; Huub Rijnaarts

Wageningen University, NL

The presence of organic micropollutants in different segments of the water cycle poses a threat to future water resources. Routine monitoring of groundwater composition in the vicinity of drinking water production locations has detected low concentrations of micropollutants. For example, in The Netherlands, approximately one-quarter of all groundwater production locations contains pesticides at concentrations that form a serious threat to future drinking water production. While these compounds are monitored, currently there is little known on the fate and transformation of these compounds in groundwater systems. Additionally, there are no technologies available to properly treat these groundwater systems.

This research aims at understanding the factors that select for natural attenuation in groundwater systems in order to design the next generation of in situ remediation, namely the treatment of low concentrations of micropollutants in oligotrophic groundwater. To this end, we take a multidisciplinary approach to understand subsurface processes and identify the conditions that select for biodegradation. We investigate the role of microbial community composition, redox conditions, and dissolved organic carbon on micropollutant biodegradation in lab and field experiments.

Microbial community composition is determined by groundwater composition and dictates biodegradation activity. For deep groundwater systems of 50-100 m it has been scarcely investigated. Groundwater was sampled at different depths at a drinking water production location for microbial community analysis based on sequencing a 16S rRNA fragment and groundwater composition. These community profiles were compared with groundwater chemistry and micropollutant concentration data. Results indicate differences in both microbial diversity and groundwater composition between wells and in depth, demonstrating the heterogeneity of the subsurface. However, subsequent sampling campaigns indicate that microbial communities in each well filter are highly stable. This stability is integral to identifying important portions of the microbial community involved in biodegradation and developing molecular tools targeting key players.

Additionally, laboratory research has been performed to unravel the roles of redox conditions and natural dissolved organic carbon (DOC) on groundwater pesticide biodegradation. A selection of key pesticides were investigated in column and batch experiments under different redox conditions with and without the addition of DOC. Results indicated that pesticides are not readily biodegraded under anaerobic conditions and that certain compounds, namely Bentazon and Chloridazon-desfenyl, are also recalcitrant under aerobic conditions. Initial results seem to indicate that adding assimilable DOC can support biodegradation under anaerobic conditions.

Together, these results present a comprehensive investigation into biodegradation of micropollutants in groundwater systems. This fundamental research thus offers the first step towards developing biodegradation-based in situ remediation technologies.

New treatment process of perchlorate impacted water

Jean-Yves Richard

SUEZ Remediation, FR

Ammonium perchlorate is used as solid fuel in the spatial and defense sector. As all anions, it is mobile in the soil and impacts locally groundwater in particular under the battlefields of the last two wars and under industrial sites where it is produced or used.

Perchlorate causes sanitary problems because it is suspected to be an endocrine disruptor. French authorities (Direction Générale de la Santé) have fixed the threshold of 15µg/L for drinking water and a lower threshold of 4 µg/L for children of less than 6 months. Limit for drinking water in the USA is fixed to 15 µg/L.

These regulatory thresholds are very low and the high stability of perchlorate in the groundwater explain why its treatment becomes a key environmental issue. Perchlorate appears today as an emergent pollutant on the European market of polluted soils.

Treatment of perchlorate impacted groundwater is usually performed by filtration through ion exchange resins. Because regeneration is very complex and expensive, resins saturated with perchlorate are usually incinerate. Disposal in hazardous waste landfill is not possible because of pyrotechnic property of perchlorate saturated resins.

Perchlorate biodegradation is possible in anoxic condition and ion perchlorate is used as terminal electron acceptor instead of oxygen. The involved bacteria are ubiquitous and are also often able of nitrates respiration.

SUEZ has developed a new process of biofiltration to treat groundwater impacted by perchlorate. This extensive biofilter includes a granular bed of low thickness saturated with water. The delivery of a carbon source in the effluent and presence of organic matter in the top layer of the biofilter allow transition and preservation of anoxia, best condition for studied biodegradation. A deep layer contain active biomass for biodegradation.

The first tests in the laboratory has allowed to validate the feasibility and the main operating parameters. A pilot-scale biofilter (10m x 10m) was realized on-site to test the hydraulic system and efficiency of unclogging system using reeds.

A first industrial application was performed to treat strongly polluted groundwater near the ground source zone containing ammonium perchlorate. Biofilter allows the biodegradation of 15kg of perchlorate per day. Treatment system accepts perchlorate concentrations higher than 100 mg/l and allows to reach a residual concentration at ppb level (µg/L), near drinking water threshold.

Biological treatments applied to extreme environments and pollutions

Christophe Chene; Maxime Emery, Carole Macon¹

¹ SOLEO Services, FR

Microorganisms are adapted to a large panel of environments, from the most common to the most extreme. These adaptation properties confer them special capacities (high pH stability, extreme temperature resistance). It is the same in very contaminated environments. Using indigenous microorganism's ability to degrade pollution in extreme environments can sometimes be the best remediation strategy, both technically and economically. Nevertheless, the success of such a treatment requires a thorough knowledge of the context, design and required monitoring. Soléo Services presents here how a biological solution can be most effective where chemical or physical process fail? How to approach this type of complex problem? How to design and to implement such a strategy of cleanup? What are essential management tools to a good management of the remediation process? Finally, some case studies of complex biological treatments will be presented.

Find the best strategy for soil cleanup is not easy and often requires adopting a scientific approach suited to the complexity of the environment. An advanced feasibility study can allow designing an effective and economic biological strategy. Biodegradation of pollutants efficiency by certain microbial species can be proved in the literature, but the real conditions may often present limiting or inhibiting effects. Soleo Services has a number of accomplishments and ongoing biodegradation projects in extreme conditions. One of them was led on pH 10 groundwater, impacted with acetone (260mg/l), isopropanol (17000µg/l) and 1,2 dichloroéthane (18000µg/l). *Sphingobacterium mizutaii* is known to degrade acetone, *xanthobacter autotrophicus* GJ10 is known to degrade 1,2-DCA, but was is it possible in these extreme conditions? Laboratory respirometric tests showed no O₂ consumption during the first 25 days (adaptation time), but then activity started. Results showed >98% acetone and >96% 1,2 DCA decrease. Biostimulation was effective with no toxic effect, no need of buffer or nutrients addition. A following 3 months field pilot test showed until 79% acetone and 91% 1,2 DCA decrease depending of the areas. Global treatment often can't begin before having validated these feasibility testing steps. The right management of such a project in extreme conditions requires certain skills, and a multidisciplinary team to insure an efficient monitoring. Some adaptations can be necessary to maintain the optimal biodegradation rates (nitrogen and phosphorous addition, wells unclogging, injection flows regulation...). Specific analysis allows following the evolution of biodegradation and the preservation of good conditions. Besides target pollutants, a monitoring of the by-products or indigenous microbial communities and their degradation genes, allows to confirm if microorganisms of interest develop correctly. Molecular biology tools are actually used to follow a field pilot test on pH 13 groundwater impacted with benzene (600mg/l). Ribosomal intergenic spacer analysis (RISA), PCR and RT-PCR functional genes analysis (benzene monooxygenase, benzene dioxygenase and catechol dioxygenase) help monitoring adaptation of bacteria to environment.

Application of chemostat systems for adaptation of microbial communities to emerging pollutants

Baptiste. A.J Poursat¹; Martin Braster²; Rick Helmus¹; Rob J.M Van Spanning²; W. Pim de Voogt¹; Wilfred F.M. Röling²; John. R Parsons¹

¹ University of Amsterdam; ² VU University Amsterdam, NL

Persistency of organic pollutant in aquatic and soil ecosystems is strongly connected to the biodegradation capacity of native microbial community. Microbial degradation is one of the major processes that affect chemical persistency. However, not all microbial communities have the capacity to efficiently degrade emerging chemicals. Several investigations have shown the adaptation capacity of microbial communities to new chemical. In their natural environment microorganisms tend to adapt to pollutants upon long term exposure, allowing for the development of efficient and fast degradation over time. This adaptation capacity of microorganism could be used to develop adapted inoculum in an objective of bioremediation in order to degrade emerging pollutants that were initially persistent.

The aim of our project is to study microbial adaptation to persistent chemicals using long term exposure in various culturing systems. This in turn might lead to a faster rate of degradation of chemicals that were initially persistent. Our approach is to expose microbial communities from activated sludge, growing in chemostat and batch culturing systems, to different chemicals for a long term and under defined conditions. Three molecules are used in this project; 4-chloroaniline, N-Methylpiperazine and Metformin. These products are considered as emerging pollutants and are environmental persistent according to the ready biodegradation testing. The biodegradation capacity of pre-exposed inoculum is assessed in biodegradation testing and changes in community structure are followed by Illumina amplicon sequencing in time. Removal of tested chemicals and their transformation products are determined by LC MS/MS. Results of this experiment are expected to show biodegradation capacity enhancement of the inoculum after pre-exposure. They will result in a better understanding of the relationship between microbial adaptation and biodegradation performance. Ultimately they will also allowed a better prediction of the biodegradation outcome and the design of adapted inoculum with enhance degradation capacity for specific molecules.

ThS 3a.4: Bioremediation of aliphatic/aromatic hydrocarbons and fuel-additives

Bacterial populations driving the biodegradation of the 4-ring PAHs benz(a)anthracene and chrysene in polluted soils

Sara N. Jiménez-Volkerink¹; Joaquim Vila²; Magdalena Grifoll¹

¹ Universitat de Barcelona, ES; ² University of North Carolina at Chapel Hill, US

Biodegradation of high molecular weight polycyclic aromatic hydrocarbons (HMW PAHs) in polluted soils is assumed to be accomplished by the cooperation of different microbial populations undertaking interconnected metabolic pathways. Due to their low water solubility and chemical stability, benz(a)anthracene (BaA) and chrysene (CHY) are resistant to extensive microbial degradation, being enriched in the end-point residues after biological treatment. Therefore, there is much interest in understanding the mechanisms that modulate their transformation and eventual mineralization. Although a few bacterial strains able to attack BaA and CHY have been reported, little is known about the microbial populations, interactions and enzymes involved in the in situ biodegradation in polluted soils.

The general aim of this project is to obtain and thoroughly characterize minimal bacterial communities able to completely degrade BaA and CHY, to isolate their bacterial components, to describe the functions involved (genes and enzymes), and to confirm the modeled processes in real polluted soils. Here we present the results obtained through two different approaches: i) retrieval of BaA and CHY-degrading minimal communities and isolation of degrading strains; ii) analysis of the structural and functional changes in the microbial community of soil microcosms spiked with the targeted PAHs.

BaA and CHY-degrading minimal communities were obtained from a creosote-polluted soil by a dilution-to-extinction method. After the identification of the bacterial components by 16S rRNA PCR-DGGE analysis, isolation was attempted using complex media for oligotrophic bacteria. Phylotypes in BaA-degrading communities included members of Rhizobiales, Bradyrhizobium and Mesorhizobium. These taxa were also present in CHY-degrading communities, along with members of Achromobacter, Pseudoxanthomonas, Pseudomonas and Alcaligenaceae. The relevance of these phylotypes in the polluted soil was confirmed by mining in pyrosequencing data for total (DNA) and active (RNA) populations from a previous bioremediation assay.

In our second approach, we assessed the biodegradation dynamics of BaA and CHY and the microbial community structure shifts in small-scale sand-in-liquid microcosms inoculated with the creosote-polluted soil. Microcosms were spiked either with BaA or CHY as sole carbon source, by both compounds together, or by the ready oxidation product of BaA, benz(a)anthracene-7,12-dione (BaA-dione). Throughout incubation, PAHs were extracted and analyzed by GC-FID; along with 16S rRNA PCR-DGGE analysis of the total bacterial DNA. The degradation kinetics of CHY, BaA and BaA-dione, suggested a cometabolic attack of BaA and CHY when found together. Analogous populations could possibly degrade BaA and BaA-dione, as they presented similar biphasic kinetics. Molecular analysis of the total bacterial populations throughout the biodegradation of these compounds did not show relevant differences in a quantitative or structural level. Therefore, analysis of the active (RNA) populations is being performed to elucidate the key players driving the in situ degradation of BaA, CHY and BaA-dione.

Surfactant foams for enhanced in situ bioremediation of PAHs

Vincent Langlois¹; Tahani Farah¹; Douglas O. Pino Herrera¹; David Huguenot¹; Nicolas Fatin-Rouge²; Julien Maire²; Yoan Pechaud¹

¹ Université Paris-Est Marne-la-Vallée; ² Université de Bourgogne Franche-Comté | Institut UTINAM, FR

Background/Objectives:

A novel approach to the problem of hydrocarbon contamination in soil is the use of foam as potential alternatives to solve transport problems throughout heterogeneous zones. Within the French RNA MOUSTIC* project that involves academic and industrial partners, we study the development of foam as a carrier of active matter (oxidant, micro-organisms, nutrients) to overcome the current limits for the in situ regeneration of heterogeneous unsaturated zones contaminated by PAHs.

In the present work, we study the development of foam as a carrier of micro-organisms, nutrients and oxygen in soil to enhance in situ bioremediation by bioaugmentation and/or biostimulation foam assisted strategies. Several advantages for using foam technology in conjunction with bioremediation appear: (i) foams tend to flow through porous media more uniformly avoiding channeling effects, (ii) foams provide a transport carrier for dispersing nutrients and bacteria because of the adsorption of bacteria to gas/liquid interface, (iii) foams can deliver and retain air to enhance biodegradation. In this context, the aim of this study is to distribute micro-organisms and nutrients carried by foam in order to degrade low bioavailable pollutants.

Approach/Activities:

Biocompatibility screening has been performed to identify the foam formulations that did not affect the microbial activity and viability: (i) of indigenous microbial species (for natural attenuation and biostimulation strategy) and (ii) of a consortia that will be carried out by the foam in bioaugmentation tests. This consortia has been selected (in bioreactor) directly from a real contaminated soil, based on their ability to degrade PAHs (phenanthrene). Once the biocompatible foam formulations have been selected, the influence of the nature and concentrations of nutrients and of micro-organisms on the foamability and foam stability has been evaluated. To study the transport of the foam and the transfer of the nutrients and micro-organisms, 1-D experiments will be performed. The pressure gradient during injection will be controlled. The transport and transfer of micro-organisms, nutrients and oxygen will be first investigated in model soils (glass beads of different particle size distributions, sands, etc.). These experiments on simple systems will improve our understanding on the mechanisms involved. The foams will be injected into the column and mass balances will be performed by collecting over time the effluent to quantify residual nutrients concentrations (for biostimulation) and microbial cell concentrations (for bioaugmentation). To evaluate the distribution of micro-organisms sorbed at different locations in the column, the soil column will be separated in different parts to perform respirometric assays on each. It will thus be possible to quantify aerobic activity of bacteria and thus indirectly to estimate the quantity of bacteria sorbed to the soil and to assess their homogeneity within the column.

In-situ aerobic bioestimulation of a heavily etbe-polluted site

Laura Izquierdo¹; Diego Corcho Sánchez¹; Marc Viñas²; Miriam Guivernau²; Patricia Piñuela³

¹ Invesoil Consultores Medioambientales sl; ² Institute of Agrifood Research and Technology [IRTA]; ³ Compañía Logística de Hidrocarburos, CLH S.A., ES

In 2011, a massive and nonquantifiable diesel – gasoline spill affected an oil pipeline from Bajo Guadalhorce alluvial aquifer in Andalucía (Spain). Initial investigation revealed the existence of two big delimited plumes: Plume 1, a free-product one encompassing slow and medium solubility hydrocarbon compounds (GRO-BTEX and DRO range) whose maximum length was 360 m, and Plume 2, heavily polluted with ETBE (gasoline additive) [maximum 190.000 µg/l – 160.000 µg/l] which due to its high water solubility reached a maximum length of 900 m.

Preliminary remediation strategies in 2012, consisted to extract and pump the LNAPL fraction for preventing plume spreading. Concomitant ETBE-biodegradability lab tests by using groundwater microcosms from plume 2 revealed the existence of abundant autochthonous ETBE/TBA-degrading microbial populations encompassing a high ETBE/TBA-degrading capability under aerobic conditions and an optimized nitrogen and phosphorous supplemented dose (100CCOT:10N:1P). Moreover, classical and molecular biology techniques were developed to quantify potential ETBE degraders in the autochthonous microbial community in plume 2.

In 2015, after the confirmation of free-product removal in the monitoring wells, remediation equipments were shut down. In-situ biostimulation was performed enhancing oxygen availability throughout emitter-based strategy and adding supplemental inorganic N and P sources (K₂HPO₄ and NH₄NO₃). Initially, the biostimulation process was implemented in a 170 m length ETBE plume with 19 monitoring wells and ETBE concentrations in the range 2000-13.500 µg/L and mean TBA concentration at 100- 120 µg/L .

Physic-chemical parameters such as temperature, conductivity, pH, dissolved oxygen and ORP, nutrients amendment and ETBE/ TBA concentrations were monitored as well as, the evolution of the indigenous microbial population (total heterotrophic population and ETBE degraders by miniaturized Most Probably number (MPN); qPCR of ethB and 16S rRNA genes and high throughput sequencing).

After one year of in-situ biostimulation impacted wellpoints decreased from 19 to 6, while ETBE concentrations in groundwater were dramatically reduced achieving 100-4.000 µg/L and TBA at 141 µg/L . Microbial assessment during in-situ biostimulation showed an important increment of ETBE degraders (both by NMP and qPCR assessment) . High throughput sequencing (MiSeq sequencing) of autochthonous microbiota in plume 2, revealed an enrichment of known ETBE-degrading Actinobacteria-based phylotypes such as OTUs belonging to Rhodococcus and Mycobacterium genera, which has been proposed as the potential microbial key players during in-situ biostimulation process.

As a conclusion, a successful in-situ biostimulation strategy in ETBE-polluted aquifer has been implemented. Combining previous lab-test feasibility data at field conditions linked with culture-dependent and molecular techniques seems to be a good strategy for further biostimulation actions at field scale, thus reducing analytical holding times and lowering budgets for this purpose.

Comparison of landfarming amendments to improve bioremediation of weathered petroleum hydrocarbons in Niger Delta soils

David Brown¹; Jonathon Smith¹; Samson Okoro²; Kim Bye Bruun²

¹ Shell International Petroleum Co. Ltd; ² Shell Petroleum Development Company of Nigeria Ltd, NL

Large scale landfarming experiments were conducted in Nigeria to study an extensive range of amendments for their impact on bioremediation of weathered Bonny light crude oil-contaminated soils. In this work the effect of nutrient addition, biosurfactant, *Eisenia fetida* (earthworm) enzyme extract, bulking and sorption agents and soil neutralization were tested. It was found that these treatments were successful in removing up to 53% of the total petroleum hydrocarbon in the soil within 16 weeks. Comparisons between treatments demonstrated that most were no more effective than nutrient addition alone. One strategy that did show better performance was a combination of nutrients, biochar and biosurfactant. This multipart treatment was found to remove 23% more TPH than nutrients alone. From an implementation perspective, the use of various strategies to improve landfarming performance needs to be balanced with financial costs and the practical considerations related to treatment application. Based on the work presented in this paper, all the treatments would be considered less attractive than fertilizer only because they are no more effective or would cost significantly more and be difficult to implement.

Attenuation rates of both bulk TPH and Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) are provided. These values represent one of the largest and most scientifically robust datasets for the Niger Delta region. An inverse correlation between attenuation rates and hydrocarbon molecular weight was observed with heavy fractions showing much slower rates than lighter fractions. Despite this difference the bioremediation process resulted in significant removal of all TPH compounds independent of carbon number.

Experimental Analysis and Modeling of Mechanisms Involved in the PAH-contaminated Soil Treatment using a Slurry Bioreactor

Douglas O. Pino Herrera¹; Yoan Pechaud¹; David Huguenot¹; Yannick Fayolle²; Sylvain Pageot²; Nihal Oturan¹; Giovanni Esposito³; Eric D. van Hullebusch⁴; Mehmet A. Oturan¹

¹ Université Paris-Est; ² Irstea; ³ University of Cassino and Southern Lazio; ⁴ UNESCO-IHE, FR

Polycyclic Aromatic Hydrocarbon (PAHs)-contaminated soils are a great environmental and public health concern nowadays. Further research is necessary to develop environmental friendly biotechnologies that allows public and private sectors to implement efficient and adaptable treatment approaches. Aerobic soil-slurry bioreactor technology has emerged as an effective and feasible technique with a high remediation potential, especially for silt and clay fractions of the soil, which often contain the highest pollution levels and are hard to treat with conventional approaches. However, mechanisms involved in the PAHs removal in the bioreactor are still not completely understood. In addition to the biological processes, important mass transfer mechanisms need to be considered (oxygen gas-liquid mass transfer, sorption-desorption, volatilization, etc.). In general volatilization is not considered in the studies whereas, in some conditions (high aeration rate), it can be a major mechanism of light PAH removal. Besides, the soil composition and concentration in the reactor may strongly influence fluid viscosity, which is a key parameter governing the hydrodynamics and thus, the mass transfer phenomena. Therefore, process optimization requires a fine understanding of the operational parameters' influence on the mechanisms involved in the removal of PAHs from soil.

The main goal of this research work is to study, understand and model the influence of soil loading, composition, and operating conditions on the gas-liquid mass transfer phenomena (oxygen transfer and PAHs volatilization) occurring in a soil-slurry reactor. Experiments were performed in a 6L glass standard bioreactor designed to control hydrodynamic conditions and temperature. Air is injected from the bottom through a porous glass sparger. Mechanical agitation is performed by a marine propeller connected to a motor. Clay has been selected as model soil and phenanthrene as model PAH molecule in this preliminary stage. Soil concentration, air superficial velocity and stirring rate were varied to study their influence on the oxygen and PAHs gas-liquid mass transfer phenomena. Rheological behavior of soil/water matrix was measured with a capillary rheometer.

Oxygen transfer tests showed that for a given air superficial velocity and stirring rate, the oxygen transfer coefficient in soil/water matrix is reduced in comparison with clean water and varies negatively with the soil concentration. Moreover, the soil/water matrix could be assimilated to a non-Newtonian fluid with shear-thinning behavior (mainly pronounced for high soil content). Also, the phenanthrene transfer coefficient varies linearly with the air superficial velocity, for a given stirring rate. The influence of solids concentration and operating conditions (air flow and stirring rate) on apparent viscosity, oxygen transfer, PAH volatilization and biodegradation rate will be modeled using experimental data. Moreover, a general model including all mechanisms studied will be developed, calibrated and validated using experimental data with both a model spiked soil and a real contaminated soil.

ThS 3b.1: In situ chemical oxidation (ISCO) I

Remediation of petroleum hydrocarbons in contaminated sediments by using magnetite-catalyzed chemical oxidation

Muhammad Usman¹; Khalil Hanna²; Pierre Faure³

¹ University of Agriculture, Faisalabad, PK; ² Ecole Nationale Supérieure de Chimie de Rennes; ³ Université de Lorraine, FR

The soil and water pollution by petroleum hydrocarbons is of great health and environmental concern. Chemical oxidation treatments are showing great potential to remediate contaminated matrices. This laboratory study was aimed to remove petroleum hydrocarbons from contaminated sediments by using magnetite catalyzed Fenton-like (FL) and activated persulfate (AP) oxidation. Contaminated sediments having different physicochemical characteristics were sampled from three different locations including (i) S1: Le Guilvinec harbor, (ii) S2: Toulon military harbor and (iii) S3: petroleum industrial channel situated in different regions of France. Hydrocarbon index in three sediments was in order of S1 (3.69 mg/g) > S2 (5.54 mg/g) > S3 (9 mg/g). Similar order was obtained for total organic carbon (TOC) which was 1.85%, 4.96% and 8.39% in S1, S2 and S3, respectively. These sediments were subjected to chemical oxidation in batch slurry system at circumneutral pH. The GC-FID was used to monitor the abatement of hydrocarbons.

Obtained results indicate that significant degradation of hydrocarbons (40-70%) was obtained by using magnetite as a catalyst during chemical oxidation (FL and AP). On the other hand, soluble Fe(II) was unable to act as a catalyst due to its precipitation at circumneutral pH. Treatment efficiency was comparatively lower in S2 that might be correlated to higher carbonate contents (28.43%) that could act as oxidant scavenger. A good correlation was observed between hydrocarbon index and extractable organic matter highlighting the non-specific nature of chemical oxidation. Our results did not indicate any availability limitation associated with the target hydrocarbons. No significant by-products were detected under our analytical conditions. For being the first study to report chemical oxidation of petroleum hydrocarbons in real contaminated sediments, it has practical implications to design a remediation strategy for polluted matrices.

Soluble organic substances extracted from compost as amendments for Fenton-like oxidation of contaminated sites

Daniela Zingaretti; Francesco Lombardi; Renato Baciocchi

University of Rome Tor Vergata, IT

In the last decades, in situ chemical oxidation (ISCO) has become an attractive remedial option for treating many organic pollutants in subsurface and groundwater. Within the available ISCO formulations, based on the use of oxidants such as hydrogen peroxide, potassium permanganate or sodium persulfate, the Fenton process, based on the reaction between H_2O_2 and ferrous iron and the consequent production of the highly reactive hydroxyl radical, proved to be effective for the remediation of sites contaminated by a wide range of organic pollutants. However, in most cases for improving the performance of hydrogen peroxide, the injection of amendments is also required. Namely in order to increase the contact time of the oxidant and hence the radius of influence of the treatment the hydrogen peroxide lifetime needs to be enhanced by using a stabilizer such as KH_2PO_4 . Furthermore in a Fenton-like process, based on the use of hydrogen peroxide catalysed by iron and manganese minerals naturally occurring in soils, a chelating agent, that keeps iron in solution, is also adopted to improve the effectiveness of the treatment. However many questions were recently raised regarding the environmental impacts of these stabilizing and chelating agents. Hence, efforts have been placed to improve the sustainability of this treatment testing new amendments, characterised by a lower environmental impact. Among these, humic acids have been tested in a Fenton process since these substances are able to form complexes with metal ions and can also act as sorbents for hydrophobic organic compounds. However from our knowledge all the studies available in literature have investigated the effects of synthetic humic acids. In this study, instead, we have tested the performance of a Fenton-like process carried out adding as amendments the humic substances extracted from compost obtained from organic waste. Fenton-like lab-scale tests with the extracted humic acids were performed on a soil-water system artificially contaminated by chlorophenol and the obtained results were analysed in terms of hydrogen peroxide lifetime and chlorophenol removal. As reference, control tests applying synthetic humic acids or a traditional stabilizing agent (KH_2PO_4) or a chelating agent (EDTA) were also performed.

The obtained results showed that the use of the humic acids extracted from compost are able to increase the hydrogen peroxide lifetime similarly to a stabilizing agent, with a 40% residual hydrogen peroxide concentration still observed in solution after 24 h. On the other hand, the use of the extracted humic acids proved also effective for the chlorophenol removal showing a behaviour similar to the one of a traditional chelating agent.

These findings hence suggest that the use of the humic acids extracted from wastes within a Fenton-like process could allow to replace at the same time the H_2O_2 stabilizer and the chelating agent. In this way a further value is given to a waste material, in line with the concept of circular economy introduced by the European Council.

Remediation of Diesel Contaminated Soil by Alkali Activated Persulfate

Miguel Angel Lominchar; Aurora Santos; Fernando Pardo; Arturo Romero

Complutense University of Madrid, ES

Contamination of soil by hydrocarbon from oil spills is a serious and common problem all over the world. Due to these compounds have low solubility in water, they are usually found as Non Aqueous Liquid Phases (NAPLs) and remediation of the affected soils involves several steps, being the extraction of the remaining free phase the first action that should be accomplished. However, residual contamination cannot be adequately eliminated by this procedure and further treatments are required.

Among current techniques, In Situ Chemical Oxidation has proven to be an effective technology in the remediation of soil polluted by hydrocarbon. Activated persulfate has been increasingly used as oxidant to remediate hydrocarbon contaminated groundwater and soils due to its lower oxidant demand and higher stability in comparison with other oxidants. Persulfate can be activated thermally, by transition metals (usually iron) or by alkali, being this last the more recent and less studied activation method. However, at high pH conditions ($\text{pH} > 11$), alkaline activation is very productive in generating sulfate and hydroxyl radicals capable to destroy the organic pollutants.

In this work, a soil contaminated by a fuel spill from tank storage has been treated by alkaline persulfate. The studied soil was obtained from a train maintenance facility located in Madrid (Spain) where the water table was located at 9 m b.g.l. According to the physico-chemical characterization, the soil had alkaline pH (about 8.4), low percentage of organic matter ($\text{SOM} = 0.48\%$) and loamy sand texture. Labile iron was measured as 13 mg/kg. TPH content was measured as 5000 mg/kg.

Experiments were conducted by using 50 mL PTFE centrifuge tubes with PTFE screw caps as batch reactors, stirred isothermally ($20\text{ }^\circ\text{C}$) in an orbital shaker. 10 g of polluted soil ($< 2\text{ mm}$) were treated with 20 ml of aqueous solution, with the corresponding concentration of the reagents (persulfate and sodium hydroxide). Persulfate concentration range employed was from 105 to 420 mM and NaOH:PS molar ratio used were from 2:1 to 4:1. Initial pH was over 12 and reaction time was extended up to 30 days.

At the selected reaction time, two PTFE tubes were sacrificed and centrifuged. Supernatant was separated to determine pH and remaining oxidant concentration. TPH in soil was extracted by organic solvent and the organic phase was withdrawn and analyzed by GC-FID equipped with a capillary DB-1 column ($30\text{ m} \times 0.25\text{ mm i.d.} \times 1\text{ }\mu\text{m}$). Fingerprint of fuel was also determined being the lineal C17 and C18 paraffinic fractions the most representatives of the fuel.

According to the results, TPH conversion was higher than 70% at the operation range studied.

Use of an Organic Compound to Activate Sodium Persulfate: Fundamental Science and Key Characteristics

Michael Mueller

PeroxyChem, AT

Background:

Activated Klozur® persulfate has been implemented for over 10 years to successfully remediate sites impacted with a wide assortment of contaminants of concern ranging from petroleum hydrocarbons; such as BTEX and DRO, oxidizable chlorinated solvents such as tetrachloroethene and trichloroethene, and reducible organics such as carbon tetrachloride and 1,1,1-trichloroethane. The ability to treat different contaminants has been attributed to the activation method and the formation of the sulfate, hydroxyl, and superoxide radicals. Conventional methods of activating persulfate include iron chelates, alkalinity, heat, and hydrogen peroxide.

Objectives:

The use of organic substrates* to activate persulfate is based on recent research, and has the potential of being a low cost alternative with the benefits of i) ease of implementation, ii) greater degree of control over the rate of activation, and iii) the ability to produce both oxidative and reductive radicals.

Activities:

A series of bench and pilot scale tests have been conducted assessing this novel activation method. The tests were conducted in a series of batch reactors, evaluating i) the rate of reaction with different contaminants of concern, ii) persistence of persulfate, iii) effect on geochemical parameters, and iv) potential degradation pathways.

Case study will be presented on organic activated persulfate applied in a field application to treat residual TPH at an active petrol station site.

Summary:

This presentation will discuss the existing methods of activating persulfate, and introduce data collected on the science and key characteristics of organic persulfate activation. Critical parameters include i) the type and concentrations of organic compounds, ii) conditions that favor the formation of reductive radicals, and iii) treatment of selected contaminants of concern. Finally, the field implementation of this new organic activator will be discussed.

Keywords: ISCO, Klozur, persulfate, activation, organic

*Patent Pending USPTO Application 13/848,092

Surfactant Foams For Enhanced In Situ Oxidation of PAHs

lheb Bouzid¹; Julien Maire²; Emmanuelle Brunol³; Nicolas Fatin-Rouge³

¹ Université de Bourgogne Franche-Comté | Institut UTINAM; ² Université de Bourgogne Franche-Comté|Institut UTINAM; ³ Université de Bourgogne Franche-Comté, FR

Background/Objectives:

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic priority contaminants that long-term impact the use of polluted resources (soil, water, ...). Because of their high viscosity and affinity for soil particles, tars display relatively low mobility and many contaminations are situated in the unsaturated zone. Nowadays, in situ treatments are preferred because they can avoid some dissemination risks and costs with respect to historical ways of management. However, the use of in situ treatments is currently limited by preferential pathways for fluid flow that oppose to the homogeneous treatment of the polluted zone. Within the MOUSTIC project (French acronym for Foams for in situ treatments of vadose zones contaminated by hydrocarbons) that involves academic and industrial partners, surfactant foams are thoroughly assessment at lab and field-scales for their ability to deliver strong oxidants and microorganisms for the synergistic removal of adsorbed PAHs. The use of surfactant in combination with oxidant has been proposed in order to improve the availability of adsorbed PAHs during the oxidative treatment. However, the flow of solutions into polluted soils remains very sensitive to preferential pathways. Moreover, it is through a raise of costs and dissemination risks. In order to warrant the homogeneous distribution of oxidant within the polluted zone, we have studied the possibility to use surfactant foams to inject it. To the best of our knowledge, the delivery of strong oxidants by foams in order to selectively degrade PAHs a never been reported.

The aim of this study is to distribute strong oxidants homogeneously in presence of surfactants in order to selectively degrade low available pollutants.

Approach/Activities:

Lab studies have been carried out in order to reach targeted properties (homogeneous delivery of oxidant, PAHs desorption and selective oxidation) at low pressure for foam injection. The implementation has been made based on chemical stability of the injected fluid and selectivity of the oxidation. A study in solution allowed the identification of optimal reaction conditions and stable metabolites. The study of PAHs contaminated soils ranging from 1 to 10 g kg⁻¹ of different permeabilities was carried out in 1D- and 2D-reactors. These tests have allowed to study the injection modes that warrant the homogeneous dispersion of the oxidant, the mobilization of PAHs and their selective oxidation. The degradation of oxidant, pollutants and surfactant have been studied through mass balances in order to determine the optimal conditions with respect to yield and selectivity. Benefits of using foams for the PAHs oxidation in vadose zone is discussed with respect to surfactant solutions and pure water.

ThS 3b.2: In situ chemical oxidation (ISCO) II

Abatement of chlorinated compounds in groundwater contaminated by HCH wastes using ISCO with alkali activated persulfate

Aurora Santos¹; Jesus Fernández²; Lucía Perez¹; Miguel Angel Lominchar¹; Sergio Rodriguez¹; Carmen Dominguez¹; David Lorenzo; Arturo Romero¹

¹ Universidad Complutense de Madrid; ² Government of Aragon, ES

Technical Hexachlorocyclohexane (HCH) is a mixture containing several isomers, mainly α -HCH (53 - 70%), β -HCH (3% - 14%), γ -HCH (11% - 18%), δ -HCH (6% - 10%) and ϵ -HCH (3% - 5%). The gamma isomer, also known as lindane, is the only one with intense insecticidal properties [1].

All isomers of HCH are toxic by inhalation, ingestion or by direct contact with the skin and manufacture and commercialization of lindane in the EU is prohibited. Besides, it was included in the list of persistent organic pollutants (POPs) in the Stockholm Convention in 2009 [2].

Lindane production was inefficient due to approximately 8 to 12 tons of the remaining isomers were produced for each ton of lindane [3]. In many cases these wastes were not properly managed being uncontrolled dumped in the vicinity of the production facility. The surroundings of Sabiñanigo, a small town located in the province of Huesca (Spain), can be considered a megasite contaminated by HCH wastes, illegally disposed off by the company INQUINOSA (1975-1992), polluting the groundwater with risk of contamination of Gállego River [3].

Developing of methods for abatement of HCH and other chlorinated compounds in groundwater of these areas is of great interest. In this work, In situ Chemical Oxidation (ISCO) using alkali activated persulfate has been tested for elimination of HCH isomers and other chlorinated compounds (mainly chlorobenzenes) found in the Sabiñanigo groundwater. Influence of variables as persulfate concentration (42- 200 mM) and alkali to persulfate molar ratio (1:1 to 4:1) on chlorinated compound abatement have been studied. Reactions were carried out in batch way at 20°C. Reaction time ranged from 0 to 40 days. Samples were periodically withdrawn and analyzed during this time interval.

Chlorinated compounds and organic intermediates were identified and quantified by GC/MS using (SPME) and Head Space. Salt addition was used to enhance pollutant adsorption on the fiber. The concentration of PS was determined by titration with KMnO_4 .

At the condition used, the pH remained above 12 after NaOH addition and a significant remaining persulfate was obtained after 40 days. After alkali addition HCH isomers were quickly hydrolyzed to trichlorobenzene (TCB), being the major compound 1,2,4 trichlorobenzene. TCB were further decomposed more slowly. Other chlorinated compounds originally present in this groundwater are chlorobenzene (CB) and dichlorobenzene (DCB). A kinetic study for the abatement of CB, DCB and TCB has been accomplished, being this study required for the design of a reliable remediation project by this technology.

***In situ* chemical oxidation (ISCO) of PAH-contaminated soils: soil (pre)heating for effectiveness increase**

*B er enice Ranc*¹; *Pierre Faure*²; *Marie-Odile Simonnot*²; *V eronique Croze*³; *Catherine Lorgeoux*²

¹ ICF Environnement; ² Universit  de Lorraine; ³ Element-Terre, FR

Polycyclic aromatic hydrocarbons (PAHs) are found in all environmental media and more specifically in soils: in Europe, more than 30 000 PAH-contaminated soils have been identified but the total number has recently been estimated at over 250 000. PAHs exhibit very little availability in soils; consequently, specific soil remediation techniques must be applied. At high PAH concentrations, *in situ* chemical oxidation (ISCO) has been extensively studied. It involves injecting oxidants into soil to convert organic pollutants into less harmful chemical compounds such as carbon dioxide. However, if oxidation is not complete, PAHs may be transformed into oxygenated compounds, especially oxygenated polycyclic aromatic compounds (O-PACs), which may be potentially toxic, mutagenic, carcinogenic and also more mobile.

Permanganate and persulfate oxidation have shown their effectiveness. Both oxidants react following electron transfer mechanism, but persulfate can be activated in order to form sulfate radicals (SO₄^{•-}) and/or hydroxyl radicals (HO[•]), which are less persistent but stronger and faster oxidants.

Aged soils inherited from former industrial sites (especially based on coal use or transformation) exhibit very low contaminant availability implying weak reactivity face to bioremediation and chemical oxidation. A way to increase oxidation effectiveness is to pre-heat soil in order to enhance PAH desorption and increase PAH availability.

As a matter of fact, moderate thermal treatments (< 100  C) would play a decisive role in chemical oxidation, exhibiting different effects: i) activation of the oxidant, ii) increase in oxidation kinetics and iii) increase in pollutant availability.

The objective of this work is to evaluate and compare the contribution of the three previous effects on the increase in chemical oxidation effectiveness. Batch experiments combining chemical oxidation by permanganate or persulfate with thermal treatment were performed with an aged PAH-contaminated sampled on a former coking plant site.

Thermal treatments were applied prior (60 or 90  C under Ar -1 wk) or during oxidation (60  C - 1wk). PAHs and O-PACs degradation/formation were monitored. Oxidant doses were based on the Stoichiometric Oxidant Demand of the extractable organic fraction of soils by using organic solvents, which is more representative of the actual contamination than only the 16 US EPA PAHs concentration frequently used for the calculation. Higher temperatures resulted in higher pollutant degradation. Two treatments were about twice as effective as the others: soil preheating to 90  C followed by permanganate oxidation and soil heating to 60  C during persulfate oxidation. Our results reveal that permanganate was more sensitive to PAH availability than persulfate. The improvement of the persulfate effectiveness during oxidation with thermal treatment was largely due to its thermal activation.

Such results underline the potential increase of the effectiveness of ISCO treatments applying (pre)thermal treatments and is now apply at the field scale on experimental plot (2x3 m and 0.6 m of deep - 3 t of soils).

ISCO feasibility – focus on what is important in the field!

Geert Wijn¹; Tessa Pancras¹; Marlies Bos¹; Jurgen van der Wal¹; Federico Nava²

¹ Arcadis Netherlands; ² Arcadis Italia

A former pharmaceutical site, located in a city to the south of the Italian Alps, is contaminated with a mixture of contaminants, including chlorinated methanes and chlorinated benzenes. Several remediation technologies were evaluated, including in situ chemical oxidation (ISCO). A general feasibility study had already been undertaken by an analytical laboratory, prior to acquiring the project. The purpose of the initial analytical study was to determine whether the contaminants could be degraded using ISCO. The laboratory tests showed good degradation of the contaminants, and based on these results, it was decided that ISCO could be an option for the site.

On review of the information, it was ascertained that the amounts of oxidant used during the laboratory study were extremely high and that it would be difficult to translate this solution to the field. Besides the practical issues, the costs would have been exorbitant. Furthermore, the feasibility testing only focused on degrading the contamination, not on the practical application of the oxidant. Therefore, an additional feasibility study was executed, focusing on the practical issues of applying ISCO at the site. The focus was on the geochemistry of the soil, and based on these results five types of ISCO degradation tests were selected which used feasible amounts of oxidants. The results were then used to enable the most optimum activation technology to be selected.

Results:

The more pragmatic feasibility tests showed that with even with oxidant amounts up to 50-100 times lower than used during the initial feasibility study it was still possible to achieve very high contaminant concentration reductions (90-100%). More importantly, the tests also highlighted some practical issues associated with ISCO application; the reaction of the oxidants with the soil was quite strong, which was caused by a combination of the high soil alkalinity and a high amount of iron available for the reaction. Combined with the silty nature of the soil, it was determined that there would be challenges associated with evenly distributing the oxidants throughout the soil mass. Based on the results of the laboratory tests, the active distribution reaction and the positive side effect of volatilization of the contamination, a neutral Fenton oxidation has been chosen as remediation technology for a pilot test on site. The pilot test is currently being executed (November 2016) and focusses on the distribution of oxidants in the soil and on the effect of the chemical oxidation on the contaminant concentrations in the less permeable layers.

Conclusions:

The study has demonstrated that it is very important to not only focus ISCO feasibility studies on the degradation of the contaminant present, but to also focus on the practical issues associated with the application of ISCO in the field. Extremely high amounts of oxidants used in ISCO laboratory feasibility studies cannot always be translated to a field execution. Furthermore, practical issues like injectability, reaction with the soil, natural available catalysts and reaction of oxidants with the soil should also be considered and addressed.

Integrated Physical and Advanced ISCO Remedial Strategy for TPH Impacted Groundwater

Guido Piepoli¹; Alberto Leombruni; Alberto Piepoli; Michael Mueller

¹ A.S.T.C. Remediation srl, IT

Background

The combined use of physical and chemical remediation approaches synergistically increased groundwater treatment rate and efficiency, saved costs, and met an inflexible remedial deadline on a IT project. The use of a specific surfactant and recovery technologies followed by an ISCO phase provided benefits that none of the common remedial technologies used alone could achieve so rapidly. Central to this, was the use of Klozur® SP persulfate alkaline activated, the chosen oxidant for this in situ chemical oxidation (ISCO), because of its proven ability to treat the site contamination. In fact, Klozur® SP persulfate is ideal for contaminated source zones and hot spots that require rapid treatment. When properly activated, Klozur persulfate provides an unmatched combination of oxidative power, versatility, and control that can be delivered both safely and cost effectively.

Aim

When the redevelopment of a residential building with small business units in the city of Milan was proposed, site investigations revealed a significant petroleum hydrocarbon impact within the soil and groundwater following historic leakage from underground storage tanks (UST's). The detected concentrations were up to 2900 mg/kg in the soils near the source area. All the area was surrounded with diaphragms located until the depth of 27 m. The subsurface contamination threatened to derail the redevelopment program and a rapid remediation strategy was needed to reduce concentrations to IT regulatory limits. A.S.T.C. Remediation was involved in the site investigations (MIP) and in the development of bench and field tests, as well as in the full scale application.

In 2011, Klozur® SP field test was performed as treatability study. Approximately 400 m³ of most impacted soils have been treated within a week of injection. Due to the results of the field test, the Klozur® SP full scale project was approved by the Authorities. In 2015 ASTC Remediation applied an alkaline persulfate activated ISCO treatment following by an enhanced oil recovery technology based on surfactants. The specific carbon-based compound has been recirculated into the aquifer for reducing the secondary adsorbed source. A total amount of 30.000 kg of Klozur® SP persulfate activated was injected into the impacted aquifer along with NaOH solution through a polygonal grid of 50 injection points from 12 m and 18 m bgl.

Conclusion

By integrating chemical oxidation using Klozur® SP persulfate activated and a physical recovery system, A.S.T.C. Remediation was able to rapidly reduce high concentrations of hydrocarbons in the soils and groundwater of the site to the IT regulatory limits. The site closure was accomplished by the Authorities in October 2016.

Remediation of Poly- and Perfluoro Alkyl Substances: New Remediation Technologies for Emerging Challenges

Jake Hurst¹; Ian Ross¹; Jonathan Miles¹; Jeff Burdick; Erika Houtz¹; Tessa Pancras¹

¹ Arcadis, GB

Poly- and perfluoro alkyl substances (PFAS) comprise a diverse class of contaminants which include PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid). PFAS are not amenable to bioremediation or conventional chemical oxidation and are difficult to remediate in situ in soil and groundwater systems. Further complicating the remediation challenges are the presence of precursor PFAS that are often present at locations where AFFF (aqueous film forming foam) has been released and are not analysed for by standard analytical laboratory methods (US EPA method 537). These precursors can act as a source of perfluorinated carboxylates and sulphonates, as some precursors are less mobile but they all will biotransform over time forming perfluorinated compounds as dead end daughter products.

Remediation of PFAS impacted sources and plumes will require multiple approaches to achieve objectives to address sources and evolving plumes often to be protective of human health via treatment of water abstracted as a potable supply. PFAS are relatively ubiquitous in the environment at very low concentrations, but point sources such as some industrial or many domestic landfills, areas used for fire training, some biosolids applications and locations of manufacture of PFAS themselves or derivative products could all be point sources of high PFAS concentrations, potentially causing elevated concentrations local to these sites.

Innovative and emerging remediation solutions for PFAS include a number of types of technologies to address highly concentrated source zones, mitigate mass flux of impacts to aquifers or address PFAS in abstracted water. Use of granular activated carbon (GAC) to treat PFAS will only effectively remove a proportion of these contaminants from groundwater, whilst offering a very low binding capacity for PFOS (as compared to hydrocarbons), so can be costly. Challenges of more comprehensive PFAS treatment in water are currently addressed using technologies such as reverse osmosis or nano-filtration but Arcadis will present for data on easily regenerable sorbent media showing initial promise at removing both long and short chain PFAS including PFBA (perfluorobutanoic acid). There are new precipitation technologies for water treatment, novel ion exchange resins and sorptive media (RemBind[®]) which show promise and will be summarized.

Conventional chemical oxidation, which promotes formation of the sulphate and hydroxyl radicals as strong oxidants appears ineffective against some perfluorinated compounds, such as PFOS (perfluorooctane sulfonate). However, recent laboratory work has demonstrated that activated persulfate could be capable of degrading some PFAS and results of recent trials with the ScisoR[®] technology will be presented.

Recent results from laboratory trials using novel sorbent media for water treatment containing long and short chain PFAS and results of oxidation trials on PFAS will be presented. The presentation will also discuss a case studies showing the effective remediation of multiple PFAS impacted site in Europe.

ThS 3b.3: Immobilization techniques

Immobilization of an Arsenic Contamination by Oxidation and Co-precipitation with Iron

Marian Langevoort¹; Charles Pijls¹; Frank Volkering

¹ Tauw bv, NL

At a former production site of the herbicide monosodium methyl arsenate (MSMA) high groundwater concentrations of MSMA and the reduced species arsenite (As(III)O₃⁻), which was used as raw material for MSMA production, are causing unacceptable migration risks. A laboratory-scale feasibility study was performed to identify remedial options.

In the first phase of the study experiments were performed to assess different methods for treating the arsenic-contaminated groundwater. Mobilization of arsenic species by pH adjustment or by the addition of carbonates was found to be ineffective. Immobilization by the addition of H₂O₂ and FeSO₄, however, showed promising results. Oxidation of MSMA and arsenite to the less mobile arsenate (As(V)O₄⁻) and oxidation of the soil by hydrogen peroxide creates favorable conditions for arsenic precipitation and adsorption to the soil matrix. Addition of iron further stimulates the arsenic immobilization by the formation of oxidized iron species (various iron oxides and hydroxides). This increases the adsorption capacity and causes co-precipitation of arsenic with the oxidized iron.

In the second phase, the arsenic immobilization was studied into more detail. Immobilization and remobilization experiments were performed to determine the feasibility of reaching the target values and as a basis for the design of a pilot test. Experiments were performed in microcosms with soil and groundwater samples from the site. H₂O₂ was added to the soil/water slurry to obtain a redox potential of at least 250 mV. FeSO₄ was added as a source of iron for co-precipitation and the pH was neutralized to facilitate precipitation. Different Fe/As ratios were tested.

Different initial arsenic concentrations were tested. At an initial concentration of 41,000 µg/l arsenic, applying a Fe/As ratio of 3 resulted in 96.8% reduction of the arsenic concentration. At the high initial concentration of 2,200,000 µg/l arsenic, a Fe/As ratio of 5 was required to reach 99% reduction. Increasing the Fe/As ratio leads to a further increase in the concentration reduction. Microcosms without addition of FeSO₄ also showed immobilization of As. At a low initial arsenic concentration (3,800 µg/l) a reduction of 96% was observed, but at the intermediate initial arsenic concentration the reduction without iron was only 17%.

Remobilization tests were performed with soil from the immobilization experiment containing arsenic in concentrations up to 1,500 mg/kg d.w.. Uncontaminated groundwater from the site was used for the leaching tests at L/S 10. After a period of six weeks, less than 1% arsenic was remobilized from soil amended with FeSO₄. Soil from microcosms without addition of FeSO₄ showed arsenic remobilization of about 25-30%.

The results of the study clearly demonstrate that MSMA and arsenite at the site can be immobilized by chemical oxidation processes. Addition of iron increases the immobilizing effect by causing co-precipitation of arsenate with iron. Co-precipitated arsenate was found to be more stable than arsenate bound to the natural soil. A pilot test using this promising approach for the arsenic contamination is foreseen.

Immobilisation of elements by iron and alkalinity in nine contaminated soils and mine residues without vegetation, growth of *Dactylis glomerata* and reduction of contaminant concentration in leaf

*Pierre Hennebert*¹; *Patricia Merdy*²; *Chen CHEN*; *Alexandre Parker*

¹ INERIS; ² Université de Toulon, FR

Some contaminated soils and mine tailings or residues are so phytotoxic (especially sulfidic tailings or process residues) that they are bare or with a very scarce vegetation for decades. Without amendment and soil development, these materials do not evolve into soils.

Nine contaminated soil or mine residues, most of them without vegetation, were treated at laboratory, in lysimeters or at field: excavated urban subsoil from Marseille (F), heavily Cu polluted soil from Bordeaux area (F), bare pyritic Pb and Zn mine tailings in sandstone from Alès (F), flotation tailing dumps, Campo Pisano, Sardinia (I), As and Pb mine residues and tailings from Marseille area (F), marsh downstream of a zone of mine tailings, Sa Masa, Sardinia (I), acid mine tailings with adapted vegetation, Saint Laurent le Minier (F), Pb and Zn mining residue in dolomite and pyritic tailings, St Félix (F), and pyritic process residues (MR3-1, F), with a control forest soil, Aix-en-Provence (F). The pH of these materials was in the 2.4 – 8.3 range, and total contaminants concentration were for some very high (As: 4 – 1300 mg/kg, Cd: 1 – 250; Cu: 1 – 10 000; Pb 10 – 20000; Zn 10 – 4000). The soil improver rich in iron and alkalinity was washed bauxite residue, treated with gypsum to lower the pH to pH 8.5 and called “modified bauxite residue” (MBR). The leachable (10 L deionised water/kg DM, EN 12457-2) fraction of 20 major and minor elements were measured one month after addition of 0.1% to 30% of MBR. Other portions of 400 g of materials were amended with 0, 10% or 30% of MBR, with NPK fertilizer at agronomic rate, with 1% compost, and sown with a common cultivated grass, *Dactylis glomerata* at spring 2016 in Aix-en-Provence (F). For two materials, *D. glomerata* was grown in lysimeters (for one year and two years), and for one material two-years field plot plant was used. In June 2016, the aerial part of *D. glomerata* were harvested and their contaminants measured.

The leaching concentration of phytotoxic elements are immobilised (frequently up to the limits of quantification - LOQ) for inputs between 0.3% to 30 % MBR, depending of the material. Leachable cations (Cd, Cu, Zn), anions (As, Cr, Sb), and major potentially phytotoxic elements (Fe, Al, Mn) are easily immobilised up to LOQ (< 0.1 mg/kg or < 0.5 mg/kg). Among the 8 materials with leachable lead, this element is immobilised up to the LOQ (< 0.8 mg/kg) in 4 materials, and to 1 to 2 mg/kg in 4 other materials. Growth of *Dactylis glomerata* was poor or zero for untreated material in small pots, moderate in amended pots, and luxurious in lysimeters or field plot. The decrease of foliar concentration is correlated with the decrease of leaching concentration with MBR addition. Foliar concentrations of all elements (excepted Pb) are reduced up to a 10 to 100 factor, and up to the concentration of the uncontaminated control soil for lysimeters (St Félix, MR3-1) and field plot (St Félix). For Pb the foliar concentrations are reduced in pots by a factor 10 with 30% of MBR, and are larger than the control (3 mg/kg) for St Félix (62 mg/kg) and MR3-1 (8 mg/kg). Iron and alkalinity of MBR are effective immobilisers for contaminants.

Natural neutralization of acid mine drainage and its effect on the bioavailability of Cu and Zn in Cu rich mine waters

Franziska Klimpel¹; Gijs Breedveld²; Gudny Okkenhaug³

¹ University of Oslo; ² University of Oslo/ Norwegian Geotechnical Institute; ³ Norwegian Geotechnical Institute/ Norwegian University of Life Sciences, NO

Acid mine drainage pollutes soil and water in many areas close to active as well as former mining sites as it has a high acidity and often contains elevated concentrations of heavy metals. There are numerous different remediation methods that have been employed and it is important to find an individual solution for each mining site as site characteristics may vary. Folldal and Sulitjelma are two former mining sites for copper and sulfur in Norway. Since their closure, both mines experience problems with elevated concentrations of copper and zinc in the mine water that flows into a river or lake respectively. In Folldal especially the elevated copper concentrations have been identified as a problem as they cause the absence of fish in the Folla river, which receives the mine water. Currently, several possible remediation options are investigated for their feasibility with the main goal being a reduction of the copper concentrations. One of these options is the natural neutralization of the mine water with water from a close by river with high alkalinity before leading it into the river/lake. This results in precipitation of minerals (mainly iron oxyhydroxides) out of the mine water to which the copper can sorb. This study investigates the effect of different dilution factors of mine and river water on the precipitation of iron oxyhydroxides and the sorption of copper. By analyzing the precipitates, filtered and unfiltered water samples and the usage of DGTs (Diffusive gradients in thin-films), it can be determined in which fractions copper is found and how much is bioavailable. Modelling the dilution process gives further information about the specification of copper for the different dilution factors. The analytical work will be finished this year, and the results from the study will be presented at the conference.

Field Demonstration of Foam injection in Aquifer to Block a Source Zone of Chlorinated Solvents

Clément Portois¹; Olivier Atteia¹; Nathalie Guiserix²; Antoine Joubert³

¹ Bordeaux INP ENSEGID; ² Renault SAS; ³ SERPOL, FR

Background. The presence of Dense Non-Aqueous Phase Liquids (DNAPLs) in soils and groundwater is caused by accidental spillages and represents a long term persistent source of contamination. The inherent chemical properties such as low solubility, high density, and adsorption to soil matrix of these compounds make them particularly problematic. Likewise, heterogeneity between different layers of aquifers leads to trapped and residual DNAPLs, which are difficult to remove by traditional flushing techniques. In the laboratory foam has been used in few experiments to displace DNAPLs to increase the recovery of these contaminants. The present work is part of an Industrial French project that promotes the use of innovative technology for remediating an old polluted site. The aim of this project is to use foam as a blocking agent to confine a source zone of chlorinated solvents (mainly Trichlorethylene).

Approach. Experimental site studies highlighted a Chlorinated Solvents (CS) source characterized by high concentrations of CS in groundwater near old deposit tanks (source zone). CS are spread in two aquifers and high concentrations are found in the boundary of the experimental site. After a progressive installation of wells, aided by modeling, 8 injection piezometers were built around the identified source zone by injecting foam. 4 monitoring piezometers were built downstream to follow before and after foam injection the evolution of flux (using Passive Flux Meter PFM) and concentration of CS.

Design of injection. Pre generated foam were injected at the same time in two piezometers. In total, foam was injected into 6 piezometers (two of the eight piezometer were not enough permeable). Pressures were continually recorded and gives information on foam generation around the piezometer. Gas and liquid flow were also recorded along the process. Slug tests were performed before and after foam injection in order to define the blocking property foam around injection piezometers.

Results. All slug tests show a reduction of the hydraulic conductivity surrounding the piezometer by a factor 100. Groundwater analysis over time from the monitoring piezometers shows a slow decrease of dissolved CS before reaching a plateau. PFM were re installed and confirm reduction of CS flux from the source zone, given an indication of the containment of the source zone by the foam.

Application of ferrates for arsenic removal from groundwater

Monika Stavelova¹; Martin Kovar; Roman Vokac; Jan Slunsky; Jan Kolarik; Jan Filip

¹ AECOM CZ, CZ

Ferrates are a general name for compounds of iron in a high oxidation state - Fe(IV), Fe(V) and Fe(VI), which show highly oxidizing effects and form non-toxic ferrous oxides and oxohydroxides that can act as coagulants. Laboratory tests have confirmed an interesting application potential for these compounds in the area of water treatment technologies. In 2014 an affordable technology for production of ferrates for industrial application was successfully developed and implemented. AECOM researched the possibility of application of ferrates to treat ground water with a naturally elevated content of arsenic (As, arising from regional geological conditions). During reaction of ferrate and As from groundwater, a very strong covalent binding occurs between Fe and As within three to five minutes. Subsequently it is necessary to finely separate the resulting micro-flakes containing hydroxides of Fe and As. Actual groundwater was tested from two sites (site MEZ, site KLU) each with an As content of approximately 100 µg/L, i.e. ten-fold greater than the Czech limit for drinking water (10 µg/L as stated in Regulation 252/2004 Sb). Based on successful laboratory tests, a technological process for separation of As using ferrates was designed, on which basis a mobile pilot plant with capacity of 100 L/hour for on-site testing was constructed. Configuration of operational pilot testing involved: a) addition of ferrate (5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L), b) pH adjustment to pH 7 using diluted HCl, c) adding polymer flocculant, d) sand filtration, e) microfiltration through 10 µm and 1 µm, f) ultrafiltration through 0.45 µm. All pilot tests were performed in duplicate. The quality of cleaned water achieved by the mobile testing device from both sites (KLU and MEZ) complied with the requirements for drinking water – the final As and Fe concentrations were both lower than the required limits of 10 µg/L As, and 200 µg/L Fe and a substantial disinfection effect was also observed. The minimal doses of ferrate for effective treatment to below the requirements were 10 mg/L for the MEZ site and 15 mg/L for the KLU site. During the washing of filters of the pilot test equipment no measurable quantity of sludge was detected. The main practical advantages of the tested technology in comparison with other technologies are therefore the minimal consumption of reagents, minimal production of waste sludge with As content and the associated disinfection effect.

Acknowledgement: This study has been funded by the Technology Agency of the Czech Republic within the research project Nanobiowat (No. TE01010218), and by AECOM CZ, s.r.o.

ThS 3b.4: In situ and ex situ chemical reduction techniques

DECHLORED: In situ implementation as a demonstration project of a chemical process for the reductive dechlorination of chlorinated solvents in polluted groundwaters

Ioannis Ignatiadis¹; Stéphanie Betelu¹; Romain Rodrigues¹; Stéfan Colombano¹; Clement ZORNIG¹; Patrick EPARDEAU²

¹ BRGM; ² BREZILLON, FR

DECHLORED project aim was to: i) develop and prove the efficiency of novel in situ chemical reductive dechlorination (RDC) processes for chlorinated solvents (CSs) in the saturated zone of polluted aquifers by using strong reducers and ii) illuminate, by an improved monitoring, the field under RDC process. The current communication presents the work accomplished to implement in situ enhanced procedures for the RDC of CSs and determine the processes performance. The selected site, Néry-Saintines (France), polluted since 30 years, presents today a well-documented pollution with a majority of CSs (mainly TCE, 2,2-DCE, 1,1-DCE, VC, TCM).

The processing of all analytical data allowed highlighting the existence of a slow natural RDC. It also allowed selecting the right place for the pilot (40.5m width, 25m length x 25m depth). Hydrogeological surveys, preceding the treatments, were realized in order to dimension the pilot and to establish the initial pollution state of the pilot zone to be used as reference. Thus, several analyses and samplings, carried out in August 2014, permit to analyze the CSs content in 12 piezometers (PZ), comprising 3 future injectors (DCI1, DCI2 and DCI3) and 9 control PZs i.e. 3 per injection line.

The pilot principle was to investigate 3 different reagent treatments by injecting into the sandy water table by means of 3 injectors at 4 levels in each one according to ratios defined during the preliminary experiments. Moreover, this part is confidential and will not be presented here. The 3 treatments were: 1) Line 1 (DCI1) Sodium Dithionite, DT; ii) Line 2 (DCI2) Nano-sized zero-valent iron particles, nZVI and iii) Line 3 (DCI3), DT+nZVI. These 3 injections were sufficiently spaced in distance and time to avoid interactions between the 3 reactive zones. During and after the treatment application, the 9 control PZs were used for regular and judicious representative samplings at 2 different depths. This leads to: i) comfort the data acquired by multiparametric probes, ii) provide T, pH, redox, alkalinity, chloride, sulfate, Fe(II) and total Fe contents, iii) analyze CSs and estimate the process performance (reduction percent, R).

With DT alone, R is very high (95%) for the nearest control (5 m from injector DCI1). The second (at 10 m) and the third (at 25 m) controls have lower R, ranging respectively between 5 and 55% and 0% and 35 %. With nZVI alone, R is fairly high (30 to 45% initially), in the 3 control PZs. If, thereafter, R decreases at the first PZ, it increases at second and third, until the extinction of the effect by a higher R at the third. With nZVI and dithionite, R is very high (85%) for the nearest control (5 m from injector DCI3). The second (at 10 m) and the third (at 25 m) piezometers have lower R, ranging respectively between 5 and 55% and 30% and 55 %.

By analyzing the nature and relative abundance of each individual CSs at each sampling operation, extremely interesting results appeared. Indeed, according to the reducer treatment, the distance between injector and control PZs, the depth of sampling, and the sampling date, relative abundance varies and permits to confirm or discover chemical RDC mechanisms.

HCH dechlorination by zero valent iron micro and nano particles

Aurora Santos¹; Carmen Dominguez¹; Sergio Rodriguez¹; Jesus Fernández²; David Lorenzo¹; Arturo Romero¹

¹ Universidad Complutense de Madrid; ² Government of Aragon, ES

Lindane (also known as γ -Hexachlorocyclohexane or γ -HCH) is a manmade organochlorine insecticide produced mainly after the Second World War until the 1990s and widely used throughout the world for agricultural and public health purposes during the last decades. The application of technical HCH, t-HCH (a mixture of α , β , γ , δ , and ϵ HCH isomers) and purified lindane (the only HCH isomer with insecticidal properties) has resulted in environmental contamination of global dimensions. Uncontrolled dumps of the HCH wastes have produced a relevant contamination of soils and groundwater in the nearest of the production facilities.

Due to the high chloride content of the HCH molecule, reduction over zero valent metals is a promising alternative, being zero valent iron (ZVI) the most common metal used drawing on its activity, abundancy, low cost and benign environmental impact [1]. Based on the iron particle size, ZVI can be used as nanoparticles (nZVI) and microparticles (mZVI), being the former much more studied in this process due to the high intrinsic activity of nanosized materials. The viability of ZVI for in situ applications (injection or Permeable Reactive Barriers, PRBs) in HCH degradation in soil and groundwater will be a suitable and cost-effective option depending on the long-term integrity and performance of the microparticles and the stability of the nanoparticles. Recently, influence of different salts, temperature and mZVI concentration have been tested in lindane dechlorination with promising results [2].

In the current work, the attention is focused on the application of both mZVI and nZVI to decontaminate groundwater from a site polluted by HCH wastes in Sabiñanigo (Spain). Commercial sources of ZVI (micro from Honagas and nano from Nanolron) have been used for this scope. Groundwater was characterized being the main pollutants chlorobenzene, dichlorobenzene and HCH isomers. Chlorinated compounds and organic intermediates were identified and quantified by GC/MS using SPME with fiber immersed in the aqueous phase.

Runs were carried out both in batch and continuous operation (in the last case, column studies were accomplished). Effect of iron loading and groundwater composition on degradation of chlorinated pollutants were studied and a kinetic expression was obtained as a function of these variables. Depending on the iron loading and the type of iron source, the required time for total dechlorination of Chlorinated Organic Compounds (COCs) ranged from minutes to days. Therefore, in spite of further research should be accomplished, the use of ZVI seems to have a good potential in remediation of soils and groundwater polluted by HCH wastes.

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In Situ Chemical Reduction for the remediation of chlordecone contaminated soils

Christophe Mouvet¹; Bastien Collet²; Sébastien Bristeau¹; Mathilde Senergues³; Luc Rangon⁴; Jean-Marie Gaude⁵; Thierry Woignier⁶

¹ BRGM, FR; ² ADEME, ³ APAVE; ⁴ IRD; ⁵ Cirad; ⁶ University of Montpellier, FR

Chlordecone (CLD), a highly persistent organochlorine pesticide, represents a major source of contamination of French West Indies (FWI) ecosystems (e. g. soil, surface, ground and coastal waters). Restrictions exist on the marketing of food products and statutory limitations on human consumption have been issued. Furthermore, several studies report that chronic exposure to CLD leads to hepatotoxicity, raise early child development and pregnancy complications and increase the risk of liver and prostate cancer. Without the implementation of soil remediation, contamination is expected to last for decades to centuries according to soil type. In the present study, In Situ Chemical Reduction (ISCR) has been evaluated at field scale for the remediation of soils contaminated by CLD.

The study was conducted in a 1 000 m² nitisoil plot of the Lamentin plain (Martinique) which chlordecone soil concentration was $0,7 \pm 0,3$ mg/kg (mean and standard deviation, $n = 24$). Six modalities were studied: no amendment (control), addition to the top 30 cm soil of 4% (dw/dw) of coarse (30 % < 50 μ m) Zero Valent Iron (ZVI), 4% fine grain ZVI (98 % < 50 μ m), 6 % Daramend, 6 % Daramend with bagasse instead of alfalfa, or 6% of a mix, prepared by BRGM, of coarse ZVI and local bagasse. All amendments were incorporated to the soil using machinery commonly used in banana plantations. Some compaction of the soil was achieved before irrigation was applied intermittently over the 3-month experiment with standard sprinklers. Soil redox potential was regularly monitored and soil samples taken over the 0 – 30 cm layer were extracted by ASE and analysed for CLD and transformation products by GC/MS/MS.

The mean redox potentials were lowered down to - 250 mV three days after incorporation of the fine ZVI, vs. + 600 mV in the control plot, and between - 10 mV and + 30 mV during the 94 days following incorporation of the standard Daramend. Values down to - 440 mV were recorded in some soil samples treated with fine ZVI. The mean CLD soil concentration was lowered in all modalities, with a 11 % decrease for Daramend bagasse, 35 % for standard Daramend, 43 % for coarse ZVI + bagasse, 54 % for coarse ZVI and 69 % for fine ZVI. The dechlorination effect of ISCR was proven by the detection of CLD transformation products with up to 4 Cl less than the parent molecule. The main CLD transformation product is the same in all ISCR treated modalities at all sampling dates: a mono-dechlorinated CLD, 5- or 5a-hydroCLD (CAS nomenclature). This mono-hydroCLD represents up to 69 % of the residual CLD concentration and does not accumulate in the soil. The other main transformation products are the 5,6- or 5a,6-di-hydroCLD, another di-hydroCLD, a tri-hydroCLD, and traces of a tetra-hydroCLD.

Compared to the very limited efficiency of microbiological degradation of CLD in optimized laboratory conditions (maximum 3 %), and knowing that preliminary studies show the 2 main CLD transformation products formed by ISCR to be less toxic than the parent compound, ISCR appears a very promising way of tackling the issue of CLD soil contamination in FWI.

Media for In-situ and Ex-situ Treatment of Radioactively Contaminated Groundwater

Nick Atherton¹; James Graham²

¹ Sellafield Ltd; ² The National Nuclear Laboratory, GB

The Sellafield Nuclear Site has a long history of supporting the civil nuclear industry. As the site comes to the end of operations, there is a greater emphasis on waste retrieval and decommissioning to reduce the risk associated with the site. An example is the retrieval of waste from a series of waste storage silos. A plan for managing the potential for leakage of contaminated water during the waste retrieval is required; including potential technologies to mitigate groundwater contamination.

The main groundwater contaminants are technetium-99 (Tc-99), strontium-90 (Sr-90) and carbon-14 (C-14). Concepts for both in-situ and ex-situ mitigation were developed. These consisted of: a funnel and gate Permeable Reactive Barrier (PRB); treatment by injectable reactive media; and a Pump and Treat (P&T) system. The in-situ techniques shared the similar treatment media, although the direct injection allowed the use of liquid amendments as well as slurries. The ex-situ treatment of groundwater was a two stage process of water softening followed by ion-exchange. Simple laboratory testing assessed the potential performance of each concept under relevant environmental conditions.

The laboratory experimental programme focussed on testing a wide range of treatment media with Sellafield soils or simulants. Zero Valent Iron and Granular Activated Carbon were selected for in-situ treatment of Tc-99; sodium dithionite was also chosen as a liquid amendment. For Sr-90, apatite and clinoptilolite were selected as solid/slurry amendments and calcium citrate phosphate as a liquid amendment to form apatite in-situ. Treatment media for ex-situ groundwater treatment included a range of commercially available ion exchange resins for Tc-99 and Sr-90 treatment; the water softening stage also had the potential to treat Sr-90 and C-14. A series of batch and column experiments was completed on each media.

For in-situ treatment Tc-99 assessments, the tests demonstrated that GAC and ZVI soil mixes both immobilised nearly all the Tc-99 in the groundwater. Sodium dithionite liquid effectively removed all of the Tc-99, however it was noted that the strongly reducing conditions released redox sensitive metals such as arsenic and selenium. The Sr-90 sorption tests demonstrated that both the clinoptilolite and apatite performed well under static conditions, although the apatite was less effective in the column tests and a strong dependency on column flow rate was measured. Calcium citrate phosphate batch tests suggested that apatite was formed; however the reaction did not appear to the same extent in column tests using a more concentrated formulation.

For ex-situ groundwater treatment, the water softening stage successfully removed competing ions and a proportion of the C-14 and Sr-90. The ion-exchange test results showed that all materials could reduce both Sr-90 and Tc-99 concentrations below drinking water standards.

The results showed that a range of commercially available treatment media could be used for the in-situ and ex-situ treatments of Tc-99 and Sr-90 contaminated groundwater. The ex-situ water treatment also benefitted from the removal of C-14.

Chemical Chromium(VI) reduction – how to find the right reagent?

Marlies Bos¹; Denny Schanze; Tessa Pancras; Geert Wijn; Wim Plaisier; Joop Verhagen, Rudi Pelgrum

¹ Arcadis Netherlands, NL

For the remediation of a large site in Spain impacted with hexavalent chromium, Cr⁶⁺, Arcadis applied biological and chemical reduction to reduce Cr⁶⁺ to the less mobile and less toxic trivalent chromium, Cr³⁺. Extensive literature is available on several Cr⁶⁺ remediation techniques, but determining which reagent would be most suitable was not obvious. Laboratory testing proved to be of great value to the development of an appropriate remediation strategy.

During the project multiple laboratory studies were executed in order to identify the best applicable reagent: to stimulate biological reduction (e.g. whey and molasses) and for chemical reduction (e.g. ferrous iron sulfate, sodium dithionite (DT) and sodium metabisulfite (MB)).

As the application of whey, molasses and iron sulfate are widely accepted, these reagents were tested first. As a result biological reduction appeared to not be applicable at high Cr⁶⁺ concentrations while almost complete reduction of Cr⁶⁺ (>99,9%) was achieved using iron sulfate. Based on these results five injection events were undertaken with iron sulfate applied in high impact zones and whey in the plume area. Although this approach has led to a significant reduction of Cr⁶⁺, in some high impact zones the reduction was still insufficient.

In order to increase the treatment efficiency it was decided to assess the effectiveness of DT and MB as alternative reagents. Some literature suggests that they are effective by reducing Fe³⁺ to Fe²⁺ and subsequent indirect reduction of Cr⁶⁺ by the formed Fe²⁺. In fact the site soil contained a lot of precipitated Fe³⁺ (partly originating from previous iron sulfate injections). Other literature states that dependent on pH both reagents could also reduce Cr⁶⁺ directly. For MB most literature suggests that a low pH (<5) is required, but creating acidic conditions is undesirable because additional chemicals would be required and it increases the risk of Cr³⁺ mobilization. DT theoretically seemed to be the better choice, but due to health and safety concerns (sodium dithionite is classified as spontaneously combustible), MB was also tested.

The results indicated that both DT and MB were effective in direct reduction of Cr⁶⁺, also under neutral pH conditions. Moreover divalent iron became available for indirect reduction. Therefore additional iron injection will not be necessary. Cr⁶⁺ reduction of >99,9% could be achieved at reagent concentrations that would be applicable in the field. Moreover the formed Cr³⁺ was immobilized, as long as the buffering capacity of the soil was capable of preventing pH decrease when higher MB/DT concentrations were applied. Subsequently long-term batch tests showed that the reduction was durable.

Depending on recent monitoring results an additional injection event may be undertaken using MB as the applied reagent.

This project reminds us (again) that it is important to combine theoretical knowledge, laboratory study and on-site field experience in order to develop the most effective remediation strategy. This is because every site is unique and has its own specific characteristics which can significantly influence the applied remediation techniques.

ThS 3c.1: Physical and Thermal technologies for site remediation

Electrochemical elimination of PFASs

Andreas Tiehm; Kathrin Rachel Schmidt; Hanna Ulrich; Michael Gierig

TZW: DVGW-Technologiezentrum Wasser, DE

Per- and polyfluoroalkyl substances (PFASs) seem to advance to the groundwater pollutant of the decade. More and more monitoring shows more and more contamination situations and also the limitations of the current available treatment techniques. PFASs are persistent to biodegradation and conventional oxidation processes such as ozonation. Nowadays, sorption is the technique most often used to remove PFASs from contaminated groundwater. Here, the main limitation is the low loading capacity of e.g. activated carbons especially for short-chained PFASs. Thus, there is a high need to investigate and propose alternative treatment options.

In this study electrochemical degradation of PFASs on boron-doped diamond (BDD) electrodes was demonstrated. Laboratory experiments were performed with model solutions and contaminated groundwater containing 0.26 up to 34 mg/L PFASs and a high organic background with 13 mg/L dissolved organic carbon (DOC).

Electrochemical decomposition of PFASs resulted in the formation of shorter chained molecules. Thus, the longer the chains the faster the elimination. With prolonged oxidation time, degradation of up to 97% sum PFASs and up to 98% DOC was achieved along with fluoride release. Specific energy consumption decreases with increasing PFASs concentration. Thus, a prior concentration step of target substances makes electrochemical treatment more energy- and cost-efficient.

The groundwater used contained chloride and bromide which were oxidized to perchlorate and bromate. Also AOX (adsorbable organic halides) were formed. Thus, toxicity before and after electrolysis needs to be assessed in order to develop treatment conditions avoiding the formation of critical byproducts. Process modifications could consider material properties, reaction conditions and reactor construction.

The results of electrochemical degradation were compared with the outcome of membrane filtration and conventional sorption techniques. Nano filtration and reverse osmosis need further treatment steps. The tested sorption materials considerably differed in their performance to adsorb PFASs. Taking into account the specific material costs one conventional activated carbon was most efficient in removing PFASs from contaminated groundwater.

In conclusion, electrochemical treatment represents a promising approach for PFASs removal. Based on the results of this study, further studies into process optimization and the benefits of combining different treatment technologies are encouraged.

Surfactant Foam Flushing For In Situ Recovery of Heavy Chlorinated Hydrocarbons of DNAPL In An Alluvial Groundwater

Nicolas Fatin-Rouge¹; Delphine Kaifas²; Julien Maire¹; Aurélien Triger²; Pierre-Yves Klein²; Antoine Joubert³; Alain Dumestre³; Stéfan Colombano⁴; Hossein Davarzani⁴; David Cazaux⁵; Cédric Marion⁵; Quentin Giraud⁶; Benoît Paris⁶

¹ University of Bourgogne Franche-Comté; ² Sol Environment; ³ SERPOL; ⁴ BRGM; ⁵ INOVYN; ⁶ INTERA, FR

Background/Objectives. The remediation of heavy and recalcitrant chlorinated hydrocarbons (HCs) DNAPLs in deep saturated zone is challenging, as conventional treatments reach their limits: Pump and treat has limited recovery yield (60% at its best) and surfactant enhanced dissolution is costly and risky as contaminants are dissolved in the aqueous phase. Whereas foams have been used for decades for enhanced oil recovery (EOR) into heterogeneous geological layers, their use as remediation fluid is newer because the contexts are very different. Indeed, the treatment in unconsolidated shallow undergrounds, able to remove pure phases of pollutants to reach ppb-levels in low permeability aquifers while protecting them and preventing soil upheaval is more challenging. Literature is scarce on DNAPL remediation using foam. Most publications only deal with fundamental mechanisms without considering all the practical parameters required for field-scale application. To the best of our knowledge, only one assessment of foams for DNAPL removal at field-scale has been reported, using them to block high permeability zones and improve the sweeping efficiency of surfactant solutions.

Within the SILPHES project (French acronym for Innovative Solutions for the Remediation of Aquifers Contaminated with Chlorinated Compounds) that involves academic and industrial partners, foams have been thoroughly assessment at lab and field-scales for their performances and applicability as flushing and delivery fluids.

Approach/Activities. This work presents a complete evaluation of physical and chemical parameters affecting applicability of the foam process for environmental remediation. Surfactant foams have been assessed for treatment of a historical contamination made of a mixture of heavy and recalcitrant HCs located at the bottom of a sandy aquifer of moderate permeability (~40 Darcy), 8-12 m below ground surface. Lab studies were performed with field materials (soil, DNAPL). Foams have been assessed to improve the HCs DNAPL recovery pushing it in its residual state to recovery wells where it is pumped out. The study consisted in systematic evaluation in 1- and 2-D cells of the effect of injection modes and parameters on operational parameters (pressure gradient, propagation rate, surfactant consumption...) and treatment parameters (DNAPL recovery, uncontrolled migration, HCs dissolution...). Comparative results with surfactant solutions are discussed. Lab results are completed by a field-test assessment carried out in a 1000 cubic meter cell.

Results/Lessons Learned.

The foam technology allows to enhance significantly the recovery of pure phase of HCs after pump and treat operations. Using foam as a flushing fluid, up to 60% of DNAPL residual can be recovered at pressure gradient lower than 90 kPa m⁻¹ and propagation rates around 3 m day⁻¹. In contrast to soil flushing with surfactant, flushing with foams allows a strong reduction of risks, duration and costs. However, if the foam technology is disruptive, efficient and sustainable for the recovery of DNAPL in low accessibility source zones, its use critically depends on fluid formulation and operating parameters.

In Situ Smoldering Combustion (STAR) for the Treatment of Contaminated Soils: Challenges Encountered & Lessons Learned In Providing a New Remediation Technology to the Industry

Gavin Grant; David Major; Grant Scholes

Savron, CA

STAR is an innovative in situ remediation technology based on the principles of smoldering combustion where the contaminants are the source of fuel. This presentation presents background information on the technology and case studies of field tests highlighting lessons learned for the successful implementation of the technology.

The first case study involved the STAR treatment of two contaminated horizons (DNAPL and LNAPL) in a fine sand unit at a former Gasworks Site in northern Michigan. Self-sustaining smoldering combustion was achieved in both the LNAPL and DNAPL zones resulting in a Radius of Influence (ROI) of approximately 2.4 meters with an average propagation rate of approximately 0.3 meters per day. However, air flow fluctuations during the first test lead to premature quenching of the combustion reaction. This work demonstrates the importance of a steady air supply on the smoldering combustion process as even mild variability of the air flow rate can result in heat losses that will impact the ROI at a given location.

The second case study involved the first in-situ field application of a surrogate fuel (emulsified vegetable oil [EVO]) to support combustion of high volatility compounds including Gasoline Range Organic (GRO) and Diesel Range Organic (DRO) compounds at a former refinery in Michigan. Successful injection and combustion of EVO resulted in a more robust smoldering reaction, with an increased ROI as compared to the "standard" STAR test. Total Petroleum Hydrocarbon (TPH) concentration reductions of greater than 90% were achieved in the target treatment zone, with approximately 20% of the mass destroyed via combustion and 80% volatilized and subsequently captured and treated at surface through a soil vapor extraction (SVE) system.

The third case study involved the STAR treatment of Navy Special Fuel Oil (NSFO) within a former tank farm area in Virginia. The field test demonstrated that the smoldering reaction successfully treat contaminated soil located both above and below a discontinuous clay layer. A combustion ROI of approximately 2.25 m with an average propagation rate of 0.25 m/day led to TPH concentration reductions in soil from over 14,000 milligrams per kilogram to a few hundred milligrams per kilogram.

The final case study involved the full-scale STAR treatment of a former manufacturing facility in New Jersey. The results of pilot testing were used to develop a full-scale STAR design consisting of approximately 1500 surficial fill ignition points and 500 deep sand ignition points and two treatment systems (air distribution and vapor collection / treatment system) to remediate an approximately 14-acre footprint of contaminated soils. Progress to date and challenges overcome during full-scale operations will be discussed.

Thermal treatment of TCE for a 30 m deep source in granite

Gorm Heron¹; Steffen Griepke Nielsen¹; Anthony Caravella¹; Erik Pearson²

¹ TerraTherm, US; ² Ramboll Environ

A 30 m deep TCE source area was treated thermally in 2015-2016 using Thermal Conduction Heating. The heaters delivered energy uniformly from 0 to 32 meter depth, leading to boiling point temperatures from top to bottom. After removal of most of the mass, and achievement of diminishing returns, the heating system was turned off ahead of schedule. Each heater boring had a co-located vacuum extraction well to ensure pneumatic capture - allowing TCE to be extracted from any open fractures during the heating period. A prepackaged Tier-One vapor treatment system was used - allowing a brief weekly visit by an operator, and unmanned operations with automated adjustments and dial-in capabilities. The data was recorded automatically and posted on a web-page with visibility for the client and the regulators at any time. Design details and results will be presented for this unique thermal approach, along with key lessons learned for remediation in fractured bedrock.

Thermal enhancement of coal tar pumping in saturated porous media

Nicolas Philippe¹; Hossein Davarzani¹; Manuel Marcoux²; Stéfan Colombano¹; Delphine Kaifas³; Aurélien Triger³; Pierre-Yves Klein³

¹ BRGM; ² IMFT; ³ Sol Environment, FR

PAHs are main constituents of coal tar, which is found on coking plant wastelands. The pumping rate of these DNAPLs is generally low due to its viscous nature and its high residual saturation. The goal of this study is to investigate effects of temperature on coal tar recovery and determine if a thermal enhancement can improve the pumping efficiency.

Coal tars used in this work were sampled from a pilot site of a former coking plant. In order to understand how thermal remediation would enhance coal tar recovery, we first investigated temperature sensitivity on coal tar properties including density, viscosity, interfacial tension and contact angle with water. Viscosity is affected by temperature and showed a five-fold decrease when coal tar is heated from 10 °C to 50 °C. Other coal tar parameters, like wettability, were not significantly altered by temperature changes. The lack of wettability variations due to temperature indicate that coal tar residual saturation should not be affected by thermal enhancement. However, the decrease in its viscosity shows that coal tar under the water table can be remobilized by heating processes. As a consequence, the recovery rate of coal tar would effectively increase, if a thermally enhanced pumping is used.

We also conducted drainage-imbibition experiments of coal tar – water system in a one-dimensional column to determine the impact of temperature on capillary pressure-saturation curves. A model has been developed to predict coal tar recovery, using COMSOL Multiphysics® in a two-dimensional tank and isothermal conditions. The theoretical results were compared to experimental pumping tests performed in laboratory in a two-dimensional tank to validate the numerical model.

The next step is to perform the experiments in non-isothermal cases and to improve the numerical model by coupling coal tar - water flow with transient heat transfers in order to realistically model a thermally enhanced pumping. This is necessary to determine quantitatively how temperature affects the coal tar recovery rate in order to enhance the processes.

ThS 3c.2: Thermal technologies for site remediation

Application of in situ thermal treatment to enhance light non-aqueous phase liquid recovery rates

Nicolas Barbian; Jake Hurst; Mark Webb; [Ian Ross](#)

Arcadis UK

The physical properties of light non-aqueous phase liquid (LNAPL) play a large role in determining the likelihood of its functional mobility and potential to act as an ongoing source of contamination – either through volatilization to soil gas or dissolution of constituents into porewater or groundwater. The physical properties and behaviour of LNAPL beneath a site can be quantified through a combination of field testing, such as baildown tests, laboratory analysis such as forensic testing and literature datasets. This data can then in turn be used to predict the likely recoverability of LNAPL from the subsurface, and guide the setting of remediation criteria associated with LNAPL removal. Certainty in recovery rates can be further improved through the implementation of pilot testing.

In the UK, the process of risk assessment can be used to help evaluate whether LNAPL recovery is a remediation requirement for sites affected by historical contamination events. This case study highlights an active manufacturing site where LNAPL recovery was required, following the development of a robust LNAPL conceptual site model and evaluation of potential risks associated with the LNAPL remaining in situ. Assessment of the recoverability of the LNAPL through theoretical calculations alongside pilot testing demonstrated that recovery would be challenging using in situ techniques. The pilot test was extended to trial the impact of thermal treatment, heating the subsurface and thus resulting in a reduction in LNAPL viscosity. The pilot test was designed to provide sufficient information about the subsurface to enable a full-scale remediation strategy to be developed and implemented.

The approach used to investigate and delineate the impact by LNAPL, the design of the pilot testing for enhanced LNAPL recovery through thermal treatment and the design and results of the full-scale remediation will be described, sharing learning around a successful method applied to enhance LNAPL recoverability.

Thermal remediation of 5-CAT, DCB, TCE and VC using a combination of steam and conductive heating adjacent to a commercial railroad track.

Niels Ploug¹; Max Jensen¹; Gorm Heron²; Steffen Griepke Nielsen²

¹ Krüger A/S; ² TerraTherm, DK

Background

A former chemical dumpsite in Switzerland established on both sides of a commercial rail road track was excavated during 2013 – 2015. However at 1750 m² of the site the contaminants migrated to a depth where excavation was impossible due to risk of the railroad track.

Simplified, the geology is 5 - 6 meter of low permeable clay till underlain by a high permeable aquifer with a substantial groundwater flow of approximately 100 m/year. The target compounds were primarily Vinyl chloride, Trichloroethylene, 1,2 Dichlorobenzene, Chlorobenzene and 4-Chloro-2-Methylanilin (5-CAT) with boiling points ranging from -13 °C to 241 °C. This means that a treatment temperature of 100 °C will only provide partial treatment of the high boiling compounds.

The contamination is situated in a heterogeneous, low permeable unsaturated zone extending approximately 6 meters below ground and in a gravelly aquifer below the unsaturated zone. More than 98% of the mass is situated in the unsaturated part of the remediation zone. The groundwater aquifer has a substantial flow of approximately 100 m/year.

Aim

The challenge was to heat the high permeable aquifer and also ensure that the interface between the unsaturated zone and the saturated zone is heated thoroughly. To remediate the unsaturated zone, and at the same time provide remediation of the underlying groundwater, a combination of steam enhanced extraction in the saturated zone and Thermal Conduction in the unsaturated zone was implemented. The target treatment temperature for both unsaturated and saturated zone was 100 °C knowing that part of the unsaturated zone would reach higher temperatures due to the nature of thermal conduction.

Conclusion

The site has been remediated to the given criteria. The purpose of the talk is to show what cleanup levels was achievable with these higher boiling compounds using the approach. A comparison between design and actual key parameters such as energy consumption, temperature distribution etc. will be provided. Heating in the absolute vicinity of the rail road tracks were monitored and results of this survey will be discussed.

Steam-air injection in fractured bedrock: completion of a CHC-remediation at the site Biswurm (Villingen-Schwenningen, Germany)

Oliver Trötschler¹; Hans-Peter Koschitzky¹; Bernd Lidola²; Isabell Kleeberg²; Stefan Schulze³

¹ University of Stuttgart; ² City of Villingen-Schwenningen; ³ GEOsens, DE

The soil and aquifer system below a former site to incinerate liquid organic waste (CHC, BTEX, mineral oils) was highly contaminated by these chemicals. During the demolition of the plant in 2004 approximately 1,600 kg of CHC were removed by the exchange of the top soil. The remaining source zone covers an area of approx. 2,900 m². The fractured sandstone aquifers are affected down to 37 m bgs. The major contamination is located between 3 – 15 m depths. A total inventory of 10 to 50 tons of CHC was estimated. The CHC emission exceeded the regulatory limits (20 g/d) by a factor of 20.

In 2009 VEGAS accomplished a pilot trial of steam-air injection upon request of the problem owner, the city of Villingen-Schwenningen. The test field extended to 2,000 m³ of fractured rock including the upper aquifer. The horizontal thermal radius of steam propagation was determined to be 5 m in the target zone. During 3 months of operation 560 kg of CHC were removed.

Based on this pilot the subsequent steam-air enhanced remediation of the source zone (2,900 m², 15 m thickness) was designed. 32 two-level injection wells and 37 soil vapour extraction wells (SVE) were installed on nine treatment sections. The steam-air injection phase (400 kW heating power) was calculated to last 33 months. The total costs were estimated to be 3.2 million EUR to treat 40,000 m³ of sandstone.

The steam-air driven remediation started in July 2012. The steam-air injection lasted until August 2016. The cooling phase will last until March 2017.

A section-wise remediation concept using in parallel 4 or 5 injection wells (300 – 500 kW heating power) and 10 to 12 soil vapour extraction wells in each section was adapted. Since the heat and steam propagation was wider than expected two sections were heated simultaneously while SVE was extracted from five sections to ensure pneumatic control. A transport distance of up to 50 m of the evaporated contaminants was observed. During the desorption phase the average temperature exceeded 88°C in 19,000 tons of heated sandstone (2 – 3 sections).

The desorption process of the CHC from the sandstone bedrock took 40 - 45% longer as expected. The remediation time was increased by 45%, the energy consumption by 30% and the total cost by 25%.

By 2016 the average CHC mass extraction was reduced from 3.5 kg/d to be below 0.3 kg/d. In 2012 the initial CHC emission by the groundwater was 400 g/d. Due to the remediation in 2015 it was reduced to 70 g/d and by end of August 2016 to 10 g/d, thus below the regulatory limit of 20 g/d. Hence steam-air injection was stopped. During the cooling phase the value in October 2016 was below 5 g/d CHC.

In total approximately 4,900 kg of CHC were removed; 4,750 kg CHC by the SVE and 160 kg CHC by the groundwater extraction.

The soil vapour monitoring indicates a mass removal of more than 95% similar to the reduction of the emission.

The EPA of Baden-Württemberg, the regional council (RP Freiburg) and the community of Villingen-Schwenningen support the application of steam-air enhanced remediation of the site. The local consultant is GEOsens, VEGAS works on the scientific supervision. The remediation company is Bauer Umwelt GmbH.

Addressing specific thermal aspects and risks in tendering In Situ Thermal Remediations

Emile Marnette¹; Bert Scheffer¹; Thierry Ruffenach²; Jean-Baptiste Guérin²; David Hiez²

¹ Tauw BV; ² Tauw France SAS, NL

In Situ Thermal Remediation (ISTR) is a remediation technique that becomes more and more widely used. It has its origin in the United States going back to the 90s of the previous century. Several American suppliers of the technique made liaisons with European contractors to serve the European market which resulted in a number of closed remediations in several countries like Denmark, France, Luxembourg, The Netherlands and Belgium.

In case the owner of an impacted site is planning to use ISTR for remediation, he generally starts a tender procedure to get a competitive bid of a contractor. The performance of ISTR requires very specialized knowledge and experiences and problem owners or their consultant not easily take the responsibility and associated financial risks to make a detailed work specification as basis for a tender. So in most cases, the work is commissioned as a design and construct-like contract (lump sum turn-key contract).

Because of the design and construct character of the tender, the conditions under which the work must be designed have to be well-defined. Tendering of an ISTR requires special attention to thermal specific aspects like e.g. heat, high electricity use, that are different from other in-situ remediation techniques. Also financial risks associated with a thermal remediation work are highly specific and have to be allocated to either the commissioner or the contractor.

Tauw has been involved in two closed In Situ Thermal remediations; one in France and one in The Netherlands. Another In Situ Thermal remediation in Brasil is currently in operation and another, large, remediation in France is in preparation.

In our presentation we will focus on the way client and consultant manage risks specifically associated with in situ thermal remediation and on how financial risks and associated costs are allocated to the commissioner or contractor, using our experiences with the ISTR projects we prepared and supervised.

Lowering the Carbon Footprint of Thermal Remediation Systems

Joanne Pennell¹; Jennifer Brett¹; Simon Tillotson; Jay Dablow¹

¹ ERM, GB

ERM was commissioned to investigate and treat legacy contamination beneath a building, at an operational manufacturing site. The main contaminant of concern within soil and groundwater was Chlorobenzene present at concentrations indicative of the presence of DNAPL. A High Resolution Site Characterisation investigation revealed DNAPL present within the heterogeneous clays, sands, silts and gravels underlying the site.

Sustainability was a key factor considered during the remedy and associated project lifecycle evaluation. In-situ thermal treatment technology was ultimately selected as the remediation technique, as the Multi Criteria Analysis conducted in accordance with the UK's Sustainable Remediation Forum (UK SuRF) framework, demonstrated this technology offered the greatest overall net sustainability benefit.

As a result of the analysis, the thermal design was built around enhancing system sustainability. For example, the remedial design included the use of gas fired burners to provide the heat input, used geochemical modeling to evaluate performance of the system if a reduction in the target treatment temperature was implemented, and used a thermal model to optimize the heater well spacing/energy input. One of the key sustainability factors included in the design was a reduction in the Target Treatment Temperature (TTT). The design paradigm for thermal remediation has traditionally been heating to or above the boiling point of Chlorobenzene (131°C) to achieve contaminant removal via volatilisation. However, ERM evaluated using a lower TTT in order to take advantage of carbon dioxide gas release to remove the contamination via gaseous stripping (a process called Low Temperature Volatilisation, or LTV). This approach allows for heating at temperatures lower than the co-boiling point reducing the TTT to circa 60°C, resulting in a significant associated energy savings.

Once the TTT had been confirmed, a thermal model was constructed using PetraSim™ PC based software. This informed the technical design and enabled heat input to be optimized, and hence the specification of the process equipment used. The model predicted a heat up time of circa 60 days and also showed that the optimum configuration comprised 26 DPVE wells and 14 gas fired heating wells within the approximately 900m² treatment area. 30 temperature monitoring points were also installed within the treatment zone to allow the heating process to be monitored and optimized.

The operational phase confirmed the design predictions and heating was completed within 56 days. The recovery system subsequently operated in isolation for several weeks afterwards to recover the remaining contamination via the LTV approach without additional heat input being required. Data showing the success of the thermal project will be presented along with an analysis of the carbon footprint of the LTV approach using the Life Cycle Analysis (LCA) Simapro PC based software. In addition, an estimated LCA will be given to compare the same project if the traditional higher temperature approach had been implemented to show the net benefit of the system from a sustainability standpoint.

ThS 3d.1: Phytoremediation of heavy metal-polluted soils and sediments

Biochar-supported phytoextraction of metals in a three-year lysimeter study

Frédéric Rees¹; Thibault Sterckeman; Jean-Louis Morel

¹ University of Lorraine - INRA, FR

Biochar, the residual solid of biomass pyrolysis, can be used in the remediation of soils contaminated by heavy metals. Biochar has been found to reduce soil metal mobility and availability for the plant, acting both as a sorbent and as a liming amendment. However, biochar can influence plant growth and plant metal uptake in metal-contaminated soils in various ways. In particular, recent studies have suggested that biochar may cause either a decrease or an increase in plant metal uptake depending on plant species.

Two identical undisturbed soil monoliths (1-m² wide, 2-m deep) were excavated in an agricultural plot from North of France in June 2009, and installed in the lysimetric station of GISFI in Homécourt (France). Soil was alkaline (pH 8.1) as a result of former liming, and presented a high contamination of Cd, Pb and Zn due to atmospheric deposition from smelters activity. In March 2013, a wood-derived biochar obtained from slow pyrolysis at 450°C was applied at a rate of 5% (w/w) in the A-horizon of one of the two soil columns. The Cd/Zn-hyperaccumulator *Noccaea caerulescens* was grown for the next three years on both lysimeters and harvested each autumn.

Our results showed that biochar improved germination of *N. caerulescens* and increased the root surface density. No significant effect of biochar on shoot metal content by *N. caerulescens* was observed. Shoot Cd content and soil Cd availability were decreased by more than 60% in the two last years compared to the first year. Overall, the total amount of Cd and Zn phytoextracted was increased in the presence of biochar. Biochar amendments may therefore be used in metal-contaminated soils to enhance not only the phytostabilization of metals but also their phytoextraction with hyperaccumulating plants, and as a result are a relevant means to reduce risk due to the presence of excess metals.

Using Thermochemical Conversion Technologies for metal-rich biomass derived from Ultramafic Soil in Brazil

Ying Jiang¹; Sergio Peres²; Humberto Santos²; Adalberto Nascimento Jr.²; Phil Longhurst¹

¹ Cranfield University; ² Escola Politecnica de Pernambuco – Universidade de Pernambuco, GB

In the UK and globally, natural metal deposits, mining and other industrial activities, have created extensive areas of heavy-metal-contaminated land. The high metal concentrations in the soil significantly restrict the potential land uses particularly for agriculture purposes. In areas with low development value, land remediation activities are largely impeded by financial and technical barriers, which resulted in a legacy of large marginal landbanks. Brazil has one of the largest ultramafic soil areas in the world containing high concentrations of heavy metals, particularly nickel (10mg g⁻¹ of dry soil average), Cu and Co.

Growing suitable energy crop on these contaminated sites presents an opportunity for renewable energy production through thermochemical conversion of the harvested biomass. Further environmental benefits can be achieved where suitably selected plant species remove or stabilise heavy metal contaminants in the soil.

This abstract describes an ongoing international collaborative research programme. Currently, indigenous biomass samples were collected from nickel and copper mining sites in the State of Pernambuco, Brazil, where high concentrations of Ni, Cu and Co were found in the soil. The selection criteria for plants are based on the biomass yield and metal accumulation factor. In the next stage of the project, proximate and ultimate analyses will be carried out on the collected biomass samples. In addition, a comprehensive determination of metal contaminants in biomass will be conducted using ICP-MS. To further understand the thermochemical behaviours of the biomass samples, a series of TGA tests have been planned. This will be followed by lab scale gasification and pyrolysis trials on biomass samples under a variety of operational parameters to optimise the energy output. To understand the fate of elemental contaminants in the biomass, ash and liquid residuals derived from gasification and pyrolysis trials will be acid digested and the metal contents will be determined using ICP-MS. In addition, gaseous elemental emission in flue gas will be collected in impingers and analysed for metal concentrations.

This study provides valuable information to enable application of thermo-chemical process for bioenergy recovery from plant biomass derived from high metal content soil in Brazil without competing with food crop productions.

We anticipate all experimental work described will be completed by March 2017 and the project outcomes will be ready for presentation at the AquaConSoil2017 conference.

Citric acid alleviated Chromium (Cr) toxicity in Lemna minor L. by improving antioxidant enzymes defense system and enhanced phytoextraction of Cr

Mujahid Farid¹; Rasham Sallah-Ud-Din; Rashid Saeed; Shafaqat Ali; PhD/Muhammad Rizwan; Hafiz Muhammad Tauqeer

¹ University of Gujrat, Gujrat, Pakistan, PK

Phytoextraction is an eco-friendly and cost-effective technique for the removal of toxins, especially heavy metals and metalloids from water and contaminated soils. Lower metal bioavailability often limits the phytoextraction. Organic chelators can help to improve this biological technique by increasing metal solubility and mobility. The present study was aimed to investigate the possibility of improving phytoextraction of chromium (Cr) by the application of citric acid (CA) through Lemna minor L (duckweed). For this purpose, healthy plants were collected from nearby marsh and placed in hydroponics under controlled conditions. Initial metal content both in marsh water and plant was measured along with physico-chemical properties of marsh water. Different concentrations of Cr and CA were applied in different combinations after defined intervals. Continuous aeration was supplied and pH maintained at 6.5 ± 0.1 . Results indicated that increasing Cr supply significantly decreased the plant growth, biomass, photosynthetic pigments, leaf area and activities of antioxidant enzymes (like Catalase (CAT), Ascorbate peroxidase (APX), Superoxide dismutase (SOD), Peroxidase (POD)) of Lemna minor while the addition of CA alleviated Cr induced toxicity and enhanced Cr uptake and its accumulation in Lemna minor. Thus, the data indicated that CA application enhanced Cr uptake and minimize Cr stress in plants and may be beneficial in accelerating the phytoextraction of Cr through Lemna minor L.

Environmental metabarcoding as a relevant tool to reveal structure and composition of microbial communities at phytomanagement sites

Michel Chalot¹; Julie Foulon¹; Cyril Zappellini¹; Alexis Durand¹; Benoit Valot¹; Damien Blaudez²

¹ Université de Bourgogne Franche-Comté; ² Université de Lorraine, FR

Poplars (Salicaceae) are now increasingly chosen for the reforestation of post-agricultural lands and the revegetation of areas that have been degraded by industrial or environmental pollution as well as renewable sources of biomass for bioenergy production. Despite a long history of use in phytomanagement strategies, the impacts of poplar trees on the structure and function of microbial communities that live in the soil remain largely unknown. As a first step towards tree-based phytoremediation, we have adopted a metabarcoding approach that employs the high-throughput Illumina MiSeq platform to investigate the potential variance caused by the site's history, soil structure and density plantation. We compared two contrasting contaminated areas in France. We hypothesized that the implementation of poplar stands would significantly and differentially shape the fungal and bacterial communities. The poplar phytomanagement regimes led to a significant increase in soil fertility and a decreased bioavailability of Zn and Cd, in concert with changes in the microbial communities. The most notable changes in the relative abundance of taxa and OTUs unsurprisingly indicated that root and soil constitute distinct ecological microbial habitats. The poplar cultivar was an important driver, explaining 12% and 6% of the variance in the fungal and bacterial datasets, respectively. The overall dominance of saprophytic fungi, e.g., *Penicillium canescens*, might be related to the decomposition activities needed at the experimental site. Conversely, Basidiomycota accounted for a much higher percentage of the fungal community in poplar root samples at one site. The root bacterial communities were dominated by Alphaproteobacteria and Actinobacteria, and the soil samples were dominated by Alphaproteobacteria and Acidobacteria. Overall, ectomycorrhizal root symbionts appeared to be highly constrained by soil characteristics at the phytomanagement sites. Our data support the view that mycorrhizal inoculation is needed in highly stressed and nutrient-poor environments. We believe that this study is relevant to the field of environmental microbiology because it reveals the contrasting consequences of poplar implementation on the microbial communities at phytomanaged trace metal-contaminated sites.

Agromining of Ni on industrial by-products

Marie Rue¹; Baptiste Laubie²; Gaylord Machinet³; Emile Benizri⁴; Marie-Odile Simonnot²; Jean-Louis Morel⁴

¹ Laboratoire Sols et Environnement _Laboratoire Réactions de Génie des Procédés; ² Laboratoire Réactions et Génie des Procédés; ³Microhumus; ⁴ Laboratoire Sols et Environnement, FR

Agromining is the chain of processes that uses plants to extract metals from matrices and their subsequent recovery from the biomass. Hyperaccumulator (HA) plants are able to accumulate one or several metals at high concentration. For nickel (Ni), the threshold concentration for hyperaccumulation is fixed at 1 000 mg kg⁻¹ of Ni in dry matter of shoots. HA plants can be used to extract metals from soils that are either contaminated or naturally rich in Ni. Then, Ni can be recovered from plant biomass by hydrometallurgical processes to obtain commercially valuable products.

Some industrial by-products contain high amounts of metals that could be recovered with agromining providing the first step of the chain, i.e. growing plants, is feasible. Such materials are generally very toxic due to their high content in metals and inadequate properties for plants (pH). Hence, agromining requires adaptation of by-products to decrease their toxicity and enhance metal uptake by plants. This work was designed to determine the most suitable substrate that would allow HA growth and metal accumulation on an industrial sludge derived from surface treatment process.

The metallic sludge contained 0.5% Ni, and high levels of Zn, P and Fe. In addition pH was very acidic. Preliminary experiments had shown that mixing sludge with by-products, like treated soil, allowed germination and plant development. But toxicity was too high and the presence of various metals in the sludge limited Ni uptake by HA.

Here we formulated three substrates in a similar way: i) sludge was mixed at 10% (dry weight) with a biologically treated soil, ii) sludge was amended with CaCO₃ (2,5% m) prior mixing with the treated soil, and iii) sludge was added without mixing at the surface of treated soil. The HA *Leptoplax emarginata* was chosen. Tests were conducted in both controlled conditions in pots and in mesocosm placed under the outside conditions at the GISFI experimental platform. In the latter leachates were collected and analysed.

Results showed that plants survived in all treatments. Survival was higher with sludge amended CaCO₃, that increased pH and decreased metal mobility. In all treatments HA accumulated Ni in their shoots. The highest performance was obtained with treatment iii) in which sludge was added to the substrate as a surface layer.

In conclusion, this work demonstrated that growing plants on industrial by-products exhibiting harsh properties is feasible with appropriate amendments. It showed also that the performances of agromining are dependant on the formulation of the substrate.

ThS 3d.2: Phytoremediation of complex pollutant mixtures

Phytoremediation of a highly chlorinated organic pollutant, by exploiting a fungal-bacterial consortium native to the contaminated field

Karen Van Geert¹; Griet Van Gestel²; Lieve Crauwels²; Thomas Van Humbeeck¹; Lennert Lammens¹

¹ Arcadis Belgium; ² OVAM - Flemish Waste Agency, BE

By using phytoremediation as a remedial technology, plants are used for the remediation of soil and groundwater contamination. Plants can contribute in different ways to the remediation of contamination, for example by keeping the contamination at the location by extraction of water by plants or degrading the contamination by stimulation bacteria living in symbiosis with the plants.

Until now, phytoremediation is only used to a limited extent in Flanders.

Phytoremediation is more than “greening” a classical remediation technology: it is a clear choice for a sustainable remediation alternative: by choosing another concept, the CO₂ footprint of the remediation can be drastically reduced.

In this study, the possibility to remediate an industrial site contaminated with the highly chlorinated organic pollutant, chlorendic acid, a fire retardant by exploiting bacteria and fungi native to the site is investigated. Plants may enhance bioremediation by promoting the growth and activity of contaminant-detoxifying micro-organisms in soil. Moreover, trees with a high transpiration rate, like poplar, draw in high amounts of contaminated groundwater and bring it into close contact with the degrading micro-organisms. The ultimate goal of this research is therefore to isolate chlorendic acid-degrading micro-organisms and to test their bioremediation efficiency in combination with poplar.

To find suitable micro-organisms, bacteria and fungi were isolated from soil, rhizosphere and roots of poplar and grasses growing on a chlorendic acid-contaminated site. Of the 75 isolated fungal strains, 4 significantly lowered the concentration of chlorendic acid after 2 weeks, one even to 29% of the original concentration. These degrading fungi were further investigated for laccase and peroxidase activity and production of hydroxyl radicals, to understand the mechanisms of degradation. After selective enrichment of a soil sample, 1 bacterial consortium was found to significantly decrease the concentration of chlorendic acid, but only to 94% of its original concentration. The role of the isolated fungi in the degradation of chlorendic acid therefore seems more important than that of the bacteria. However, the isolated bacteria can still be important because they can promote plant growth. Therefore, they were screened for different plant growth-promoting traits, after which a consortium was selected, consisting of chlorendic acid-degrading fungi and plant growth-promoting bacteria. The effect of inoculation of poplar with this consortium on the bioremediation efficiency is currently being evaluated in a greenhouse experiment.

Rare earth elements (REEs) accumulation and fractionation in *Phytolacca americana*, a REE hyperaccumulator

*Ming Yuan*¹; *Mei-Na Guo*¹; *Wen-Shen Liu*¹; *Chang Liu*¹; *Hermine Huot*¹; *Jean-Louis Morel*²; *Ye-Tao Tang*¹; *Rong-Liang Qiu*¹

¹ Sun Yat-sen University; ² INRA, Université de Lorraine, CN

The wide spread use of rare earth elements (REEs) has resulted in problems for soil and human health. *Phytolacca americana* L. is a herbaceous plant widely distributed in Dingnan county of Jiangxi province, China, the soil of which has high levels of REEs. An investigation of REE content of *P. americana* growing naturally in Dingnan county was conducted. The highest measured concentration of total REEs in the leaves of *P. americana* was 1012 mg kg⁻¹. Plant REEs concentrations decreased in the order of leaf > root > stem. In addition, *P. americana* exhibited a preferential accumulation of light REEs (LREEs) during the absorption process (from soil to root) and a preferential accumulation of heavy REEs (HREEs) during the translocation process (from stem to leaf). In order to figure out how *P. americana* accumulates REEs, a series of hydroponic experiments were conducted. When supplied with 0-250 μM REEs in the nutrient solution, the biomass of *P. americana* plants were enhanced by 161% from 1 - 10 μM REEs but were inhibited by 72% at > 100 μM REEs in solution. The total REE concentrations of *P. americana* were increased from 282 mg kg⁻¹ to 7754 mg kg⁻¹ by low levels of REEs supply (from 1 μM - 100 μM) but decreased to 5745 mg kg⁻¹ by high levels of REEs (250 μM). Fractionation patterns between plant organs showed that *P. americana* tended to select HREEs during the stem-to-leaf translocation process. The whole plants of *P. americana* also tended to accumulate HREEs, and the ratio of HREEs to the LREEs was ranged from 1.26 to 1.48. This indicates that certain organic ligands may be involved in the HREEs transfer processes in *P. americana* especially during the root-to-shoot translocation process. REEs concentration in the root of *P. americana* could be inhibited by the presence of Ca in solution (0.1 mM - 10 mM), and the ratio of LREEs to HREEs in root decreased from 0.74 to 0.68. This implies that REE uptake by *P. americana* may be via a Ca ion channel, and LREEs are more likely to enter into the root of *P. americana* through it. However, The REEs concentration in the root of *P. americana* was increased by the presence of excessive Fe (200 μM), but the related mechanisms is not clear yet. Further studies are necessary to better understand the absorption and tolerance mechanisms of REEs in *P. americana*, which may contributed to future application of this plant in phytoremediation of soil contaminated by REEs.

Rhizorremediation: the key role of brassica napus in the recovery of health of soils contaminated with metals and diesel

Rafael G. Lacalle¹; Unai Artetxe¹; María Teresa Gómez-Sagasti¹; Carlos Garbisu²; José María Becerril¹

¹ University of the Basque Country; ² NEIKER-Tecnalia, ES

Contamination affects a large amount of soils, making them unproductive and dangerous. Contaminated soils are frequently characterized by the simultaneous presence of several contaminants, which increase the complexity of the problem. Traditionally, physical-chemical techniques have been used for contaminant elimination. Besides being economically unattractive, these techniques do not consider soil health as an important ecological aspect. By contrast, other techniques use plants (phytoremediation) or bacteria (bioremediation) to extract, stabilize or degrade the contaminants. These technologies are environmental-friendly, as they promote the ecological functions and services of soil, specially its capacity to sustain life. Phytoremediation is commonly used to restore metal contaminated soils, whilst bioremediation is often applied to enhance the degradation of organic compounds. However, it is necessary to develop a technology that can fix both problems at once. Rhizoremediation proposes the combined use of phytoremediation and bioremediation. Hence, the main aim of this work was to evaluate the effectiveness of a rhizoremediation technology of a soil with mixed contamination (metals and diesel) using biodiesel production species for such as *Brassica napus* (rapeseed) and native microorganisms of the rhizosphere.

A greenhouse experiment was carried out using 2 types of soil, one amended with organic matter from urban organic residues and the other without the amendment. Both soils were artificially contaminated with metals (1500 ppm Zn, 500 ppm Cu, 50 ppm Cd) and diesel (6000 ppm), leaving also non-polluted soils as control. Half of each subgroup was planted with *B. napus*, and the other half was left unplanted. Rapeseed plants after 2 months of growing were harvested and soil and plant samples were analyzed. The physical-chemical (concentrations of contaminants) and biological indicators (plant and microbial properties) of soil and plant health were measured.

Our results showed a positive effect of plants on microbial communities (biomass, activity and functional biodiversity) in all treatments. Plants in contaminated soils grew as much as those growing on non-contaminated soils and were able to tolerate and extract metals from soils (specially, Cd and Zn). Total phytoextraction rate was generally higher in amended soils probably due to the higher plant biomass. Degradation of diesel was higher in planted pots. The organic amendment had also a positive effect on soil microbial properties and reduced Cd bioavailability, whereas Zn and Cu bioavailability was increased. In conclusion, *B. napus*, an oil crop used for biodiesel production, is a good candidate for rhizoremediation of soils with mixed (metals and diesel) contamination due to its capacity to improve soil health and decrease contaminants of soils.

Acknowledgements: This experiment was financially supported by the Ministry of Economy and Competitiveness (MINECO) of the government of Spain, by the project: NANORRIZORREM: Risorremediación asistida con nanopartículas para la recuperación de suelos con contaminación mixta. (AGL 2015-64481-C2-1-R)

Phytocontainment of groundwater contaminations as a cost-effective and sustainable alternative for pump & treat

Frank Volkering¹; Edward Gatliff²

¹ Tauw bv; ² Applied Natural Sciences, Inc., NL

In the Netherlands, almost all sites with urgent subsurface contaminations have been addressed. A large number of these sites has been remediated, whereas others are being managed. A recent Dutch inventory revealed that almost 2300 sites are being actively contained, most of which via pump & treat systems. Maintaining a pump & treat system for decades is costly, unsustainable, and requires long-lasting management efforts. Being the owner of many of these sites, the government is interested in alternative containment options. In addition, many industrial companies are struggling with the perpetual task of groundwater containment.

The use of trees can be an attractive alternative to the classical hydraulic containment via pump & treat. Using relatively simple engineering solutions like the TreeWell® system, it is possible to use the natural water uptake by trees to contain mobile groundwater contaminant plumes, in near surface as well as in deeper aquifers, including deep horizons within an aquifer. This type of phytoremediation is termed phytocontainment.

In the United States phytocontainment is being applied successfully at many contaminated sites, making it a proven technology. These applications have resulted in rules of thumb for the design and implementation of a phytocontainment.

This presentation at AquaConSoil 2017 will give an introduction to phytocontainment and a comparison between phytocontainment and classical containment via pump & treat. The presentation will include aspects such as required space, performance, costs, monitoring and maintenance, and sustainability assessment. The design, implementation, and results of a full-scale phytocontainment installation at an industrial site in the Netherlands where 240 poplar trees are used to contain a mobile groundwater contaminant plume will be presented. Further results of several successful phytocontainment applications in the US will be discussed.

Combining bioremediation methods with bioenergy production at field scale

Daniel Mirgorodsky, Märten, A., Riefenstahl, M., Pietschmann, S., Fürst, D.² Merten, D., Kothe, E., Büchel, G.

Friedrich Schiller University Jena, DE

Soil and water pollution by heavy metals and radionuclides (HM/R) is a major concern in many areas of the world, influencing the health of local populations, the use of the natural resources and the environmental equilibrium. In particular, soil, surface water and groundwater are likely to get an important input in different of these persistent pollutants, compromising the biosphere including humans on large areas. Bare soil or heaps are furthermore more likely to erode through the action of wind and precipitation, causing an eluviation of soil parallel to a spreading of contaminants in the air and water phase.

In this context, field scale investigations are applied to areas of moderate HM/R contaminated substrates at the test sites Gessenwiese and Kanigsberg, near Ronneburg, to investigate phytoremediation strategies (USER-project, PTKA, FKZ 02S9194). Here, the main focuses lie on designing sustainable landscapes by reducing the bioavailability of contaminants with carbonatic soil material (rendzina) and microbial amendments (VA-mycorrhiza *Rhizophagus irregularis*, actinobacteria *Streptomyces mirabilis* P16-B1), as well as the production of renewable energy with metal tolerant plants (*Festuca rubra*, *Secale multicaule*) within a short-rotation-coppice (SRC, landfarming). In this connection, production of woody biomass with fast growing plants (*Betula pendula*, *Sorbus aucuparia*, *Alnus*, *Pinus*, *Salix*) in SRC provides a positive effect on biodiversity and erosion protection.

Furthermore, quantification of biomass productivity and HM/R-transfer within the soil-plant-water system by using soil and microbial amendments are scopes of this project, and should lead to reduction in leaching of HM/R and soil erosion as well. Therefore, soil hydrological measurement stations and a lysimeter station are installed to get information about distribution, changes, transfer and output of HM/R in the water phase.

Additionally, biomass productivity, plant vitality (1) and erosion processes (2) should be monitored with a multispectral camera (1) and a high resolution camera System (2) (accuracy 5 mm) installed on a microdrone (project TerraSensE, FKZ 13007-715).

ThS 3e.1: Nanoremediation: from lab investigation to field application

Investigations of three-dimensional transport and sedimentation properties for nano iron particles in column experiments

Anke Wiener; Jürgen Braun

University of Stuttgart, DE

The utilization of zero valent iron nano (nZVI) particles (70 – 120nm) for remediation of contaminated soil and groundwater is a promising new technology. Due to the usage of nZVI in reactive barriers, their ability to degrade a variety of contaminants is already well known. Advantages of nZVI are the high reactivity and the possibility of targeted injection in form of aqueous suspensions. However, for a sustainable and economical treatment, it is essential to determine crucial transport and sedimentation properties of different nZVI slurries in porous media.

Various factors have to be considered for the characterization of the transport properties. Aquifer quality (q(GW), K, porosity) influences injection conditions and thus transport radii. The size of a contaminated area and the mass of contaminant controls mass of nZVI required, properties of nano particles (size, density, agglomeration behavior) impinge on the composition of the injection suspension (concentration, viscosity, additives). In order to select optimal injection conditions and to correctly track changes of these factors during experiments, the accuracy of analytical methods and of monitoring technologies utilized is an important element as well.

At the research facility for subsurface remediation – VEGAS (University of Stuttgart) experiments are conducted to link research of nano particles on laboratory scale with end-user applications. The goal is the homogeneous implementation of a defined mass of nZVI particles in a given reaction zone. By conducting column tests, different nZVI suspensions can be optimized regarding their transport in radial flow systems. Therefore, a one-dimensional column system – Cascading Column System – was designed. Results of the column system can be used for planning large scale injections and to predict particle distribution for empirically determined transport length.

The characterization of constitutive relations between particle – particle in the suspension (agglomeration) and particle – porous media (sedimentation, blocking) is a challenge. Additional single column tests were performed to describe the transport processes (advection, dispersion, sorption) which change for different experimental conditions. Results of these tests will be used to provide input parameters for a numerical model.

For all experiments a newly developed set-up including a specific measurement technology was used, which allows for the monitoring of all influencing factors. Particularly, space and time dependent propagation velocity of nZVI particles as well as the the distribution of the mass of sedimented nZVI can be measured qualitatively and quantitatively with a specially designed magnetic susceptibility sensor.

The presentation is a review of current research results for transport and sedimentation properties of different nano particles with a specific focus on the set-up and monitoring methodologies.

This investigations were conducted in the framework of the research project NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) funded by the European Commission FP7

Rapid arsenate removal from contaminated water by two-dimensional nanosheet iron oxides

Zhou Yin; Hans Hansen¹

¹ University of Copenhagen, DK

Two-dimensional metal oxide nanosheet materials have attracted attention as high-affinity and capacity sorbents due to their large surface areas and high densities of surface functional groups. A new type of 2D iron hydroxides termed Single Sheet Iron oxides (SSI) can be prepared by oxidation of layered FeII-FeIII hydroxides. The SSIs are expected to consist of single sheets of trioctahedral FeIII (hydr)oxides with a similar composition as trioctahedral Fe(OH)₃ layers in layered FeII-FeIII hydroxides (green rust, GR). In this investigation, SSIs were synthesized by anion exchanging the chloride form of GR with dodecanoate, followed by solid state oxidation with dioxygen and delamination in alkaline solution. AFM and TEM images showed that SSIs are 1 nm high and has lateral dimensions of 100 to 200 nm. The material also contained particles with stacks of SSIs. The measured BET (N₂) specific surface areas ranged between 210 and 240 m²/g. The kinetics of arsenate adsorption onto SSI was rapid, reaching equilibrium within 30 minutes. All isotherm data were fitted to the Redlich-Peterson isotherm model with the exponent n in the range between 0.8 and 0.9, thus indicating a non-ideal monolayer sorption to SSI that approached the ideal Langmuir condition.

Measurements of zeta potential revealed that the point of zero charge of SSI was 8.6~9, which favored the As(V) adsorption on SSI surface even at neutral pH. The maximum arsenate adsorption capacity of SSI was estimated to 0.76 mmol/g at pH 4 (57 mg/g, 1.41 mmol As per g Fe). With increasing pH in the range of 4-9.4, arsenate sorption decreased to 0.33 mmol/g. Under similar conditions ferrihydrite show sorption capacities of 0.75 mmol As/g (pH 7) in 1h, and ferrioxyhite show sorption capacities of 0.46 mmol/g (pH 7) after 7h.

Arsenate sorption to SSI is comparable to previous studies of phosphate sorption to SSI with sorption capacities of 2.54 mmol/g (pH 5). In this case, X-ray photoelectron spectroscopic analyses indicated the formation of inner-sphere Fe-O-P surface complexes. Both arsenate and phosphate have strong binding with SSI with similar binding mechanism. Thus, with high adsorption capacity, binding ability, and fast kinetics of arsenate removal, SSI is a promising sorbent for removing arsenate in drinking water.

Study of iron and hematite nanoparticles production by top to down approach and its reactivity for groundwater remediation

Vicenç Martí¹; José Antonio Benito¹; David Ribas¹; Maria R. Martínez¹; Miroslav Černík²; Irene Jubany³

¹ Technical University of Catalonia, ES; ² Technical University in Liberec, CZ; ³ CTM Technological Centre, Foundation

Two examples of production of nanoparticles at lab scale by using top to down approach with milling and associated tests of reactivity of the produced particles are presented.

In the first example, a new milling based in two step method for nZVI (nano Zero Valent Iron) production was developed. First step was focused on wet milling in MEG (Mono Ethylene Glycol) and in second step the addition of micronized alumina. The method produced the abrasion of the grinding media and breakage of flakes formed in the first step. Milling parameters such as: alumina concentration, grinding media load, chemical composition and diameter were optimized to finally obtain 100% of the volume of ZVI below 1 μm .

Characterization of the produced nZVI was compared with other commercial products obtained by top to down and bottom up approaches. Granulometry, morphology, chemical composition, BET surface area and suspension stability was assessed in all the samples.

The developed particles (e.g. mean particle diameter of 0,16 μm (by SEM), specific surface area of 29,6 $\text{m}^2\text{-g}^{-1}$) showed excellent properties compared to commercial products, highlighting reactivity and suspension stability. Reactivity towards Cr(VI), PCE (tetrachloroethene) and TCE (Trichloroethene) showed to be several times higher than the commercial nZVIs also when reactivity was normalized to specific SEM surface area and Fe (0).

The second example is top to down fabrication of nanoparticles from micronized hematite mineral. In this case the study optimizes the wet milling of micronized hematite in water a dispersant and evaluates the adsorption of As (V) from a real contaminated groundwater from Langreo (SP) onto the initial and milled mineral.

Milling time from 6 to 20 h and concentration of sodium polyacrilate (PA) from 0 to 10 g-l^{-1} was tested. Best results were obtained for more than 10 h and PA concentration above 5 g-l^{-1} . Under these conditions, average size was decreased from 2067 nm to 140-150 nm and BET surface area increased from 12,2 to 77-100 $\text{m}^2\text{-g}^{-1}$.

Previous batch adsorption equilibrium and kinetic tests were performed with synthetic solutions from 0 to 20 mmol-l^{-1} (1,5 mg-l^{-1}) of As(V) standards and initial hematite micronized mineral. Results were satisfactory adjusted to Freundlich isotherms with equilibrium time around 20 h.

Batch experiments with two different real groundwater from the studied site and milled hematite were performed by mixing 0,3 grams of mineral and 20 ml of groundwater samples for 20 h. The milled samples showed to exhaust almost all As(V) in solution with a range of 92-164 microgram As-g⁻¹ mineral that were about two-three times the values of the initial mineral (50 microgram As-g⁻¹ mineral).

The present research work has been funded by the projects NANOREM "Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment" (7FP, grant agreement 309517) and NANOATTENUATION (CGL2014-57215-C4-4-R) from Spanish Ministry of Science and Innovation. Authors acknowledge to Tecnalia Foundation for supplying the contaminated groundwater sample from Langreo linked to the EU project Re-Ground.

MNM3D: a modelling tool for simulation of nanoparticle injection and transport in 3D geometries

Carlo Bianco; Tiziana Tosco; Rajandrea Sethi

Politecnico di Torino, IT

The design of a field-scale injection of engineered nanoparticle (NP) suspensions for the remediation of a polluted site requires the development of quantitative predictive models for the system design and implementation.

In general, micro- and nanoparticle transport in porous media is controlled by particle-particle and particle-porous media interactions, which are in turn affected by flow velocity and pore water chemistry. During the injection, a strong perturbation of the flow field is induced around the well, and the particle transport is mainly controlled by the consequent sharp variation of pore-water velocity, and by the hydro-chemical properties of the injected fluid. Conversely, when the injection is stopped, the particles are transported solely due to the natural flow, and the influence of groundwater geochemistry (ionic strength, IS, in particular) on the particle behaviour becomes predominant. Pore-water velocity and IS are therefore important parameters influencing particle transport in groundwater, and have to be taken into account by the numerical codes used to support nanoremediation design.

Several analytical and numerical tools have been developed in recent years to model the transport of colloidal particles in simplified geometry and boundary conditions. For instance, the numerical tool MNMs was developed by the authors of this work to simulate colloidal transport in 1D Cartesian and radial coordinates. Only few simulation tools are instead available for 3D colloid transport, and none of them implements direct correlations accounting for variations of groundwater IS and flow velocity.

In this work a new modelling tool, MNM3D (Micro and Nanoparticles transport Model in 3D geometries), is proposed for the simulation of injection and transport of nanoparticle suspensions in generic complex scenarios. MNM3D implements a new formulation to account for the simultaneous dependency of the attachment and detachment kinetic coefficients on groundwater IS and velocity. The software was developed in the framework of the FP7 European research project NanoRem and can be used to predict the NP mobility at different stages of a nanoremediation application, both in the planning and design stages (i.e. support the design of the injection plan), and later to predict the long-term particle mobility after injection (i.e. support the monitoring, final fate of the injected particles). In this work MNM3D is used to model a 2D pilot scale injection of CARBO-IRON® in a small scale flume carried out at the VEGAS facilities in the framework of the NanoRem project. Moreover, the long term fate of an hypothetical release of nanoparticles into the environment from a landfill is simulated.

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Field-Scale Performance of Non-stabilized and Surface-Stabilized nZVI Particles for CHCs– contaminated Groundwater Treatment

Petra Skácelová¹; Jana Oborná¹; Ondřej Lhotský²; Ivo Medřík¹; Josef Kašlík¹; Jan Filip¹; Vojtěch Stejskal³

¹ Palacký University in Olomouc; ² DEKONTA, a.s., CZ, ³ Technical University of Liberec, Czech Republic

Innovative technologies for groundwater and soil remediation based on nanoscale-zero valent iron (nZVI) particles engaged an interest of many researcher and field engineers during two last decades. They are regarded as effective tools for chlorinated hydrocarbons (CHCs) and metals removal. [1] For the successful application of nanoparticles in groundwater remediation it is crucial to fully understand the reactivity and migration ability of the material used. Therefore, batch experiments or pilot applications under field-relevant conditions should be performed. To the best of our knowledge, there are only few full scale field applications of nZVI followed by long-term monitoring in Europe. [2]

The aim of this study was to compare remediation efficiency and environmental changes (including nanoparticles migration and fate) caused by application of nZVI at two contaminated sites, both polluted mainly by CHCs. The first locality, situated in north-western part of Czech Republic in the area of chemical plant, is characterized by high concentration of perchlorethylene (PCE) reaching up to 40 mg/L. The site was remediated using 200 kg of surface stabilized NANOFER 25 S (suspension concentration 2.2 g/L) that was applied in November 2014. The second monitored site, located in area of pharmaceutical company in eastern part of Czech Republic, polluted mainly by trichloroethene (TCE) in concentration up to 200 mg/L and was treated by 150 kg non-stabilized NANOFER 25 (suspension concentration 20 g/L) in September 2016.

At both sites, the groundwater and soil were periodically sampled during at least six months after the remediation event. In-situ and ex-situ measurements of physical-chemical parameters, contamination levels, nZVI migration and fate and changes in biota were performed employing field-ready laboratory equipment as well as advanced analytical techniques (head-space gas chromatography-mass spectrometry, atomic absorption spectrometry, inductively coupled plasma-mass spectrometry, X-ray-powder diffraction and ⁵⁷Fe Mössbauer spectroscopy).

By such robust combination of experimental approach, we proved the good nZVI migration over distance of at least two meters, significant decrease in contamination level, and we identified reaction products formed by nZVI oxidation.

This work was supported by grant from the EU FP7 (project NANOREM, No. 803103031) and Technology Agency of the Czech Republic "Competence Centers" (project No. TE01020218).

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ThS 3e.2: Advances and future perspectives of nanoremediation

Cost-effective optimizations of nZVI based Nanoremediation technology

Miroslav Černík¹; Petr Kvapil²; Paul Bardos³

¹ Technical University of Liberec; CZ; ² Photon Water Technology s.r.o.; ³ r3 Environmental Technology Ltd.

The proposed session will present the major advances made in the application of nanoremediation in recent years within more than 100 deployments of this technology in various research and commercial projects worldwide. The uptake of its two main process alternatives, ISBR and ISCR, has been much greater for the following reasons: 1. Relatively simple and effective deployment of soluble materials into the aquifer body, 2. Public and regulatory acceptance of the release of reactive materials into the environment (compared to engineered nanoparticles in certain countries), 3. Sufficient number of well-described demonstration sites and related documentation describing the deployment and materials, 4. Lower material costs.

Various informational gaps that have limited the uptake have been addressed by the NanoRem project performed within FP7, but the price competitiveness remains a barrier.

This free session explores new approaches to bringing nanoremediation processes to more affordable levels. These are based on integrated nanoremediation concepts. For example, combined processes of nanoremediation with synergic physical, chemical and biological processes like DC enhanced nanoremediation (INR-DC process) or biologically enhanced nanoremediation.

Integrated processes based on a combination of nanoremediation and biological or/and chemical processes are an emerging approach to dealing with this cost barrier, and achieving the additional benefits of nanoremediation at a market-ready price.

DC enhanced nanoremediation (INR-DC) directly addresses the cost barrier and also has a broader range of treatable issues, in particular in dealing with contaminant source management, where large volumes of contaminant may otherwise rapidly exhaust any deployed NPs. The application of nanoparticles with the support of a DC electric field at a low intensity leads to a significant increase in the total efficiency of this remedial method. This new method was first confirmed in the laboratory (2009), and subsequently during long-term monitoring at the Horice site (Czech Republic (2010)). The method was also successfully implemented within a different environment at the Spolchemie site (Czech Republic). The method was used at this site to establish a geochemical barrier in order to limit the outflow of contaminant from the site.

This special session will include the following paper and a discussion session:

- Two presentations describing these integrated approaches: INR-DC and NR + bio.
- A presentation describing how these technologies are being brought to the market, focusing on INR-DC.
- A presentation describing the application guidance
- To conclude, an open discussion on appropriate uses and CLM market feasibility

NanoRem: Nanoremediation for Soil and Groundwater Clean-up - Possibilities and Future Trend

Hans-Peter Koschitzky; Alexandra Gens; Joachim Roos

University of Stuttgart, DE

NanoRem is a research project with 29 partners from 13 countries, funded through the European Union's 7th Programme for research, technological development and demonstration under grant agreement no 309517. NanoRem focused on facilitating practical, safe, economic and exploitable nanotechnology for in situ remediation of soil and groundwater. This was undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of nanoparticles (NPs), market demand, overall sustainability, and stakeholder perceptions. The project was designed to unlock the potential of nanoremediation processes from laboratory scale to end user applications and to support both the appropriate use of nanotechnology in restoring land and water resources and the development of the knowledge based economy at a world leading level for the benefit of a wide range of users in the EU environmental sector.

NanoRem aim was to demonstrate that the application of NPs is a practical and reliable method for soil and groundwater remediation. NanoRem provided a direct link between SME (small and medium sized enterprises) on the production side and SME on the application side of groundwater remediation using NPs. NanoRem's six goals were to

- (1) Identify the most appropriate nanoremediation technological approaches to achieve a step change in remediation practice
- (2) Develop lower cost production techniques and production at commercial scales of nanoparticles (NP)
- (3) Determine the mobility and migration potential of NP in the subsurface, and relate these both to their potential usefulness and also their potential to cause harm
- (4) Develop a comprehensive set of tools for design, application and monitoring practical nanoremediation performance and determine the fate of NP in the subsurface
- (5) Engage in dialogue with key stakeholder and interest groups to ensure that research, development and demonstration meets their needs, is most sustainable and appropriate whilst balancing benefits against risks
- (6) Carry out a series of full scale applications in several European countries to provide cost estimations and performance, fate and transport findings

All results and detailed information are available at www.nanorem.eu. The NanoRem Toolbox focuses on the needs of decision makers, consultants and site owners. It provides the respective output in three levels:

- (I) Twelve 2 to 4-page bulletins include the most relevant information in a condensed and concise way
- (II) Detailed information on available nanoparticles and tools
- (III) Other dissemination products and selected project reports

The bulletins are available as download and in printed form:

- Nanotechnology for Contaminated Land Remediation - Possibilities and Future Trends Resulting from the NanoRem Project
- Appropriate Use of Nanoremediation
- Generalised Guideline for Application of Nanoremediation
- A Guide to Nanoparticles for the Remediation of Contaminated Sites
- Development and Application of Methods for Monitoring Nanoparticles in Remediation
- Forecasting Nanoparticle Transport for Soil Remediation
- Six NanoRem Pilot Site-Bulletins

NanoRem's main results and some future trends will be presented.

Nanoremediation - a consultant's perspective

Petr Kvapil¹; Jaroslav Nosek²; Miroslav Černík²; Paul Bardos³; Corinne Merly⁴

¹ Photon Water Technology s.r.o., CZ; ² Technical University of Liberec; CZ; ³ R3 Environmental Technology Ltd; ⁴ BRGM Rhône Alpes, FR

While great advances have been made in the application of nanoremediation, with more than 100 field applications worldwide, (perceived) cost remains an important market barrier. The main competing in situ remediation alternatives to nanoremediation for these contaminants are in situ biological reduction (ISBR) and conventional forms of in situ chemical reduction (ISCR) using reducing agents such as micro zero valent iron (-ZVI) or sodium dithionite.

Nanoremediation has not achieved the same levels of market uptake as these methods. This is as probably related to five broad barriers, two of which are inter-related, i.e. (1) a prevailing public unease about the environmental release of NPs and (2) regulatory concerns that engineered particles released as an environmental technology may have unforeseen impacts on water and the environment. (3) In addition, effective deployment of the technology proved to be more complex and was perceived to be associated with (4) higher input costs. (5) The fifth barrier is a lack of well-regarded demonstration site reports.

Conventionally, ISCR and ISBR (In-Situ Chemical and Biological Reduction) are primarily pathway (plume) management interventions with a limited scope for addressing source contaminants. They have a limited effectiveness against several important contaminants such as fuel oxygenates, fluoridated organics and various other recalcitrants, they may cause modifications to aquifer properties that render them unacceptable under certain circumstances, and ISBR may also be subject to process stall. Nanoremediation has greater applicability for source term treatments and greater potential for less (bio)degradable contaminants. It may also be more suitable for aquifers sensitive to inputs leading to sulphates or taints of biological origin, by virtue of the low degree of spreading of the particles and their relatively short half-life.

Moreover, nanoremediation can offer a number of additional niche benefits, including greater speed, greater versatility (for example in terms of source term treatment or where conditions are inhibitory to biological processes), and potentially lower overall aquifer impacts.

Integrated processes based on combination of nanoremediation with biological or/and chemical processes are an emerging approach to dealing with this cost barrier, and achieving the additional benefits of nanoremediation at a market-ready price. This paper reviews the market readiness of nanoremediation from a consultants point of view; taking into account changes in understanding following the recent NanoRem project (www.nanorem.eu) and reviewing opportunities for the development of price competitive nanoremediation in practice.

Long-term performance of milled zerovalent iron particles for in situ groundwater remediation

Milica Velimirovic¹; Vesna Micic Batka¹; Melanie Auffan²; Luca Carniato³; Doris Schmid¹; Daniel Borschneck²; Stephan Wagner¹; Frank von der Kammer¹; Thilo Hofmann¹

¹ University of Vienna, AT; ² CNRS; ³ Delft University of Technology

The nanoscale zerovalent iron (nZVI) particles are widely used with high success in removal/degradation of a variety of environmental contaminants under laboratory conditions. However, high production costs, mobility of nZVI particles limited to a maximum of a few meters due to the rapid aggregation of primary particles, and limited effectiveness of the iron surface to serve as an electron donor for longer period due to fast depletion of nZVI particles after side reaction with groundwater constituents were main technical obstacles for rising the full potential of this technology.

For that reason, submicro-scale milled zerovalent iron particles were recently developed (milled ZVI, UVR-FIA, Germany) by grinding macroscopic raw materials of elementary iron as a cheaper alternative to products produced by solid-state reduction. Although the factors and processes affecting milled ZVI particles transport mechanism in porous media were studied in detail, there has to date been no detailed study on milled ZVI particles long-term active performance/corrosion mechanism after in situ application. Therefore, lab-scale batch degradation experiments were performed to provide valuable data on the reactivity, life-time and aging mechanism of milled ZVI particles during degradation of trichloroethene (TCE), which are necessary in order to access their potential for groundwater remediation.

The life-time of milled ZVI particles was investigated by measuring the H₂ production as a consequence of ZVI anaerobic corrosion in the presence of aquifer material originating from two contaminated sites and artificially contaminated anaerobic water. The apparent corrosion rate and consequently the life-time of milled ZVI particles are in the same order of magnitude for both geochemical conditions (177-186 mmol kg⁻¹ d⁻¹), indicating a similar fate of milled ZVI particles at both industrial sites. In addition, it was observed that the presence of sulfate can enhance the reactivity of Fe⁰ to some extent by possibly removing passivating iron oxides and hydroxides from the Fe⁰ surface and consequently increasing the number of reactive sites. In order to fully understand corrosion mechanism, the morphological, structural, and compositional changes of milled ZVI particles were evaluated by using SEM, X-ray diffraction (XRD) and Iron K-edge X-ray absorption spectroscopy (XAS). SEM data show that the magnetite/maghemite are the predominant minerals after 49 days of milled ZVI exposure to two different geochemical conditions. XRD/XAS data show that at the end of experiment 34 ± 8 % of milled ZVI iron was corroded and/or precipitated. This is in accordance with the numerical modeling and consequently simulated magnetite precipitation (49-54 %). Finally, this study shows that under investigated conditions a similar fate of milled ZVI particles at both field sites can be expected.

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 309517.

ThS 3g.1: Combining chemical oxidation with other technologies

Low permeability and high heterogeneity: really a no-go for in situ remediation at a reasonable cost?

Laura Simone; Thomas Held

Arcadis Germany GmbH, DE

Most in situ remediation methods rely on the potential for contact or connection with the contaminant in the polluted media. Consequently, the permeability is extremely low and/or the geology is highly heterogeneous, most in situ technologies are not technically efficacious, and the few feasible ones can be excessively expensive. Thus, contamination in low permeability or highly heterogeneous soils was considered in the past as a significant challenge to remediate using in situ techniques. However, new techniques are proving successful.

An example site in western Germany where low permeability conditions are present, with contamination being remediated using in situ techniques applied in association with modification to geologic conditions, will be described. The site was contaminated by chlorinated volatile organic compounds (mainly trichloroethene, TCE). The contamination, represented by dissolved phase contaminants and suspected residual dense non-aqueous phase liquid (DNAPL), had drained into backfill material, had contaminated the perched water present, and permeated into the underlying clay layers. In some areas the TCE had penetrated through the clay and contaminated the aquifer in the unit below, consisting of bedrock (weathered to low permeability soil).

Initially, a remediation system (dual phase extraction, pump and treat and high vacuum soil vapour extraction) was designed and operated from 2001. The perched water extraction was ceased in 2012, since the remediation target levels were reached. However, the remediation in the lower layers had been less successful, which was believed to be as a result of residual contamination in the clay layers continuing to act as a source for the dissolved phase impact to the bedrock aquifer.

In order to increase the effectiveness of the ongoing remediation, a review of new and emerging remediation technologies was undertaken to identify the options available for addressing residual contamination in the clay layers. Thermal remediation was initially identified as a plausible option to close the remediation at the site within less than 3 years with high certainty of success. However, due to the high estimated costs, a range of technically viable alternatives were also considered, and comparing probable costs and closure probability, allowed development of a ranking of approaches. Fracturing of the clay layers, with injection of in situ chemical oxidation (ISCO) reagents (permanganate) represented the best compromise of all evaluated technologies. The project subsequently developed based on a phased approach. The first steps consisted of a pre-design investigation including a high resolution 3D-source delineation, geotechnical and geochemical soil and groundwater investigation, as well as hydraulic testing. Based on these results, the remediation strategy will be further refined and investigated in more detail in a bench and/or pilot scale.

The experience at this site showed that the state of the art remedial technologies offer different alternatives, even at not extremely high costs to tackle contaminations under conditions which used to be considered prohibitive.

Sustainable tools for the remediation of soils and wastewater polluted by emerging pollutants

Emilio Rosales Villanueva; Marta Pazos Currás; M. Angeles Sanroman Braga

University of Vigo, ES

Nowadays, a great variety and substantial amount of emerging pollutants due to the human activity have been detected in the environment. For example, more than 700 compounds have been identified in the European aquatic environment such as pharmaceutical products, surfactants, personal care products, pesticides, ionic liquids, etc. They are chemicals with high potential to get into the environment and cause adverse ecological and human health effects and they cannot be removed by conventional technologies.

The main objective of this study is to evaluate the feasibility of several electrochemical advanced oxidation processes (EAOPs) as sustainable tools for the remediation of soils and wastewater polluted by organic pollutants such as pesticides, pharmaceutical products, personal care products or ionic liquids. EAOPs are based on the electrochemical generation of oxidants used for the degradation of the pollutants and showing high efficiency and versatility. These techniques can be considered as environmentally friendly due the reagents used [1-2]. Among them, in this study we focus our attention in the application of electro-Fenton (EF) to different environments. In relation to treatment of wastewater a comparative study of conventional processes with the EF was carried out. The results confirm that heterogeneous EF process is a promising technology to degrade different kind of organic pollutants in aqueous media and open the possibility to operate in continuous mode.

In regard to the soil remediation, the EAOPs purpose is the in situ soil restoration by the conjunction of electrokinetic treatment with Fenton's reagents. In this case, the presence of iron into the soils permits that the Fenton's reactions take place in situ by its reaction with the H₂O₂ transported across them by the action of the electric field applied. Thus, the powerful oxidant radicals (-OH) generated into the soil are able to degrade a huge number of hazardous compounds. Moreover, this fact favours the transport of the metallic species present in the soil to the electrode chambers, increasing the remediation of pollutants in the soil. The results of this study demonstrated the effectiveness of the developed techniques for remediation of the investigated polluted soils nonetheless further studies are required in order to scale up this process.

Acknowledgments

This research has been funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and ERDF Funds (Projects CTM2014-52471-R). The authors are grateful to MINECO for the financial support of Emilio Rosales under Juan de la Cierva program.

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Remediation of a hydrocarbon chronically contaminated soil by combination of persulfate oxidation and bioremediation

Rocio Medina¹; Janina A. Rosso²; Pedro M. David Gara³; Maria T Del Panno¹

¹ CINDEFI (UNLP-CONICET); ² INIFTA (CONICET-UNLP); ³ CIOp (UNLP), AR

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds in the environment generated by natural and anthropogenic activities. Because their hydrophobicity and low water solubility they are highly persistent in soil. Although the use of chemical oxidants can overcome the limitations of bioremediation, it is known that it damages the community and soil structures. We studied the effect of combined technologies, chemical oxidation followed by bioremediation, on chronically hydrocarbon contaminated soil.

A chronically contaminated soil (S0) with 214 ppm of PAHs was treated with ammonium persulfate (PS) (3.3 g PS/ kg dry soil), OxS. Microcosms of oxidized soil were incubated (25°C, 25% moisture content), for 1 year as bioremediation process, BOxS. Soil microcosms without oxidation were used as bioremediation control, BS.

The PAH concentration, PAH bioavailability (%), dissolved total carbon (% DTC), absorption and fluorescence of organic matter (OM), total nitrogen (N), sulphate (SO₄²⁻), phosphorous (P) and bacterial diversity were analysed. Hill's numbers were used as diversity measures. The results were analysed using methods from the multivariate statistic.

The PS application produced 30% of PAHs elimination and an increase of DTC and PAH bioavailability. The aqueous extract fluorescence attributed to the organic matter was higher than S0, but the relative emission from PAHs was lower. The corresponding spectroscopic analysis (E4/E6) did not show changes.

Before the oxidation, S0 showed a very high diversity being an equal community. A dramatic decline in the richness was observed after PS oxidation. The OxS community showed an uneven assemblage with a few dominant species. The Actinomycetales (57%) and Bacillales (20%) were the predominant orders. By analysis of 16SrDNA hypervariable region, we found successional changes in the community along the treatment. The low richness and uneven assemblage remained until the fifth month but with Pseudomonadales as predominant order (71%). Slowly, the bioremediation allowed that the diversity was recovery (BOxS); despite of the richness was still low in compare with S0.

At the end of the treatment, 47.5% of total PHA elimination was observed, leaving a lower DTC value in BOxS. The fluorescence intensity from OM was similar to S0 but principally as consequence of humic-like substances contribution, suggesting that the bacterial successional changes were principally to expenses of the available compound from the oxidized OM. The increment on P also suggested the effective bacterial involvement in the soil P cycle. The significantly higher SO₄²⁻ concentration seemed to no exert much effect on the soil bacterial diversity.

The bioremediation in BS after one year also showed a low richness. Although a reduced fluorescence was detected in this microcosms, the relative PAH and OM fluorescence contribution did not change.

The coupled technology studied was suitable for elimination of PAHs with the recovery of microbial diversity associated to the metabolism of oxidized OM. The multifaceted approach were useful for understanding the global process in a chronical-contaminated soil.

Multi contaminant remediation by combining in-situ chemical oxidation and airsparging - a successful case study at a challenging and operating site

Liat Coifman¹; Yinon Lapid¹; Michael Mueller²

¹ Ludan Environmental Technologies; ² PeroxyChem Environmental Solutions, IL

In recent years Israel is facing a vast development of infrastructure intended to support the national population and economic growth. Such trends are more intense in the Tel Aviv and Central districts, than in others across the country.

Increased land values have motivated entrepreneurs and local municipalities to develop those areas currently occupied by traditional Industry, or Brownfields, which are less environmentally regulated, and therefore more likely to contain soil or ground water contamination.

As a result, the need for cost – effective methods to remediate such areas is required. Concurrently, there is a necessity to avoid lengthy remediation processes and to create proactive solutions designed to enable remediation process occurring in parallel with development works. In many instances, the new use of the land – such as office towers, or gas stations on main routes - are already operational.

When time is of essence, the use of in-situ chemical oxidation (ISCO) has emerged as a preferred method to address these challenges. The primary advantages of chemical oxidation are quick results, and the lack of routine - ongoing maintenance and monitoring of a remediation system. Working conditions on these sites also require high professional and operational efficiencies, to maximize the results obtained in short intervals of time onsite.

Ludan Environmental Technologies (LET) was the first Israeli company to successfully complete rehabilitation of the capillary and saturated zone at an operational gas station.

Groundwater monitoring at the site presented high MTBE and BTEX concentrations, ranging two to three orders of magnitude over the local threshold values, dispersed across an area of more than 100 square meters.

In order to achieve maximum effect – the design team used a combination of technologies and practices, engineered to encourage breakdown of target pollutants in the saturated zone.

Oxidation was performed using activated sodium persulfate (SP); chemical reactions of the contaminant and the SP result in mineralization into harmless by-products. In order to optimize the scattering cross-section of the oxidizer an Air Sparging (AS) system was also incorporated.

Another advantage of the AS system was to ensure the introduction of sufficient oxygen into the groundwater, and thereby encouraging natural attenuation in addition to the chemical dissolution.

Results showed a significant decrease in concentrations of all pollutants; MTBE and BTEX concentrations measured following site rehabilitation were under the regulatory threshold levels in most monitoring wells. The remediation operations and periodic monitoring resulted in receiving a No Further Action (NFA) notification from the Israeli Water Authority.

The authors will present the methodology adopted to select, design, and implement this remediation process. It will include a description of the relevant work phases, challenges, lessons learned and the final results. Other comparative ISCO case studies will be referenced as well.

Combined ISCO Treatment In Petrochemical Explosive Zone (Class-I): Application Control And Safety Management

Karel Waska; Petr Beneš; Jiří Kamas; Zdeněk Vilhelm; Ondřej Šnajdar; Miroslav Minařík

EPS biotechnology, CZ

Contrary to previous decades, the complexity of remediation projects in Eastern Europe has been rapidly increasing as the sites gradually became more difficult-to-treat, be it for complexity of hydrogeological background, or due to land use limitations. This study describes the deployment of combined in situ chemical oxidation (ISCO) using the Modified Fenton's Reagent (MFR) and the activated Kloxur® SP (sodium persulfate; APDS) solution for remediation of a heavily BTEX-polluted aquifer present within the grounds of an active petrochemical plant in the immediate vicinity of explosive zone (EX-1, OSHA standard 1910.399).

Because the Fenton's reaction is known for extensive heat and gas (O₂ and volatile organic compounds – VOC as pollutant daughter products) generation, the reagent had to be modified by addition of citric acid. The MFR oxidation was based on the formation of hydroxyl radicals (Eh = +2.8 V) during the decomposition of hydrogen peroxide reacting with citric acid-stabilized ferrous ions. While the gas and heat threats to the EX-1 zone conditions were to some extent mitigated by this modification, another issue arose regarding the low reagent pH. The APDS oxidation was based on the formation of sulfate radicals (Eh = +2.6 V), persulfate anions (Eh = +2.1 V), and partially also the hydroxyl radicals, with the activation either by alkaline conditions (groundwater of pH>10 present at part of the site), ferrous ions, or hydroxyl radicals from the MFR. Despite the potentially hazardous deployment of MFR, the reagent was applied after detailed lab-bench trials with the benefits of low cost, moderate temperature increases for potential pollutant heat-desorption, and for the potential enhancement of aerobic biodegradation conditions after the reaction depletion. The APDS was applied in areas where greater reaction range (under large constructions) or smaller VOC generation were sought.

Together with functionality-verification and application optimization, the project studied tools for real time reaction control and work safety management. The monitored risk-factors included the exothermic character of MFR reaction, the corrosiveness of injected MFR, the groundwater level (concerning the depth of local utility network), and the generation of VOC. During the repeated applications, the MFR exhibited prolonged durability (weeks), greater reaction zone range (tens of meters), and gradually decreasing VOC generation, which was in contrast with the short term lab-tests. The APDS was preferably used as an initial reagent in wells where high VOC generation prevented fast MFR application due to gas bubble pore-clogging. Once the pollutant within the proximity of such well was degraded using APDS, the MFR could be used as usual. The effect of combined ISCO application on ambient microbial communities and the potential for biodegradation clean-up finishing were also evaluated using standard and molecular microbiology tools. Aside from successful decontamination of the target zone (87% - 99% of BTEX reduction in monitored wells, ongoing effort), we provide an insight on the safety and efficiency of combined ISCO treatment at the vicinity of EX-1 zone.

ThS 3g.2: Case studies of combining technologies application

Circular remediation of groundwater contaminated by hydrocarbons without water discharge

Claudia Beatrice Mosangini, Roger Midence; Marco Pagano

Ecosurvey®, IT

Ecosurvey® provide services and consultancy in the field of Green and Sustainable Remediation also acknowledged by the Eco-Innovation initiative, part of the EU's EASME program to support innovation among SMEs. (SmartStripping® - <https://ec.europa.eu/easme/en/tags/green-remediation>).

The following application testify that Green Remediation allows, not only environmental sustainable solutions, but also economical advantages and, in this case, it allowed the requalification of a dismissed industrial site neglected from 13 years due to the excessive costs of traditional remediation solutions.

The site is located in the alluvial plain at 30 km North of Bologna. The subsoil consist of alternating sediments, composed mainly by silt, sand and clay where a dozen of underground tanks used for the hydrocarbons storage have been found positioned below the groundwater table level. Site characterization activities and the Environmental and Sanitary Risk Analysis highlighted unacceptable risks for residential receptors (child and adult) in outdoor and indoor environment and an environmental risk to water resource protection for some organic parameters, mainly aromatic hydrocarbons, total hydrocarbons and MTBE.

The Remediation activities for topsoil and deep soil consisted, respectively, in a limited intervention of soil removal and in the application of a vapour barrier under the building foundation to remove the risk of inhalation.

The remediation activities for groundwater consist on a site-specific circular remediation that involves hydraulic containment and determines the continuous cycle: "extraction - treatment - injection" of groundwater avoiding wastewater discharges. The circular remediation consist of (a) passive trench drain located downstream with a recovery well to extract groundwater; (b) purification unit to treat groundwater, (c) re-injection well located upstream the contamination area to inject the treated water to generate the circulation of water; (d) passive impermeable lateral barrier for the containment of the contamination and (e) remote control to monitor the plant performances.

The project is characterized by the following important goals:

- reduction of soil handling (90% of soil resources preserved) thanks to the realization of the trench by laying a draining geocomposite (geogrid + geotextile) that collect groundwater;
- no water discharge in sewer or surface water (100% of groundwater resources preserved) due to the re-injection of the cleaned groundwater;
- low energy consumption and low environmental impacts;
- monitoring activities implemented with remote control;
- costs integrated in the project for the urban area requalification that don't exceed the 10% of the total requalification costs.

The present abstracts is related to a talk presentation about the technical and the hydrological description of the technology and the main phases of the decontamination process, as well as the current remediation results.

A multi-technique approach for remediation of a hydrocarbons contaminated rail yard site

Beate Mueller¹; Michael Petzold²

¹ Deutsche Bahn AG, DB Netz AG; ² Deutsche Bahn AG, DB Immobilien, DE

Rail yard facilities are highly specialized facilities consisting of one or more areas including engine maintenance buildings, fueling areas, track and switching areas, and track maintenance/material storage yards. In the Northern part of Berlin an oil gas production was running between 1909 and 1922. During that period, an oil tank was situated at the site and a tar pit was established for the remaining tar from the gas production. The handling of the oil and tar resulted in considerable soil and groundwater contamination of the area. The contamination mainly consists of tar oil with a high content of PAH and other aromatic compounds. Several meters of free phase tar oil are present in the source area, and a plume of contaminants, in varying concentrations, was detected down-gradient of it. Today, the contamination is located below buildings and active railways tracks, making it both difficult and expensive to apply traditional remediation strategies.

However, for the development of an effective enhanced natural attenuation concept it is at first necessary to remove as much tar oil as possible. The tar oil is the main source for the soil and groundwater contamination. Between 2013 and 2015 tar oil was extracted from four extraction wells solely without groundwater extraction. In this first period a total amount of 2.4 m³ tar oil was removed from the underground. In 2015 the tar oil extraction was combined with pumping of groundwater. From the four extraction wells, groundwater and tar oil is extracted at the same time. A considerable increase of the extracted tar oil was noticed. Since 2013 a total amount of 11.1 m³ tar oil was extracted at the site. In future, a further optimization of the tar oil extraction is planned e.g. installation of horizontal extraction wells.

The on-site groundwater treatment system comprises a packed-bed bio-reactor in two steps. In the first step of the bio-reactor hydrogen peroxide as an oxygen donator and mineral salts are added in order to stimulate the microorganisms and therefore to increase the degradation of the contaminants. The main fraction (app. 70 %) of the contaminants is degraded within the bio-reactor. The remaining contaminants are removed from the groundwater with an activated carbon filter.

In a second step several laboratory tests such as column, batch and closed bottle tests were performed in order to evaluate the enhanced natural attenuation potential. A multidisciplinary approach was established, as a combination of physiochemical analyses (groundwater monitoring), treatability study (based on batch incubations), and microbial population analyses (based on next-generation DNA-sequencing techniques), in order to evaluate the potential of the in situ microbial communities to biodegrade the target contaminants and thus choose the optimal bioremediation approach for the site.

Overall, the results indicate that organisms able to degrade of aromatic hydrocarbons are already present in this contaminated soil, and that the growth can be stimulated by adding the right nutrients and e-acceptors. These findings are used to choose the optimal bioremediation treatment for an in situ field scale test.

Combined in situ treatment technologies

Michael Wanders¹; Pim Vis²

¹ SUEZ Remediation; ² SUEZ RR IWS REMEDIATION B.V., NL

Combined in situ treatment technologies

Case study on a former military site used since a century for cleaning services and storage: Three hectares was highly contaminated with chlorinated hydrocarbons, volatile aromatics and mineral oil. The project was to remediate the soil and to redevelop the location by building houses and making monumental industrial buildings suitable for habitation.

To achieve this project and reach the customer requirements, several treatments were combined.

First, a large panel of pilot test have been made in laboratory or on site to validate the adapted treatments including capacity soil samples with H₂SO₄, Natural oxidant demand soil, Natural oxidant demand soil with KMnO₄, Groundwater level after pumping test, Temperature and groundwater level during field test ISCO Fenton's, Field test ISCO Fenton.

After a defined remediation strategy, the activities consist of: design, licenses and notifications, excavation and treating soil (10,000 m³), sheet piles, in situ remediation (60,000 m³) and environmental works.

Using the treatment technology of pump & treat for the remediation of residual contamination and also for the removal of DNAPLs (Dense non-aqueous phase liquids; hotspots) in addition to other technologies as in situ chemical oxidation followed by stimulated biological degradation.

In situ chemical oxidation : By the addition of hydrogen peroxide and iron (Fenton's reagent) very reactive hydroxyl radicals are formed to chemically break down contaminations such as tetrachloroethene and trichloroethene into harmless products.

Stimulated biological degradation : When the concentrations of contaminations sufficiently be lowered (< 1.500 µg/l) by pump & treat (DNAPLs) and in situ chemical oxidation and/or a sufficient amount of dissolved organic carbon (> 50 mg/l) is present, the remediation approach is continued with the application of stimulated biological degradation.

Because high concentrations of sulphate (> 200 mg/l) were present, a shock-load of substrate is injected as a first step (fast reduction). After that, a slowrelease substrate is injected as second step for the biodegradation of contaminations.

These activities are aligned with the redevelopment of the site.

Complex in situ remediation with construction and safety challenges

John Ulrik Bastrup; Anne Gammeltoft Hindrichsen

Geo, DK

Geo has performed a thermal remediation of a hot spot underneath and around a transformer where we had to take into account the conditions of wires and cables in the ground, which cannot withstand the heat from the remediation. In addition to this the work were performed in a high voltage area. All these factors were important for the project planning and execution. The execution phase of the source remediation was only 5 weeks, but the preparation phase was 5 times as much.

We were dealing with a project with QHSE-matters and security on the site as first priorities in project implementation. The presentation will focus on both extreme security matters and the implementation of the project under these conditions. What is there to be aware of before and during project execution and how do you optimize the project under such strict conditions.

Besides of the remediation of the source we also had to take care of the plume. Considerations while selecting the most cost effective method in both source and plume and remediation results will be shown.

Keywords for the lecture is: QHSE, HASP, Safety rules, Work in high voltage area, Thermal in situ remediation, Gas Termal Remediation (GTR), source and plume, Potassium Permanganate, Special drilling techniques, Dewatering strategy, Remediation Program, dimensioning and design, Com-plex and efficient project execution.

How do you make an optimal process for not having to make a lot of costly project changes? Many projects are hampered by costly add-on services that have emerged due to project changes. How do you avoid this in project planning - and can high focus on QHSE be beneficial for the project execution. What was the difficulty of combining both innovative methods and strict safety rules? - and how do you succeed despite difficult working conditions? This will be described in the presentation.

Remediation of soil and acid tar at the former Esso refinery Valloy Norway

Stany Pensaert; Hendrik Nollet; Joke Van de Steene

DEME Environmental Contractors, BE

The Valloy peninsula in the south of Norway hosted a refinery of Esso Norge. This site was polluted by the activities of the refinery: oil contaminations are found in the soil, and a large acid tar dump area has to be removed. At the end of the second world war, this site was heavily bombed which of course worsened the contamination situation.

After the decommissioning of the refinery a few decades ago the acid tar dump was covered with gravel and rocks in order to provide a simple capping. Over the years the cover however slowly sank into the tars, making the situation more complex.

Esso Norge decided to remediate the site and to remove all contaminated materials off-site. A lot of attention was put on the complex acid tar dump. Due to its experience in acid tar remediations DEME Environmental contractors (DEC) were involved in 2011 to carry out several field scale investigations and trials in order to separate gravels from acid tars, and find external disposal routes for the acid tars. In 2013 DEC carried out field pilot trials for the separation, segregation and treatment of the tars as can be found on the site. In addition SO₂ emission and its mitigation was investigated. The findings from the various pilot trials formed the basis of the remedial design.

DEC formed a joint venture with the Norwegian company Veidekke, called VeiDec. Veidec has won the contract for this large remediation and started full scale work in Autumn 2015. A treatment facility has been set up at the site, where soils and acid tars can be separated, and to treat the acid tars into a secondary fuel that can be used in the cement industry. The contaminated soils from the site are disposed off-site in various disposal facilities in Norway and abroad depending on their degree of contamination. The amount of acid tars to be disposed of is around 20000 ton, and the amount of soils is around 200000 ton.

The remediation is carried out under the most strict safety measured in compliance with the Exxon standards. A continuous air monitoring is carried out in order to avoid or minimize the nuisance to the residential areas around the site.

The presentation will outline the project as a case study, showing the approach of the remediation, constraints, etc.

ThS 3g.3: Combined technologies for chlorinated hydrocarbons

Integrated modeling of geological, hydro-chemical and geophysical data as a support for a combined chemical-physical and biological groundwater remediation intervention: The contaminated site of the New High Speed Railway Station of Bologna

Paolo Ciampi¹; Carlo Esposito¹; Firoozeh Arjmand¹; Giorgio Cassiani²; Gian Piero Deidda³; Marco Petrangeli Papini¹

¹ Sapienza University of Rome; ² University of Padova; ³ University of Cagliari, IT

The site of New High Speed Railway Station of Bologna (northern Italy) is historically affected by a contamination due to low and diffuse concentration chlorinated solvents, mainly PCE and TCE, resulting from spills caused by cleaning operations and maintenance of railway cars. The stratigraphic sequence featuring the subsoil of Bologna is represented by Quaternary alluvial deposits. A rhythmical alternation of coarse-grained (gravel-sand) and fine-grained (silt-clay) deposits is the most striking feature of the alluvial succession, which also implies a complex hydrogeological setting. In order to manage the contaminated site and with the aim of designing a proper remediation strategy, a first phase of activity dealt with the site characterization and was addressed to better define the hydrogeological setting, the present contamination condition and its variation over time. For this purpose stratigraphic data from several boreholes, piezometric records and results of chemical analyses of water were collected and organized in a geodatabase. The related 3D geological/hydrogeological model shows lateral variations of the stratigraphic levels and extremely articulated morphologies of the aquifers' limits, that give rise to a complex hydrogeological setting, typical of alluvial plains, featured by three separate aquifers (shallow, intermediate and deep). The first two aquifers are relevant for the contamination issue. The analysis of the variation over time of the water pollution (from 2005 to 2015) allowed us to point out: i) a low mean level of contamination with a decreasing trend of chlorinate solvents concentration (i.e. natural attenuation); ii) the presence of few "hot spots" with a contamination still slightly over the Italian threshold limits. The preliminary characterization at a small scale, supported by numerical modeling of flow and transport, allowed us to propose and test a remediation strategy that considers the geological and "chemical" peculiarity of the contaminated site. Based on the small scale conceptual model, we pointed out a site suitable to perform a pilot test aimed at assessing the reliability of the proposed solution, consisting in a new technology based on the direct injection of a dispersed colloidal activated carbon (Plumestop™, Regensis) coupled with a source of electron donor in order to enhance the biological reductive dechlorination processes. For this purpose a very robust geological model was necessary to identify migration pathways and low permeability zones: Electrical Resistivity Tomography surveys were integrated with stratigraphic logs in order to provide spatially continuous information regarding subsurface setting. Such an integrated model, able to reproduce the "geological-hydrogeological roughness" at a very high frequency, was the basis for optimizing the remediation strategies in terms of number of injection points and quantity of product to be injected. As a result, it was finally possible to implement the remediation intervention at full scale with positive results.

Treatment train strategies at operational sites: incorporation of oxidative or reductive bio-stimulation following physical removal of contamination

Richard Bewley; Matthew Dilley; Kevin Shepherd; Neil Cooper

AECOM, GB

Operational sites pose particular challenges for effective remediation due to access restrictions imposed by infrastructure and avoidance of disruption to the day to day activities taking place. Under such circumstances, treatment trains may achieve effective contaminant removal through the deployment of sequential approaches that are based on successive physical, chemical and/or biologically-based techniques corresponding to the severity of mass remaining.

At the first site, a rail facility, loss of diesel fuel had resulted in several centimetres of free product on the groundwater and a plume estimated to be in the order of approximately 500m². Three large diameter (150 mm) remedial wells were installed in the source area, initially with skimmer pumps for 'product only' recovery, later to be changed to a 'total fluids' recovery system with the addition of a dedicated oil-water separator. During an 18-month period of operation, approximately 10,000 litres of product were recovered. Following attainment of an asymptotic point of recovery, an Oxygen Release Compound (ORC[®] Advanced[™] manufactured by Regenesys Inc.) was injected at forty-eight locations throughout the source and plume areas to a maximum depth of 3 m by direct push. This resulted in a decrease in concentrations of Total Petroleum Hydrocarbons (TPH) initially ranging from 1.2 to 2.7mg/l to 0.4 – 0.9mg/l over approximately 12 months. An estimate of assimilative capacity indicated that this was equivalent to 47mg/l TPH, which was well in excess of these residual concentrations, and dominated by nitrate. To verify that ongoing natural attenuation was successful, a final monitoring round was undertaken after a further 15 months. This indicated TPH concentrations ranged from 0.5mg/l to below detection, all wells being below the target of 0.7mg/l.

At a second site, a manufacturing facility, a dual phase extraction system was used to effect mass removal of TCE and breakdown products, resulting in recovery of 1250kg over three to four years, 97% of this being from soil vapour and 3% from shallow groundwater, successfully reducing contaminant levels in unsaturated soils and substantially decreasing the lateral extent of contamination in the saturated zone. Due to the diminishing returns of contaminant recovery the scheme was decommissioned and a percarbonate-based chemical oxidation reagent, Regenox[®] was successively injected four times at up to 44 locations within the residual source zone, followed by a lactate-based hydrogen release compound (HRC[®]), which was additionally injected at a further 20 locations. This resulted in significant contaminant mass removal following mobilisation into the aqueous phase, and whilst potential localised DNAPL remained, after 18 months, the Chloride Index (a molar-based means of identifying the relative degree of reductive dechlorination) averaged 0.9 compared to 1.9 prior to treatment, demonstrating that ongoing natural attenuation was at an advanced stage.

The lessons arising from these case studies including sequencing issues and sustainability will be discussed.

Enhanced In-situ Bioremediation of a Chlorinated Aliphatic Hydrocarbon Contaminated Site, through Liquid Activated Carbon Injection: From Laboratory to Full-scale Application

Firoozeh Arjmand¹; Jeremy Birnstingl²; Marcello Carboni²; Paola Goria²; Paolo Ciampi¹; Carlo Esposito¹; Bruna Matturro³; Simona Rossetti³; Marco Petrangeli Papini⁴

¹ Sapienza university of rome; ² REGENESIS Remediation Solutions, Europe; ³ CNR; ⁴ University of Rome "La Sapienza", IT

The Italian environmental legislation is among the most restrictive in Europe, and has some of the most stringent target levels especially with regards to the Chlorinated Aliphatic Hydrocarbons (CAHs). For example, the Maximum Contaminant Levels for groundwater at the border of site properties are 1.1 and 1.5 µg/L for PCE and TCE respectively. Unfortunately, most of the traditional remediation technologies struggle to achieve these levels, particularly when rapid clean-up is required.

The University of Rome "Sapienza" has been commissioned to evaluate strategies for the management of the contaminated areas of the new High Speed Railway Station of Bologna (Italy), where a historical CAHs contamination has been found and characterized by a long-term monitoring activity (CAHs - PCE, TCE and cis-DCE - concentrations are ranged between 10-100 µg/L). Contamination is present in two aquifers with diverse geological characteristics, fine sand and lime in the superficial aquifer with a thickness of around 6-8 m, and higher permeable sand in the deeper aquifer with a thickness of 2-4 m.

A thorough investigation of the site has been carried out and integrated with a microcosm study with the presence of electron donors. Based on the results, biological reductive dechlorination was recognized as a potential approach for the site remediation but the low CAHs concentration and the consequent kinetic limitation made it unfeasible for the site. Thus, the possibility to use a new dispersed colloidal activated carbon technology (Plumestop™, Regenesis) was experimentally investigated as a site-specific remediation approach. The product, essentially a micrometric activated carbon with proprietary surface-charge modification to enable dispersion, theoretically could be easily injected in the contaminated aquifer creating an in-situ adsorption zone potentially able to quickly reduce CAHs concentration and to raise the kinetics of the biological reduction by locally increasing the bioavailable CAHs concentration at the carbon surface. With this technology, there is no need of any mechanical plant installation also no requirement for repeated applications, which is ideal on this complex site, where the presence of a busy train station, a residential neighbourhood and redevelopment works make the minimization of site activities a specific prerequisite.

The technology was co-injected with an electron donor (HRC™), to provide initial biostimulation of the treatment. We observed reduction of CHCs concentrations to non-detectable level within only few weeks from the application. The parent compounds (PCE and TCE) and daughter compound cis-DCE have shown reductions of one order of magnitude within first month. A sequential increase of vinyl chloride has been observed in subsequent monitoring data, indicating solvent degradation to be proceeding without limitation despite the significant reduction in aqueous-phase contamination. This is expected to decline again as remediation proceeds. It is anticipated that at time of the conference, further full-scale results will be available to provide information on the long-term trend of the groundwater treatment onsite.

Enhancement of zero valent iron use by electric field to remediate contaminated sites

Vojtech Stejskal¹; Jaroslav Nosek; Miroslav Černík¹; Jaroslav Hrabal²; Petr Kvapil³

¹ Technical University of Liberec; ² Mega a.s.; ³ Photon Water Technology s.r.o., CZ

The use of zero-valent iron nanoparticles for contaminated groundwater remediation is nowadays one of standard methods for in-situ removal or stabilisation of chlorinated hydrocarbons, selected inorganic anions, heavy metals and others. The effectiveness of this method depends on the geological and hydrogeological conditions which affect both the reactivity of nanoparticles with contaminants and their migration in groundwater environment. In the case of low permeability, the migration of nanoparticles is very limited and the efficiency of the method might be therefore reduced. The application of nanoparticles with the support of DC electric field at low intensity leads to a significant increase of total efficiency of this remediation ethos. It was first confirmed in the laboratory, but also afterwards during long-term monitoring at the site Horice (Czech R.). The first field experiment was conducted on the test polygon with three cathodes and anodes. These results showed a significant improvement of efficiency of his method compared with the simple use of nanoiron. Then the pilote system was extended to 9 test polygons which sufficiently covered existing contamination hotspots at the site. Within 3 years of running of enhanced remediation system, the cleanup of the site was performed. Other successful implementation of the method in different environment took place at the site Spolchemie. At this site was the method used to establish geochemical barrier to limit contaminant outflow from the site.

In principle the method is based on electrochemical reactions occurring in the neighborhood of the cathode to increase the pH and decrease of ORP. This has a positive effect on a higher and longevity used zero valent iron. In economical comparison of the method with the simple use of nanoiron, cost savings around 40% and at least 2-fold iron active time are confirmed. Technically the method requires a regular monitoring and depending on the groundwater environment a regular renewal of anodes due to their oxidation (range 6-12 months). From an ecological perspective the method leads to significantly improved results in reducing contaminant concentrations and increasing of effective time of the method.

We would like to thank the TA ČR for their financial support (project No. TE01020218, research centre "NANOBIOWAT")

Dynamic Groundwater Recirculation: A Strategy for Expedited Plume Cleanup

Allan Horneman¹; Mark Klemmer²; Wouter Gevaerts³; Thomas Held⁴; William Parry⁵

¹ Arcadis US; ² Arcadis US; ³ Arcadis Europe; ⁴ Arcadis Germany GmbH; ⁵ CSX Transportation, Inc.

The evolving understanding of groundwater transport including acknowledging the importance of the mass transfer between storage, low advection and high advection zones has led to stronger conceptual site models (CSMs) and more targeted and effective remediation strategies. Dynamic groundwater recirculation (DGR), i.e. strategic groundwater extraction combined with re-injection, is one such emerging dissolved phase remediation strategy. The most important difference between DGR and conventional pumping and treatment is the reliance on the CSM to develop a hydraulic flushing framework, a dynamic operation plan, and continuous adaptation based on actual remedial performance. The DGR approach includes targeted re-injections of treated water to generate hydraulic control, increase pore volume exchange, and thereby, significantly reduce the remedial timeframes.

This presentation will discuss the design and performance of a remedial system that was implemented to support the transfer of a high value property near Boston, Massachusetts (U.S.A.). The property transfer required cleanup of a 12-acre chlorinated volatile organic compound (CVOC) groundwater plume to strict standards within a very short timeframe.

The remedial strategy included excavation, electrical resistivity heating (ERH), and DGR. Initial excavation targeted shallow vadose zone soil CVOC impacts. The ERH system was implemented in a 2.1 acre source area to address back diffusion from clays underlying an alluvial sand and gravel aquifer. Outside the ERH area, DGR was implemented to address the dissolved-phase CVOC concentrations in the plume. The DGR system design was based on groundwater modeling to predict the number of pore volume exchanges to achieve the cleanup goals. The number of extraction and injection wells, the well positioning, and the flow rates were designed to meet the required pore volume exchange within 1.5 years of operation. The ex-situ treatment train included iron removal, air stripping, and granular activated carbon, plus a nitrogen scrub to strip oxygen from the reinjection water to limit injection well fouling. Well fouling is a significant consideration during this DGR effort as a result of prevailing reducing geochemical conditions and elevated dissolved metals concentrations.

The DGR operations have resulted in an up to three orders of magnitude reduction in CVOC concentrations in the plume with the majority of monitoring wells having CVOC concentrations below the analytical detection limit of 1 microgram per liter ($\mu\text{g/L}$). In a portion of the source zone, remaining groundwater CVOC concentrations of a few tens of $\mu\text{g/L}$ are related to residual concentrations in the clay layer below the alluvial aquifer. These residual hotspots will be addressed by a targeted excavation effort in the spring of 2017.

ThS 3h.1: Other technologies

From Laboratory to Site; Field Performance of Liquid Activated Carbon (LAC) – Lessons Learned from Multiple Geological Settings

Gareth Leonard; Jeremy Birnstingl

REGENESIS Remediation Solutions, Europe, IE

Background/Objectives

There is growing interest in the use of carbon injectable technologies to expedite groundwater clean-up through coupling adsorption of dissolved phase contaminants with biological degradation. After six years of research and development, a new in situ remediation technology was launched in 2014.

Approach/Activities

This presentation will examine the performance expectations created in the laboratory and compare this to more than 2 years of field evidence of this new technology. The talk will explore concerns and questions related to effective practical application of a dispersive colloidal active carbon including: the ability to secure adequate subsurface distribution in the field, applicability in low-permeability or heterogeneous formations, efficacy with varying contaminant concentrations and limits of treatable contaminant mass. Further important questions include long-term efficacy, and the related validation of post-sorption field degradation.

Data will be drawn from more than 20 field applications, variously addressing chlorinated solvent and hydrocarbon impacted sites and encompassing a variety of geological settings within Europe and the United States. Contaminants investigated range from chlorinated ethenes and ethanes to aromatic and aliphatic hydrocarbons and PAHs. Sites considered include legacy monitored natural attenuation (MNA) sites, dry-cleaners, active industrial sites, post-industrial development sites and petrol filling stations.

Results/Lessons Learnt

In addition, field data from recent and ongoing projects - including a site in Ghent, Belgium - will be presented to exemplify validation, performance against remediation goals and lessons learned with regard to material placement, site characterization and the importance of application-feasibility pre-testing.

Conclusion

This presentation is a 'full circle' example of how R&D based on industry need, can result in real innovation in remediation. The presentation includes an overview of 2 years of practical field experience with lessons learnt and recent European examples.

Innovative photocatalytic luminous textile for water remediation

Lina Lamaa¹; Laure Peruchon¹; Cedric Brochier¹; Chloé Indermuhle²; Eric Puznat²; Chantal Guillard²

¹ Brochier Technologies; ² IRCELYON, FR

Water contamination weakens or destroys natural ecosystems that support human health, food production, and biodiversity. Many Technologies have been developed in order to treat water pollution. It is essential to combine several technologies for abatement of different types of pollutants. To remove dissolved substances remaining after conventional secondary treatment, such as organic pollutants at trace level, tertiary treatments are needed. Advanced technologies to degrade this kind of pollutants are for example: fenton, ozone, photocatalysis...

For Fenton: The major drawback of this technology is that it is pH dependent (pH 2-4). For Ozone: In order to increase the reaction rate, ozone is coupled to H₂O₂ or UV. This technology is effective on microorganisms and on some organic pollutants, but has several drawbacks: Low O₃ solubility, high energy consumption, special securities needed due to the use of the ozone because of its toxicity for human.

Photocatalytic oxidation is a very promising technology for pollutant degradation. The main advantage of this process is its capability to remove and mineralize organic pollutants at room temperature. However, for photocatalysis, an important point is to optimize the contact between catalyst/pollutant/light. Actually the use of external light has several disadvantages: Important volume of set-up, Scattering of light, high energy consumption. Classical systems allow only surface treatment due to the use of external lamp which cannot be immersed in water and cannot treat water in volume. This limits the amount of pollution treated per volume and per energy consumed.

Thanks to the development of new flexible photocatalytic luminous material made of optical fibers, developed by Brochier technologies, it is possible to design compact photocatalytic set-up for water treatment in volume, not only in surface. The association of LED with optical fiber textile provides many advantages. Due to the optical fiber textile, the light emitted by the LED is distributed all over the surface of the textile. The photocatalyst is deposited on the surface of woven optical fiber. This combined light source and photocatalyst on the same support will ensure a homogenous distribution of light inside photocatalytic bed. The use of optical fibers as irradiance source has a major advantage with respect to the quantum yield.

The work was focused on evaluation of the activity of different photocatalytic coating using different model molecules on batch reactor. The results has allowed the selection of TiO₂ coating with the highest efficiency. In parallel, the durability of the photocatalytic optical fiber textile was performed and the excellent adhesion and stability of the photocatalyst was demonstrated. A protective layer is needed to avoid the attack of the optical fibers by the photocatalyst. The results of this innovative photocatalytic optical fiber textile are very encouraging and open new perspectives in photocatalytic reactor design, as these textiles allow a three-dimensional source of light.

Mobilization of LNAPL: 2D Tank Experiments

Marinos Stylianou¹; Konstantinos Kostarelos²; Agapios Agapiou

¹ University of Cyprus, CY; ² Chemical and Biomolecular Engineering Department, University of Houston, Houston, US

NAPL recovery efficiency is increased significantly with the use of surfactant solutions which offer two mechanisms: (i) solubilisation and (ii) mobilization. The first one relies on increasing the NAPL's apparent aqueous solubility as an enhancement to the commonly-used "pump-and-treat" method. The second mechanism is achieved by reducing NAPL/water interfacial tension, which allows the NAPL to become mobilize and be recovered faster than either P&T or solubilisation. Care must be exercised, though, to control the NAPL movement so that it is captured by production wells.

The recovery efficiency of NAPL using surfactants has been studied mainly through one-dimensional flow (column) experiments. Two-dimensional tank experiments are not commonly performed, but can provide valuable insight before the application at a field site. In this study, a sand tank experiment was conducted to study the mobilization of light non-aqueous phase liquids (LNAPL) from the subsurface prior to implementation in the field. Critical to the recovery process is preventing both viscous fingering through the LNAPL and gravity under-ride of the LNAPL bank. Both conditions are known to be preventable using proper design of the surfactant flood.

A stainless steel, glass tank (100 cm×76.6cm×13.5cm) was used for 2-D experiments. The tank was packed with silica sand ($150\mu\text{m} < d < 600\mu\text{m}$) with a CaCO_3 content $<0.5\%w/w$. After packing, the porous media was water-saturated and the pack was water-flooded using several pore volumes of water to measure differential pressure and calculate permeability of the media. The Jet-A fuel was dyed red and injected into the tank through three spill wells the penetrated down to a depth of 45cm from top of the tank. The final amount of Jet-A spilled was 3L or 11% of the pore volume (PV). The surfactant flood was designed to achieve a contact angle between the mobile LNAPL phase and microemulsion of approximately 33 degrees from the horizontal. This was a critical goal of the experiment, in addition to preventing viscous fingering. To ensure that no gels viscous phases were formed, the pressure drop across the tank was monitored during the experiment.

The results showed that the surfactant formulation achieved an adequate degree of IFT reduction, resulting in the development of a mobile LNAPL phase and, furthermore, concluded that the surfactant formulation can be used for the recovery of Jet-A fuel at the proposed site by means of mobilization. A relatively small amount of surfactant solution (on the order of 0.5 to 1.0 PV) could be used for the field application, and the predicted LNAPL/microemulsion contact angle was confirmed by experimentation, allowing for the design of an application of the low-tension flood whereby the targeted NAPL could be recovered without experiencing gravity under-ride.

Soil washing solution reuse – Selective degradation of hydrophobic organic pollutants entrapped in micelles by anodic oxidation

Clément Trellu; Yoan Pechaud; Nihal Oturan; Mehmet A. Oturan

Université Paris-Est, UPEM, FR

The cost-effectiveness of soil washing processes (SW) tightly depends on a proper management of SW solutions. Particularly, the possibility to reuse SW solutions is of great importance in order to reduce the consumption of expensive chemical extracting agents such as surfactant. Based on a detailed understanding of degradation and oxidation mechanisms, this study investigated how to degrade selectively target pollutants by using anodic oxidation (AO) in order to reuse a SW solution for additional SW steps.

Particularly, it has been pointed out that the formation of micelles at high surfactant concentration strongly modifies oxidation mechanisms and kinetics of organic pollutants during AO using boron doped diamond (BDD) anode. While the non-ionic surfactant monomers Tween® 80 (TW80) reacts quickly with BDD(-OH) (k_{obs} determined as $(2.97 \pm 0.60) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the ratio between the apparent (pseudo-first order) rate constant of p-hydroxybenzoic acid (used as standard competitor) and TW80 degradation ranged from 0.43 to 10, according to the current intensity and TW80 concentration. Results presented and discussed in this study emphasized the following mechanisms: (i) the use of low current intensity strongly reduces micelle degradation kinetics due to both steric hindrance phenomenon for oxidation of micelles at the BDD surface and the absence of mediated oxidation in the bulk; (ii) compounds solubilized in surfactant-containing solutions can be either oxidized after the degradation of the protective environment formed by micelles or if they are present as free extra-micellar compound. Therefore, selective degradation of organic compounds entrapped in micelles can be achieved by using low current intensity and high surfactant concentration. In fact, these operating conditions strongly hinder micelle oxidation, while free (extra-micellar) compounds can still be oxidized. Then, the remaining entrapped compounds can also be continuously released in the aqueous phase, according to the micellar / aqueous phase partitioning coefficient (K_m).

These results have been applied for the treatment of a real polycyclic aromatic hydrocarbon-containing soil washing solution. After 23 h of treatment at 50 mA, 83% of phenanthrene, 90% of anthracene, 77% of pyrene and 75% of fluoranthene were degraded and the treated SW solution was reused for an additional SW step with only 5% lower extraction capacity than a fresh TW80 solution. Moreover, such operating conditions during AO led to the consumption of only 1.6 kWh m⁻³. This highlights the great promises of this treatment strategy for reducing surfactant consumption and improving the cost-effectiveness of SW processes.

Sorption of MTBE by ZSM-5 and modified ZSM-5 in aqueous solution and soil

Yunhui Zhang; Abir Al-Tabbaa

University of Cambridge, GB

Methyl tert-butyl ether (MTBE) is a widely used gasoline additive and can cause harmful environmental and health risks. MTBE can easily contaminate the groundwater and soil and be accessible to the public due to its high solubility and volatility. Therefore, the contamination of MTBE in groundwater and soil has received an ever-increasing attention. MTBE is hard to be biodegraded due to the lack of carbon branches more than one carbon atom long, and hence immobilization is more suitable for the removal of MTBE. ZSM-5, a high-silica MFI type zeolite, is regarded as a suitable adsorbent for the removal of MTBE in water and soil due to its hydrophobicity and suitable pore size. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is a decisive factor controlling the adsorption of MTBE for ZSM-5. In this study, in order to discuss the relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ and adsorption capacity of MTBE, post-synthesis desilication and dealumination methods were applied to modify ZSM-5 in alkaline and acidic media, respectively. The physiochemical properties of ZSM-5 and modified ZSM-5 were characterised. Batch adsorption tests and soil column experiments were also conducted to reveal the adsorption characteristics of MTBE on ZSM-5 and modified ZSM-5 in water and soil.

The batch adsorption studies showed that the alkaline treatment can enhance the adsorption capacity of ZSM-5 for MTBE by 47 % (from 53.55 mg/g to 78.66 mg/g). The effects of different experimental parameters, such as initial MTBE concentration, contact time, initial solution pH and solid to liquid ratio on MTBE adsorption were investigated. The adsorption of MTBE onto both ZSM-5 at equilibrium was well described by Langmuir model, indicating a monolayer adsorption. For the adsorption of MTBE onto ZSM-5, the kinetic data were well fitted by the Pseudo first order model and showed that the adsorption process was completed within 72 h. The intraparticle diffusion model indicated that the adsorption rate was controlled by external mass transfer at the beginning, then the rate-control factor changed to intraparticle diffusion after 0.5 h. The pH of PZC (point of zero charge) is 5.5 and the initial solution pH and solid to liquid ratio had little effect on the adsorption capacity of MTBE on ZSM-5. The adsorption characteristics of MTBE onto modified ZSM-5 as well as the column test results will also be discussed in this study.

ThS 4a.3: Remediation goals and strategies; technical aspects

Lorentz, Gini, and Other Strange Things

Thomas Held; Kristin McClellan

Arcadis Germany GmbH, DE

Despite more than 30 years of experience, the success of groundwater remediation is still dependant, in many cases, on the 'gut feeling' of practitioners. In the last few years many of the subsurface processes that determine how accessible contaminants are to remediation process have been identified, but assessment methods are still qualitative. A quantitative approach is still lacking, based on the assumption that the subsurface is too heterogeneous to be successfully modelled mathematically. The reactive transport models that are often applied, claim to be valid only on a larger scale. The result is that we are determining timescales (and associated costs) for remediation on basis of rough estimations (with some indication of best/worse case estimates).

Since this all starts with the heterogeneity of the subsurface, we need to first be able to measure and quantify it. These measurements can be based on frequently used technologies such as cone penetration testing (CPT) and hydraulic profiling tools (HPT). The processing of the data can then produce correlations (e.g. Lorentz distribution) that give a visualization to the degree of heterogeneity which can then be transferred to quantitative metrics such as the Gini coefficient.

Being able to quantify heterogeneity enables the development of tools for the estimation of remediation timescales which primarily depend on the velocity of mass transfer processes. Other factors influencing remediation timescales are technical substrate delivery or non-productive substrate consumption. Considering all the parameters and the site-specific constraints that influence transport, simple calculation tools have been developed for a variety of remediation technologies enabling remediation timescales and end points to be determined.

Another aspect is that at the time of remediation planning there is the lack of qualitative data to assess whether the designed remediation will perform efficiently. To give an example, the success of in situ chemical oxidation (ISCO) can be influenced by the degree of aquifer saturation with non-aqueous product phase liquid (NAPL). Qualitatively we know that if the phase saturation is too high ISCO will not be effective, but at what level is the phase saturation too high? The range in which ISCO can be applied effectively is known as the operating window (OW). These OWs exist for a variety of technology-specific parameters. Applying a remediation technology outside the boundaries of the OWs may lead to inefficient remediation performance or to a situation where the remediation doesn't work at all (e.g. trying to enhance biodegradation at very low pH).

Tools for the derivation of the time needed for the remediation of a specific site will identify if the OWs are met or not. On the other hand we have worked on the delineation of the OWs for a number of parameters starting with ISCO as a most frequently used technology. This will allow us at a very early stage to exclude, for a given site, inefficient technologies, enabling focus to the application of the most promising technologies, and design of a remediation solution at the lowest possible cost.

New approach for systematic evaluation of data regarding the risk assessment at contaminated sites

Mads Møller¹; Henrik Jannerup²; Jens Aabling³; Katerina Tsitonaki¹

¹ Orbicon A/S; ² Region Zealand; ³ Danish EPA, DK

Background

Risk assessment at contaminated sites is typically based on concentration calculations, mass discharge and site specific models, and it is often solely an assessment of the impact. An evaluation of the knowledge base, data quality and the probability that the calculated impact occurs, is rarely included in the risk assessment.

Aim

The primary objective was to develop a new approach that reduces the time consumption and evaluates the quality of performed risk assessments at contaminated sites. The specific goal was to develop a tool with a high degree of transparency with respect to input data and performed assessments, in which the user easily can get an overview of the overall information foundation base that forms the basis for the risk assessment. The objective was to develop a systematic and dynamic tool that incorporates the user's knowledge and experience.

Project

The developed Excel tool is primarily designed to evaluate an already performed risk assessment, but can also be used in the preparation of new risk assessments.

The tool includes:

- A systematic methodology for reviewing investigation parameters in order to rate the strength of the knowledge base for the risk assessment. Data are collected and evaluated for four different data areas (source area, secondary aquifer, primary aquifer, and water abstraction well). This systematic data evaluation allows the discovery of data gaps.
- Establishment of site-specific target criteria for risk assessment (e.g., criteria based on concentrations, mass discharge, acceptable levels at water abstraction wells etc.).
- Visualization of the knowledge base, target criteria and risk assessments. The user performs risk assessments based on data from each of the four data areas. By evaluating all information and uncertainty, the user performs the overall risk assessment of current and potential future risk to groundwater resources and water abstraction well fields.
- Selection of further action for the site. Based on the risk assessment the user chose between following four actions 1. No immediate or future risk-case closed, 2. Low risk - establish monitoring, 3. High risk - remediation, 4. Risk can not be assessed - additional site investigations.

Conclusion

We tested the tool on four case studies. Applying the tool at these four sites resulted in clear recommendations for further action. In two of the four cases, application of this evaluation tool allows for a reevaluation of the risk assessment that suggest a lower overall risk and hereby a less costly action for the site (for example monitoring instead of remediation, or site closure instead of monitoring). The tool provided a good overview regarding the overall information foundation and potential data gaps. Use of different target criteria (concentration levels) for different data areas gave a good insight into whether the contamination poses a current or future risk for the groundwater resource or a water abstraction. Testing also showed that the tool was easy and fast to use, and it was possible to include the user's skills and knowledge into the tool.

Bioremediation at a French Airport: Enhanced Reductive Dechlorination (ERD) as a successful stand-alone solution for the treatment of a large chlorinated solvent plume under difficult geological conditions

Amelie Rognon¹; Daniel Guille¹; Kris Maerten²

¹ ORTEC Generale de Depollution / Groupe ORTEC; ² REGENESIS Remediation Solutions, Europe, IE

The process of Enhanced Reductive Dechlorination (ERD) for the biological degradation of chlorinated compounds, is now a widely used and proven in situ remediation approach. Extensive literature exists on the biodegradation of chlorinated solvents, in particular chlorinated ethenes such as Tetrachloroethene (PCE) and Trichloroethene (TCE), using electron donor technology. Nevertheless, ERD is often used only as a 'polishing step' of the plume, rather than a stand-alone primary remediation technology.

In our experience, the potential of ERD is much more powerful than a final stage to address residual dissolved phase contamination. In many cases, it is the only viable remediation option available when site conditions are difficult. This is often the case when the geology is challenging due to high heterogeneity and/or poor permeability, when site access is restricted by onsite structures or activities, and in cases where the plume is very large.

This presentation describes the results of a pilot test and subsequent full-scale application of a single injection of a controlled-release electron donor at an active industrial site located at Mérignac airport near Bordeaux (France). Long term monitoring data will be shown (up to 2 years following the single injection) and the particular challenging conditions of this site explained, including:

- Restricted access; the contamination was located on the sites of 2 different companies active in the aviation industry (manufacturing airplane parts).
- Heterogeneous Geology with very different permeabilities; gravelly clay overlying sandy gravel.
- Wide contaminant distribution; the contamination spread along the permeable bedding of a sewage system located in the gravelly clay. From here, the contamination seeped into the sandy gravel layer. This resulted in a very long plume with the potential to cross the site border approx. 700 m downgradient of the source.
- Large range in contaminant concentrations; Relatively high PCE concentrations were found in the source area (up to 14,000 µg/l), with very low dissolved phase concentrations further away from the sewage system.

The remedial approach and design will be discussed, including the choice of a controlled-release electron donor with a longevity of minimum 4 – 5 years (to reduce site disturbance and to deal with the back diffusion from the clayey top layer). An electron donor with a high volume and ability to self-distribute in the subsurface in order to reduce the number of injection locations on a large site and so minimise treatment cost. The use of 'top-down' direct-push injections, to provide a sufficient vertical distribution of the electron donor. Transition from aerobic aquifer conditions to those ideal for enhanced ERD in both geologic layers will be explained and evidence of full degradation towards ethene given.

This case study demonstrates the success of long-term controlled-release ERD as a primary/stand-alone remediation technology solution for challenging chlorinated solvent sites, including those with difficult geology and restricted site access.

Critical Steps in the Design of an Activated Persulfate ISCO Project

Brant Smith

PeroxyChem, AT

Activated Klorur persulfate has been widely implemented to successfully remediate sites around the world. Using the proper activation methods, persulfate has been shown to be able to treat a wide assortment of contaminants of concern (CoC) including: i) Petroleum hydrocarbons, such as BTEX, PAHs, F1, F2, and F3 compounds; ii) Oxidizable chlorinated solvents, such as PCE and TCE; iii) Reducible organics, such as carbon tetrachloride and 1,1,1-trichloroethane; and iv) Emerging contaminants, such as 1,4-dioxane.

Several factors are critical to successful design of an in situ chemical oxidation (ISCO) system involving activated persulfate. These factors include: i) fundamental understanding of persulfate activation chemistry, ii) interactions of site specific geochemistry with persulfate process chemistry, iii) site characterization, iv) determination of the quantity of reagents needed at each site, v) processes used to establish contact between reagents and CoCs during field implementation, vi) remedial expectations, and vii) monitoring programs.

The presentation will rely upon years of experience to discuss the above factors, with particular attention placed on how they interact. The end goal is to have a truly successful activated persulfate ISCO application.

Topics:

- 1) **Persulfate Activation Chemistry.** The persulfate anion can be activated by several methods to form powerful oxidative and reductive radicals. The most common methods of activation include high pH (alkaline), H₂O₂, iron-chelate, and heat. Each method can be used to form the oxidative pathway by generating the sulfate and, in some cases, hydroxyl radicals. With both oxidative and reductive pathways, activated persulfate can be used to treat a wide assortment of CoC's.
- 2) **Geochemical Interactions:** Each site has the potential for unique geochemical interactions with activated persulfate process chemistry. In addition, bench scale tests and their objectives, as well as scale-up procedures will be evaluated.
- 3) **Reagent Mass Estimates:** The mass of reagents required can be evaluated by several methods. The most common is to sum both target and non-target demand for the reagents, then to include a safety factor. Other common methods can be based on injection concentrations and scaling up from elaborate bench scale tests.
- 4) **Establishing Contact:** Transformative technologies including chemical oxidation are successfully deployed in situ when they establish contact between a sufficient mass of the appropriate treatment chemistry with the CoC. Common methods of establishing contact include in situ soil mixing, direct injection, and recirculation of groundwater mixed with reagents.
- 5) **Remedial Expectations:** Studies have assessed typical results of transformative technologies including ISCO, ISCR, and in situ bioremediation. This presentation will provide insights regarding reasonable expectations regarding ISCO performance.
- 6) **Monitoring Programs:** The role of monitoring programs in successful implementation of activated persulfate projects is often under appreciated. The importance such programs will be discussed, as will typical monitoring program objectives, design, and lessons learned.

Laboratory tests to investigate the effects of groundwater mobilization on Back-Diffusion phenomena in the saturated zone

Fabio Tatti; Marco Petrangeli Papini; Paolo Viotti

University of Rome "La Sapienza", IT

The presence of contaminants in low permeability zones today can represent a real limitation for a complete and effective groundwater restoration. Low permeability zones become saturated of contaminant during plume flowing bringing therefore to a slow re-distribution (Back-Diffusion) in groundwater with a process based on molecular diffusion. These zones become therefore a contamination source even when the primary one is removed. This process is the primary cause of long-term plume tailing. Experiments were carried at the lab scale to study the Back-Diffusion process and to improve possible way of its management. The process was simulated using a Plexiglas tank and Fluorescein as tracer. In the tank a high permeability layer with three different low permeability lenses was used as aquifer. To simulate a flowing contaminant plume in groundwater the tank was saturated with a solution of Fluorescein. Observation on the tracer advance in the low permeability zones by molecular diffusion were carried out. When the intrusion process reached a steady state, clean water was used by flushing fluorescein concentration. An Image Analysis procedure based on the intensity of emitted light by the tracer is proposed to evaluate the concentration and the mass of Fluorescein released from low permeability zones. By this procedure different relations to estimate the duration of the phenomenon and the amount of mass released from the lenses are obtained. The same experiment is repeated flushing water at different velocities to investigate the effects of pumping water on the low permeability lenses rate of release. The results show a not-significant decrease of the time affected by Back-Diffusion process and a slight increase of contaminants removal from low permeability lenses. The collected data demonstrate the need to manage the Back-Diffusion phenomenon using alternative remediation technologies, such as groundwater circulation wells or thermal treatments.

ThS 4a.4: Remediation goals and strategies; heavy metals and radioactivity

Management of subsurface contamination at an operational nuclear site

Bertrand Leterme; Isabelle Majkowski; Matej Gedeon; Sven Boden; Diederik Jacques

SCK·CEN, BE

SCK·CEN (Belgium) performs research into nuclear energy and ionising radiation for civilian use. In 2014, during the preparation of dismantling activities, contamination in the subsurface soil was discovered. The contaminant was mainly Cs-137 and a limited amount of Co-60, located at a depth between 1 and 2 m below the ground surface. Due to the unexpected situation, the remediation was carried out following an “emergency” procedure. As a result of a thorough screening on site, about 80 tons of soil had been excavated. In principle, the major part of the excavated soil meets unconditional release criteria. However, since removal routes are unexploited, the excavated soil is currently posing storage issues.

Following this, a consolidated strategy has been established, covering the following aspects:

- Registration of all radiological measurements performed on soils, in a centralized mapping tool;
- Implementation of dose impact studies for the present soil contamination and the potential ground water contamination;
- Enforcement of a strict procedure for the execution of fieldworks on the SCK·CEN site;
- Ensuring the protection of the environment (with special attention to the relatively shallow groundwater) and of workers carrying out fieldworks in potentially slightly contaminated areas, using a risk based approach and numerical simulations of radionuclide transport;
- Search for new/unexploited removal routes for contaminated soil;
- Evaluation of feasible decontamination methods.

More recent experience shows that, for contamination similar to the one described above, excavation should be avoided when there is a very limited risk/impact for human and the environment. Indeed, excavation might not be optimal towards the ALARA principle since no effective removal route is currently available. Instead, considering the contamination type and the subsoil characteristics, protective measures for workers and the environment may constitute a more effective contamination management policy.

Since 2015, 80 field interventions took place, 550 radiological characterization measurements have been performed and registered. Four small contaminated areas have been discovered.

Two interventions in such areas have been performed and radioprotection measures have been implemented. No excavation for remediation purposes has been performed on these sites.

Dismantling a NORM waste storage facility in the acid phosphate industry

Marine JACQUET

ARCADIS France, FR

In the early 1990s, a facility in the acid phosphate industry was dismantled, resulting in the production of more than 100 tonnes of Naturally Occurring Radioactive Materials (NORM) waste. No final management solution for these wastes had been identified. The wastes have been stored in a hermetic and impermeable storage facility located in an industrial area. As the land owner wished to develop industrial activities on the site, the NORM waste owner had to dismantle the installation and manage the primary and secondary wastes resulting from these operations.

Several issues relating to the project will be described to demonstrate how the challenges associated with NORM waste management were overcome:

The existing waste inventory was not sufficient to manage the wastes adequately. A temporary zone for screening and characterization was designed next to the installation in order to open packages, allowing sampling and characterization of the wastes.

These were stringent regulatory waste disposal requirements. A bespoke sampling and analytical programme was set up in order to obtain necessary information for adequate waste management.

Radon 222 had built up in the storage facility during the past 25 years due to Radium 226 decay. As a result, a methodology to safely ventilate the facility without uncontrolled releases of contaminated gases to the atmosphere upon opening of the facility was developed.

Exposure by human health was a potential concern. Worker and public radiation protection was evaluated for each stage in the process, namely: ventilation, storage, facility opening, screening and sampling of wastes.

Potential environmental impacts on groundwater, soil and air. These were studied and assessed carefully for each step of the project. The use of suitable protective measures were taken into account, as well as environmental monitoring before, during and after the project to assess and minimize potential impacts.

Remediation strategy for the underground uranium leach operation at Königstein (Germany) – Full flooding with residual emissions instead of pumping for eternity

Ulf Jenk; Michael Paul

Wismut GmbH, DE

Flooding of the Königstein Uranium mine was initiated in 2001 following 10 years of conceptual preparation, supported by a large number of scientific studies. Within the last 12 years the mine water level was raised up to a permitted interim level of 140 m a.s.l. with about two thirds of the mine volume being filled. The flooding process has been accompanied by an extensive monitoring programme and continuous analyses to assess the relevant hydrogeological and geochemical processes within the mine and in the surrounding field and to ensure that requirements related to mine safety be met.

Key findings regarding technological and scientific aspects of flooding have been evaluated and reported including a reassessment of earlier model predictions. This information has been used as a basis for planning for full flooding of the mine, which is connected with remediation of the mined aquifer as well as with an unavoidable limited ground water contamination in the surroundings.

Based on these planning and additional R&D-projects to support the flooding process, Wismut filed permit applications in 2011. After denial of permit application due to stringent interpretation of the Water Act Wismut entered an objection in 2013.

Application for permit is still pending. Denial of permit for full flooding would imply pumping and treating water forever and leaving one third of the mine workings without remediation in an insecure hydrologic condition. Wismut are still arguing for full flooding with a view to reaching a naturally stable ground water system in the end; although this would unavoidably entail a limited contamination of the above laying aquifer. A technical solution with regulatory approval could be a very slow, stepwise flooding over a period of about 30 years, keeping contamination of surrounding ground water within strongly limited bounds.

The paper describes the remediation strategy for the former uranium leaching operation, outlines the main technological elements and discusses the option of a sustainable solution with limited negative effects as opposed to pumping for eternity.

Statistically based decision model for lead contamination in Rotterdam

Jasper Lackin¹; Arie de Niet¹; Kees de Vette²; Ilse Meijer-Verschuur²; Marc Groenenboom³; Peter Wijn³

¹ Witteveen+Bos; ² Municipality Rotterdam; ³ DCMR, NL

In this paper we present a statistical approach for the development of a decision model for diffuse lead contamination. The key in the approach is that it takes in account the heterogeneity of the contamination in different subregions and translates it to city block level. In the end the model supports the decision on city block level based on limited measurements.

Due to lead carbonate production and application of its waste products, the municipality of Rotterdam struggles with a large scale heterogeneous diffuse contamination of lead. A bioavailability study has shown that the health risk is greater than assumed previously. The study motivated the municipality of Rotterdam in conjunction with the DCMR to develop a research program regarding the lead contamination.

The level of heterogeneity of diffuse lead pollution differs between areas in Rotterdam. Based on the development history of the city, locations of the lead carbonate producing companies and large scale historical activities, Rotterdam was divided in subregions. These subregions all have their characteristic diffuse contaminated profile which is determined with common statistical analysis. Usually measurements of contaminated soil have a skew distribution. Hence, subsequently a Box-Cox transformation was performed to get a better fit to the normal distribution.

Evaluation is based on existing data or a limited new soil survey within an evaluation unit, in most cases a city block or park. The aim of the procedure is to make a reliable statement whether the lead concentrations in all gardens in the city block are acceptable. The designed procedure requires comparing the data from a subset of the gardens in the city block to the data from the subregion it belongs to. The assumption is that the distribution of the lead contamination in the city block has the same variance as the distribution of the lead contamination of the subregion. The measured average concentration of lead in the city block is tested against an 80% reliability value of different soil limits. Therefore a safety margin between the soil limits and the lower target concentration is applied. Furthermore it is taken into account that the reliability of the mean increases as the number of samples increases. Multiple Monte Carlo simulations were carried out for each subregion varying the sample size in order to determine the test values. The result is a table for each subregion that provides the test values for different sample sizes in the soil survey and different soil limits. If the mean of the soil survey of the block of houses is below the test value it can be stated, with 80% confidence, that the contamination levels with lead in all the gardens are acceptable.

In order to establish the robustness of the methodology a sensitivity analysis was performed. Currently pilots are implemented in order to test and refine the assessment methodology.

The management and remediation of large scale mercury contamination along a waste water channel in the Canton of Valais (Switzerland) – intermediate results

David Trudel¹; Christoph Munz¹; Rémi Luttenbacher²; Renzo Cicillini²

¹ Arcadis Switzerland; ² Lonza Ltd., CH

Visp, a municipality in the upper part of the Canton of Valais (Switzerland), is home to the largest production site of Lonza. The Lonza Group is a company with around 10,000 employees producing fine chemicals, pharmaceutical and biotech products.

From the beginning of the last century mercury has been used in the plant as a catalyst for various chemical reactions (e.g. for the production of acetylene). Due to losses of mercury during the production process, a small fraction of the metal was present in the waste water from the chemical company and was transported in a channel approximately 10 km downstream until it reached the River Rhone.

The channel, originally built for the drainage of the valley between Visp and Raron, was periodically maintained by the authorities to avoid silt build-up. During the maintenance work, sediments were excavated and deposited along the side of the channel. The excavated sediments could then be removed and used to improve the quality of the soil within the neighboring fields and gardens as well as for the leveling of the terrain. A total area of approximately 9 km² is now under investigation for possible mercury contamination in soil and subsoil. These investigations are conducted by Arcadis, a large design and consulting company with a proven track record for investigation and remediation of contaminated sites.

To manage this large-scale project, the area under investigation was subdivided into a residential area, an agricultural area and the channel itself. As it was not feasible to handle all three areas simultaneously, the initial focus was on the residential area. This was due to the initial investigation identifying that some gardens contained levels of mercury that could potentially pose a risk to children playing in these gardens and, hence, being exposed to contaminated soil.

Subsequently the extent of the mercury pollution, in soil and subsoil within the residential areas, was investigated and the number of parcels of land that need to be remediated was determined. Currently, there are about 90 land parcels in need of remediation in residential areas. In order to optimize the remediation of the polluted parcels, two pilot projects were conducted in summer and autumn 2016. Based on the gained experience a remediation strategy for all the other affected parcels of land was developed. The aim is to remediate the affected parcels in the years 2017 and 2018.

To make this whole investigation and remediation process successful, Lonza and Arcadis are working collaboratively together and are actively involving all relevant stakeholder groups in regular meetings. The relevant stakeholder groups in this project are cantonal and municipal authorities, owners of the land parcels, non-governmental organizations, media (local, regional, and national), and the general public. Based on the current experience Lonza and Arcadis are confident that this project will be finished successfully to the satisfaction of all involved parties.

ThS 4a.5: Remediation goals and strategies; administrative approaches

Australian Guidelines for PFAS Contamination of Soil, Surface Water and Groundwater

Peter Nadebaum¹; Eric Friebel; Jill Woodworth; Therese Hammond

¹ GHD Pty Ltd, AU

Perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonic acid (PFOA) have been identified as contaminants of emerging concern in Australia. They are known to be persistent, bioaccumulative and potentially toxic, and have been found to be present at concentrations of potential concern at a number of sites, particularly where there has been use of fire fighting foams. Industry and public awareness of the presence of PFAS contamination at airports has grown, and litigation is occurring, including class actions by affected parties.

CRC CARE has prepared guidance on the assessment, management and remediation of PFOS and PFOA in Australia. This work has involved a working group comprising representatives of regulatory agencies, industry and research organisations; the authors of this paper are the lead researchers in the preparation of the guidance.

It is intended that this guidance will assist practitioners, regulators and site owners to effectively assess, manage and remediate soil and groundwater contaminated with PFAS compounds, and will allow more appropriate remediation and potentially reduce the cost of managing soil and groundwater contaminated with PFAS compounds.

In particular, the guidance includes information on:

- a) The extent and magnitude of PFAS contamination in Australia, where particular problems have been identified, and where significant data gaps in knowledge exist;
- b) The problem of many perfluorinated compounds being reported in analysis and where assessment should focus;
- c) Impacts on the beneficial uses of soil, groundwater and receiving waters;
- d) Ecological and human health screening levels to protect soil, surface water and groundwater for application in Australia; these screening levels consider toxicity, bioaccumulation, bioavailability and persistence;
- e) Screening levels for water and sediment with respect to bioaccumulation in fish and acceptability for human consumption; and
- f) The difficulties that arise in treating and managing PFAS contamination and reducing the risks to an acceptable level, and practicable approaches that are able to be adopted. Consideration extends to soil containment, treatment and reuse, discharge of water and effluent to receiving waters and to the sewerage system, and disposal of soil and waste to landfill.

Investigation and Remediation of Multiple PFAS Source Zones at an Airport to Safeguard a Water Supply

James Lemon; Dave Atkinson; Jonathan Miles; Ian Ross; Jake Hurst

Arcadis, GB

Guernsey, a British Crown Dependency, is located in the English Channel between England and France and represents one of the Channel Islands. Concentrations of PFAS were detected in the surface waters which are used to source drinking water supply for the Island's population. The affected catchment area, which includes one of the Island's principle water supply reservoirs, collects surface water and groundwater from within the vicinity of the islands airport. The airport was identified as a potential source for the PFAS contamination detected. The objectives of the project were to investigate: the extent of PFAS impacts within the airport and the surrounding environment; whether the existing conditions were likely to deteriorate further; and, ultimately to identify an appropriate solution protected to safeguard the Island's water supply into the future.

As an immediate step, a detailed desk based review and preliminary risk assessment was completed, looking at historic uses of AFFF foam at the airport through records of aircraft accidents, training procedures, and material storage. The outcome of this study identified eleven potential source locations which required further assessment. Site investigations followed, including extensive soil, groundwater and surface water sampling, which identified PFAS impacts at 7 of these locations. Following detailed fate and transport modelling 4 of these location were considered to require remedial action. All investigation works were undertaken on an active airport without disruption to operations.

On completion of the investigation activities a bespoke water treatment system was designed, which incorporated the installation of two below ground capture trenches across the airfield to intercept PFAS impacted groundwater. The water treatment system also collects and treats impacted surface water. With a capacity to treat up to 20 litres of water per second, the system is ensuring that concentrations of the PFAS are below drinking water criteria, prior to discharge into the wider catchment area.

Following the installation of the water treatment system, soils identified to be contaminated with PFAS in the four source zones across the airport were excavated and contained within a purpose built soil bund. The soils are encapsulated so as to isolate them entirely from the local environment, whilst also acting an acoustic barrier to mitigate noise pollution from the airfield operations.

The project highlighted the requirement to understand the history of AFFF use at airports and airfields as multiple sources zones are typical. The treatment solution reduced PFAS concentrations in the drinking water supply whilst also removing the risk of further leaching from the main source areas by isolating the contaminated material as part of wider redevelopment scheme.

When it has to be done again... challenges in the management of a decade-old “remediated” legacy site

Ariane Ancel¹; Amiel Boullemant²; Grant Douglas³

¹ Ramboll Environ; ² Rio Tinto; ³ CSIRO, FR

A minerals processing site located in southwestern France operated for almost a century (1916-2002) a wide range of industrial products – mainly magnesium – with waste materials deposited onsite. In 2005, this 16ha site was remediated with two former industrial platforms and three landfills. Shortly thereafter, liabilities were transferred to a new company with a poor data transfer. However, within a decade, it became apparent that one landfill was still chemically active causing gas emissions, fissures and potential slope instability. On-going reactivity at the site triggered a suite of environmental investigations (gas emissions, mineralogy, and leaching behaviour) to obtain a better understanding of chemical reactions and the associated risk for human and local ecosystems.

Both acetylene and ammonia were measured in atmospheric emissions while high concentrations of ammonia, hydrogen cyanide and dihydrogen in the working atmosphere were measured during coring ($\text{NH}_3 > 500$ ppm, $\text{HCN} > 30$ ppm, $\text{H}_2 > 1,500$ ppm).

In regards to mineralogy, substantial heterogeneity was apparent both vertically and horizontally, likely related to different waste deposits and internal reactions that occurred over the past decades within the landfill. Eight major groups can be identified from the analysis of the mineralogical data with four major geochemical/mineralogical associations found. The ratio of CaO/MgO was found to be an important proxy variable that could define geochemical reactivity within the pile. If CaO/MgO was < 5 then a strong likelihood existed for higher temperatures and gaseous (NH_3 , VOC, and HCN) emissions and intermediate to high pH (ca. 9.5 – 12.5). On this basis, it may be possible to subdivide waste to target intervention.

Layered double hydroxides (e.g. hydrotalcite) are found to be important passivating secondary minerals at the ambient pH (ca 9.5 – 12.5) in waste materials. Formation of additional LDH minerals is probably limited by the supply of Al.

Based on a characterization of the waste materials present, preliminary conclusions were drawn with respect to a potentially successful rehabilitation at this landfill of concern. It is suggested that in first instance, a cover be placed on the waste material to restrict further water ingress. In addition, active venting, monitoring and treatment of gaseous emissions would be undertaken to reduce the local environmental impact.

Inadequate characterization of waste materials deposited during an initial remediation phase has resulted in an on-going environmental liability. Underestimation of wastes chemical reactivity in a mineral processing landfill site led to an unstable rehabilitation ten years later. An international characterization study of the waste materials has allowed for the identification of better informed remediation options.

Flanders uses dynamic spatial modelling ('RuimteModel') for prioritization and sustainable management of contaminated sites

Griet Van Gestel¹; Johan Ceenaeme; Nina Peeters¹; Nathalie Van Trier¹; Karolien Vermeiren²; Guy Engelen²

¹ OVAM; ² VITO, BE

In Flanders, much effort has been given to collect information on all possible contaminated sites in a land information register. The next phase involves decision making on further examination, remediation and/or management of these risk sites, and on the timing of the actions. The high number of sites in combination with the wide range of possible further actions based on the – at present largely unknown – site-specific risks, induces the need for a prioritization of all sites.

The OVAM, the Public Waste Agency of Flanders, wants to prioritize based on sustainability goals, such as sustainable spatial development and the sustainable use of energy and other natural resources. This implies that a whole range of different factors needs to be evaluated together: (1) the properties of the risk sites, (2) socio-economic and physical characteristics of the environment surrounding the risk sites; (3) the current spatial planning and the expected evolution over time.

Dynamic spatial models are useful tools to support these decisions. Therefore, OVAM initiated a collaboration with VITO in order to use VITO's so called 'RuimteModel'. This model simulates land use changes in Flanders at high spatial resolutions, for about 40 different land use categories, and for 50 years into the future. The output is cartographic, quantitative and dynamic over time. The model is used by different agencies of the Flemish and local governments for policy decisions on a range of issues: urbanization, spatial planning, mobility and transport, flood prevention, resource management, ...

Indicators are developed for scoring and prioritizing sites on the relevant factors. There are 3 types of indicators representing (1) the environmental-technical characteristics reported at the sites, (2) spatial characteristics of the present land-use and activities (population, employment) at the sites and in their near surroundings, and, (3) potential for future development of the sites and their near surroundings as identified by 'RuimteModel'.

Recently, VITO and OVAM developed an application for prioritizing landfill sites in the framework of Enhanced Landfill Management and Mining. This application will be extended and improved to make it suitable for contaminated sites. It will visualize the scores of all possible contaminated sites in Flanders on the selected indicators in the form of a 'spider-diagram'. This tool allows to select and weigh sets of indicators by regional and local policy makers who are granted access to the model. It will support the prioritization on levels varying from local to regional.

In the presentation, the advantages of spatial dynamic modelling to support soil policy will be demonstrated. The tool helps to gain insight in complex issues, and allows to test various possible scenarios and solutions. It generates output in various forms, but, it is above all very visual and tangible and thus ensures that the model is a very useful instrument to involve different stakeholders in the decision making process.

In the future the OVAM envisages to develop also specific applications for brownfield redevelopment and the management of contaminated sediments and river banks.

Implications of the changes in the Polish legislation on remediation issues in recent years on the sustainable management of contaminated land

Katarzyna Jankowska; Paweł Goldsztejn

ARCADIS PL

A legal obligation to remediate contaminated land has existed in Poland for 15 years, however the origins of remediation being undertaken date back to the 1990s. In the past regulations were very conservative and based on clean-up of contaminated land to prescriptive quality standards which led to high costs, discouraging potential investors who would otherwise have regenerated contaminated sites. In the last 3 years important changes in environmental law were implemented, providing greater clarity and strongly promoting a risk-based approach. The main changes implemented to the environmental legislation resemble solutions applied in other European countries but differences in some approaches still occur. The impact of changes in legislation on sustainable management of contaminated land in Poland will be explored.

The term “remediation” refers to measures dealing with the presence of substances posing risk (contaminants) in soils or groundwater. It should lead to elimination, limitation or controlling of the amount of substances posing risk, or limitation of the migration of substances such that they will not pose further risk for environmental receptors or human health. The new regulations have implemented a less conservative approach - the requirement for soil treatment to quality standards values (remediate no matter the cost) is no longer always obliged. It is a revolution in Polish environmental law. The new rules allow for a balanced approach in terms of costs, time and effectiveness of remediation. It encourages Site owners to proceed with remediation and attracts investors to regenerate brownfield sites, often in very good locations.

Risk assessment for human health and environmental receptors is a relatively new procedure in Poland that was introduced in September 2014 as a concept. The risk assessment methodology in Poland is still under development, but likely to comprise a similar approach to those followed in other European countries. The methodology implemented within risk assessments will focus on identification of potential Source-Pathway-Receptor linkages. Currently in Poland, no legal act regulating the methodology of assessing significant risks for human health or condition of the environment, nor the reference methodology for modeling the spread of substances in soil and groundwater has been published. Therefore, European risk assessment methods are currently used, enabling sustainable decision-making in terms of the scope and final outcome of remediation, allowing in particular situations certain amount of substances of concern to be left in situ as long as they do not pose significant risk.

In September 2016 a new Ordinance on the Assessment of Soil was issued in Poland. It introduced a new scheme of how to execute a site investigation, new sampling procedures and new threshold values. The previous Ordinance did not regulate the methodology for the assessment of soil contamination and presented only contaminants threshold concentrations. The Ordinance, however, does not refer to groundwater quality issues in terms of remediation and this aspect is still not clearly regulated by Polish Law.

ThS 4b.3: Sustainability appraisal of remediation technologies and strategies

Sustainable Remediation in Brazil

Joyce Rodrigues da Cruz¹; Olivier Maurer¹; James Henderson; Carlos Henrique Araújo, Laurence Rebenne¹

¹ CH2M, BR

Currently in Brazil the topic of sustainable remediation has been treated and discussed by several working groups among environmental consulting companies, universities, environmental agencies and industries. In face of this scenario the group NICOLE Brazil and Sustainable Remediation Forum (SURF) noted the need to develop a technical document that would help all those involved in the discussions about the subject.

The challenge of the NICOLE Brazil and SURF group is to develop a White Paper talking about this paradoxical subject and its Brazilian specificities: Sustainable Remediation. Innumerable factors favor the country and its people, but they are counterbalanced in all cases by dogged circumstances out of the control of the majority of the country's approximately 169 million inhabitants. The natural resource base of Brazil alone could supply the world's food and potable water needs for the next 20 years. A growing population, vibrant economy, and cultural significance renowned the world-over have placed Brazil squarely within the world's consciousness as a growing global force to be reckoned with.

But, as every Brazilian will tell you, there are problems, though this should not be a treatise on the many economic and political difficulties, and especially the country's infamous levels of corruption, the present document has as its primary focus no less a critical concern: revitalization and restoration of the country's contaminated areas.

After decades of work in North America and Europe, it is well-known that initial efforts in those regions, focusing on restoration of contaminated areas, were largely misguided. A new methodology has taken hold, and is increasingly at the forefront: the use of green and sustainable remediation practices that have as their fundamental tents not only environmental, but also, societal and economic gain.

The present document comes at the realization that more established sources of information, largely generated by North America and Europe, do not suffice solely as the expertise needed within a Brazilian context. The document has been elaborated in collaborative fashion with experts from afar, but it is strictly "brasileiro," or Brazilian, in every sense. The undersigned are individually, and collectively, those practitioners and stakeholders most affected by the issue of contaminated lands in Brazil, and thus the most knowledgeable parties the country has to offer. The group hopes this White Paper, in so much as it serves as a robust treatment of the technical subject matter involved in Sustainable Remediation in Brazil is helpful to all affected stakeholders.

Our proposal to AquaConsoil is to present the highlights of this White Paper on Sustainable Remediation in Brazil.

Current Status of Green and Sustainable Remediation in JAPAN -An Approach of SuRF-JAPAN-

Tetsuo Yasutaka¹; Yasuhide Furukawa; Makoto Nakashima; Ming Zhang; Hisaichi Suzuki; Toichiro Maekawa; Takaaki Nishihara; Naoyoshi Yokoyama; Tetsuro Sato; Toshihiro Haramoto; Hiromi Suyama; Masafumi Funakawa

¹ National Institute of Advanced Industrial Science and Technology, JP

The environmental, economic and social impacts of contaminated sites have attracted considerable attention at the remediation activities associated with site cleanup and reuse or redevelopment. Since the 2000s, the United States and Western Europe have started to actively discuss the concept of sustainable approaches applied to contaminated sites and established SuRF (Sustainable Remediation Forum). In Japan, some institutes started studies on Green and Sustainable remediation in 2010. Geo Environment Protection Center developed CO₂ calculation tool in 2013. Tokyo Metropolitan Government and the National Institute of Advanced Industrial Science and Technology (AIST) published an integrated environmental burden calculation tool (GRADJ, Yasutaka et al 2016) and guidance associated with green remediation in 2015. For further discussion about sustainable remediation and green remediation, SuRF-JAPAN was established in February 2016.

The SuRF Japan is composed of 14 corporate members, including construction companies, consulting companies, real estate companies, municipalities and national institutes, and 8 individual members. There are two working groups: Green Remediation WG (GR-WG) and Sustainable Remediation WG (SR-WG). The GR-WG deals with (1) organizing Best-Management Practices (BMPs) from investigation to implementation of measures, (2) preparing environmental impact reduction checklists while implementing measures, and (3) developing a semi-quantitative tool. By March 2017, the results of these discussions will be compiled and technical report will be published.

On the other hand, the SR-WG is working on index extraction by considering the environmental, economic, and social impacts, according to the decision-making while implementing measures and redevelopment. Several workshops and role-playing activities have been organized. As a result of workshop, we will select the important parameters for Japan's stakeholders and compile the parameters weighting of each environmental, economic and social aspects. Research meetings, as part of this consortium's activities, have also been held to discuss brownfield sustainable redevelopment.

Comparison of international approaches to sustainable remediation across Europe, The Americas and Australasia

Paul Bardos¹; Erika Rizzo; Lisa Pizzol; Andy Cundy; Nicola Harries²

¹ University of Brighton, Brighton, UK, r3 Environmental Technology Ltd.,; ² CL:AIRE, GB

Since mid-to-late 2000s growing interest for sustainable remediation has emerged in initiatives from several international and national organisations as well as other initiatives from networks and forums. This reflects a realisation that risk-management activities can about bring environmental, social, and economic impacts (positive or negative) in addition to achieving risk-based remediation goals. These ideas have begun to develop as a new discipline of “sustainable remediation”. The various initiatives have now published a number of frameworks, standards, white papers, road maps and operative guidelines. This paper reviews approaches from several European countries, Canada, USA and Australia/New Zealand, Brazil, Colombia, Taiwan and emerging international standards.

The similarities and differences in the approaches by these outputs and general trends have been identified. The comparison is based on a set of criteria developed in discussion with members of these various initiatives, and identifies a range of similarities between their publications. Overall the comparison demonstrates a high level of consensus across definitions and principles, which leads to the conclusion that there is a shared understanding of what sustainable remediation is both across countries and stakeholder groups. Publications do differ in points of detail, in particular about the operational aspects of sustainable remediation assessment. These differences likely result from differences in context and legal framework. As this analysis was carried out its findings were debated with members of the various international initiatives. Hence the outcomes described in this contribution can be seen as the result of a sort of multi-level debate among international experts (authors) and so can offer a starting point to new sustainable remediation initiatives (for example in other countries) that aim to start developing their own documents.

Comparison of approaches for assessing sustainable remediation of contaminated sites

Gitte Lemming Søndergaard¹; Philip J. Binning; Poul L. Bjerg

¹ Technical University of Denmark, DK

It has been estimated that there are approximately 2.5 million potentially contaminated sites in Europe. Of these, approximately 340,000 sites are thought to be contaminated to a degree that may require remediation (Joint Research Center, 2014). Until recently, remediation was considered to be inherently green or sustainable since it removes a contaminant problem. However, it is now broadly recognized that while remediation is intended to address a local environmental threat, it may cause other local, regional and global impacts on the environment, society and economy. Over the last decade, the broader assessment of these criteria is occurring in a movement toward 'sustainable remediation'. This paper aims to review the available methods for assessing the sustainability of remediation alternatives.

Sustainable remediation seeks to reduce direct contaminant point source impacts on the environment, while minimizing the indirect cost of remediation to the environment, society and economy. Here we present and compare the available tools and methods for assessing the sustainability of remedial solutions and discuss some of the key issues and future challenges. The aim of a sustainability assessment is to compare the sustainability of two or more remedial solutions for a contaminated site. A sustainability assessment does not provide an absolute measure of whether remediation of a specific site is sustainable. Instead it provides a relative measure which can be used to select the most sustainable solution from amongst a number of defined remedial scenarios.

Results of the review show that most approaches use multi-criteria assessment methods (MCA) to structure a decision support process because it allows the combined assessment of criteria which may be either quantitatively or qualitatively assessed. Different combinations of environmental, social and economic criteria are employed, and are assessed either in qualitative or quantitative forms with various tools such as life cycle assessment and cost benefit analysis. Stakeholder involvement, which is a key component of sustainable remediation, is conducted in various ways. Some approaches involve stakeholders directly in the evaluation or weighting of criteria, whereas other approaches only indirectly consider stakeholder preferences.

This study has reviewed available methods for assessing and comparing the sustainability of contaminated site remediation alternatives. It is concluded that MCA methods are very useful when comparing remediation alternatives, since they allow for a joint assessment of many types of indicators; however the available tools and methods differ substantially, for instance in their selection of indicators, criteria evaluation methods, and approaches to stakeholder involvement and uncertainty analysis. Further work is needed in order to test the assessment approaches for real case studies, since to date only few documented case applications have been published. The presentation will give specific examples of approaches ranging from more qualitative assessments to more quantitative assessments of criteria.

Is sustainable remediation storing up environmental problems for the future?

Matthew Pannett

Ramboll Environ, GB

Is sustainable remediation storing up environmental problems for the future?

The concept of sustainable remediation has been around for a number of years and its value is well known. How sustainable remediation is being regulated and applied is less apparent and at times subjective, and may not fully account for future land users and interested parties. A common perception with regulators and industry is that sustainable remediation is too biased towards economy at the detriment of the environment and society. Could this could be storing up liabilities for businesses and investors in the future?

The aim of this presentation is to critically assess sustainable remediation from a commercial perspective and discuss whether, in the future, a sustainably remediated site could become an environmental liability or a concern for society or business.

Current trends suggest that investors and businesses often demand higher levels of environmental clean-up than the minimal science based standards, which are based on precautionary or low levels of toxicological concern. Factors such as the liquidity of an asset, the ability to attract project financing and corporate social responsibility mean that some 'sustainably remediated' sites may become less commercially attractive in the longer term. Furthermore, many remediation schemes are not sufficiently 'future proofed' to take into account climate change, evolving science and government policies.

To illustrate the concepts, the following themes will be discussed:

- How sustainable remediation is viewed by businesses, investors and regulators;
- Case studies of where sustainable remediation is being used to avoid 'difficult' remediation such as clean-up of DNAPL, only to pass on potential environmental liabilities to investors and developers.
- Climate change, as an example of how insufficient foresight may cause sustainable remediation schemes to fail in the future with resultant liabilities being inherited by future site owners.

The paper will conclude that:

1. When using sustainable remediation approaches it is important to consider how the residual contamination will be viewed in five, ten or twenty years' time; will businesses or regulators demand higher standards in the future which are incompatible with the remediation that was implemented?
2. It is important to understand the commercial context of the remediation – should the remediation go 'above and beyond' the science-based or sustainable requirements?
3. Where it is 'unsustainable' to remediate, or the cost outweighs the environmental and societal benefits, stakeholders should be aware of, and able to understand, the risks and liabilities which may remain, or be passed on to future site owners and stakeholders.

ThS 4b.4: Socio-economic appraisal of remediation technologies and strategies

From eternal containment to a finite solution for a contamination of a Pinch Gas Factory, technical advances and a sustainability appraisal

Hans Slenders¹; Arthur Van de Velde; Mart Jansen; Johan van Leeuwen; Jan Gerritse; Gerhard Winters

¹ Arcadis Netherlands, NL

SITE

At the Railway station of Amersfoort in the Netherlands a Pinch Gas Factory has been operative until the 1950s. At the Pinch gas factory diesel was processed into gas and an oily, creosote like waste product. This waste product was initially dumped into open lagoons at the site. As a result a huge contamination of soil and groundwater with approximately 5000 tons of LNAPL and DNAPLs was caused. Nearly 15 hectares are contaminated, making this one of the biggest remediation sites in the Netherlands and challenge to bring to an end solution. In 2000-2004 the site was redeveloped, the top soil layers remediated and a funnel and gate[®] system installed with a bioscreen in the gate. Since 2007 SBNS (the Remediation Foundation of Dutch Railways) has been looking for a finite solution for this site. In 2015 things were speeded up because SBNS will cease to exist and responsibility for the site will be transferred to the Ministry of the Environment and Infrastructure. Both parties feel responsibility for sustainable land stewardship and invited Arcadis and TTE to develop scenarios and to structure the appraisal process towards a sustainable finite solution.

In this presentation we show the benefits of the clear sustainability appraisal and the innovative hydrogeological measure. This approach fits perfectly in a national initiative to bring all "everlasting" remedial projects to an end.

TECHNICAL

The contaminant situation is mainly characterized by a large amount of thin DNAPL layers that rest upon a clay/peat layer at 13 m depth. At some spots DNAPL is found until 28 m deep in the second aquifer underneath this semi continuous aquitard. Additional delineation of the hotspots had the risk of additional punctures and DNAPL mobilization. Recently it was proven that mobile oil components (mainly PAHs) were subject to natural degradation. The plumes indeed seem stationary, at least since 1995. The newly constructed funnel however seems to partly overflow and appears susceptible to changes in groundwater flow. The bioscreen consists of an airsparging curtain that needs continuous operation and monitoring and does not seem to be effective just above the clay layer.

SELECTION OF A PREFERENTIAL SCENARIO

In a series of meetings with a group of stakeholders of NS Vastgoed, Prorail, Municipality, the Ministry and competent authorities scenarios and sustainability indicators were discussed and selected. A process similar to NICOLEs Road Map or SURF UKs Framework. The tool of pairwise comparison and reduction of choices proved to be strikingly simple and robust. The basic scenario consists of bentonite walls that close the funnel at the top and diminish the outflow. The wall in the funnel opening starts at groundwater level, and the lower wall in the gate is only 3 m above the top of the 13 m deep clay layer, thus creating a threshold that reduces the flow of the highest contaminant concentrations. Although the basic scenario (2 mln€) is sufficiently protective, an additional scenario (4 mln€) was unanimously selected that in situ removes 80% of the contaminant load and is considered to be cost-effective because it also reduces long term uncertainty.

Socio-Economic Drivers and Inhibitors of the Nano-Remediation Technology in Europe – A Scenario Approach

Stephan Bartke¹; Nina Hagemann²; Nicola Harries³; Jennifer Hauck²; Paul Bardos⁴

¹ German Environment Agency, DE; ² Helmholtz Centre for Environmental Research UFZ, DE; ³ CL:AIRE; ⁴ r3 Environmental Technology Ltd.

In order to develop an exploitation strategy that considers the medium to longer term potential market development for nano-particle enabled remediation, any analysis has to deal with an uncertain future – in particular if it acknowledges beyond the technological also the socio-economic framework determining the acceptance and application of such a niche technology with a potential of broader market distribution.

This contribution identifies key factors that foster or inhibit the evolution of the market in Europe by 2025. A scenario approach has been used to help forecast potential market developments and, more importantly, to identify the key factors. The outcomes of such an assessment are utilisable for: “real-world” business development, deducing strategies for market activities; informing policy development; and/or informing regulatory authorities.

Scenarios are internally consistent stories about potential future states. The central idea of the scenario-based approach as applied within the EU FP7 co-funded NanoRem project has been to use stakeholder engagement formats to gain strategic market, regulatory and academic knowledge on how the market for nanoremediation in Europe could develop until 2025 – thereby identifying different plausible future states and key factors determining these future states and the decision points and disruptive elements in the development of these factors.

The scenario process included two specific expert workshops and several special sessions at European conferences. As a summary, the analysis highlighted that the existence of validated data on case studies is critical for market development – in particular if this information can be told as success stories. In addition, dialogue between the stakeholders (science – industry – policy – general public) is found to be crucial. Any new technology has to prove that it is complementing or improving existing technologies at an appropriate economic cost and acceptable risks. There are no absolute blocks to an uptake of nanoremediation in the markets, but documented, validated case studies and understanding the “operational window” of nanoremediation are found to be extremely significant. Research is seen by experts as a disruptive element as results can help to deliver the required validated information – however, academics must communicate these in an appropriate way to business and regulation.

The scenario assessment approach as yielded a wealth of insights into the diversity of factors influencing the potential market emergence of nanoremediation. In particular, it helped to conclude on the strengths, weaknesses, opportunities and threats of nanoremediation technologies general market value proposition and exploitability.

Land remediation strategy under uncertain context: how can Life Cycle Assessment help?

Marie-Noelle Pons¹; Jérémy Rodrigues¹; Antoine Gérard²; Marie-Odile Simonnot¹

¹ CNRS-UL; ² PROGEPI, FR

Life Cycle Assessment (LCA) is a valuable tool to assess the potential environmental impacts of a commodity or an activity, taking into account its complete life cycle. It can be used to improve the environmental performance of strategies of degraded land rehabilitation, by highlighting their potential trade-offs: the actions implemented to restore a brownfield may cause significant degradations elsewhere, because of the commodities they require and the waste they generate.

However, many methodological issues remain to be addressed for LCA to give a thorough picture of those strategies and trade-offs. Land remediation involves (1) a strong consideration of land use and land cover change (LU/LCC) and possible Land use change (LUC) and (2) often changes in the behavior/presence of organic or metallic pollutants. Both issues are challenging to assess because of the complexity of the ecosystem processes they involve. Furthermore, uncertainties and strong variability related to the life cycles of studied strategies also contribute to question the relevance of LCA to improve environmental diagnosis and performance.

These issues have been addressed in a two-steps procedure tested on a case-study: the LORVER project. This project aims at restoring degraded soil properties to allow non-food crop production by building a soil with byproducts of agronomic interest (compost, industrial sludge, excavated soil).

Firstly, for the phase of Life Cycle Impact Assessment, robust indicators were selected regarding LULCC: areas of natural landscape appropriation and land artificialization, which address two major irreversible damages, i.e. endemic biodiversity and loss in soil quality. Other indicators related to land occupation were used to assess the loss of ecosystem services (erosion regulation, freshwater purification and supply, soil carbon storage), based on the recommendations of the UNEP-SETAC.

Secondly, an uncertainty analysis was performed using Monte Carlo algorithms. Markers were assigned to the main parameters and flows in order to keep track of their contribution to overall impacts and to discriminate contrasted scenarios. The results were computed doing a Principal Component Analysis.

They confirmed the hypothesis that LORVER constructed soils maximize environmental benefits when they use significant amounts of materials that would otherwise be landfilled. When possible, materials with high organic carbon contents (sludge, compost) are best used in agriculture, because they are generally used closer to source and avoid agricultural inputs.

Further research will help assess the optimum composition of constructed soils under the constraint of proper rehabilitation.

Monetization coupled with Life Cycle Assessment compared to Cost Benefit Analysis: a site remediation case study

Lies Huysegoms; Valérie Cappuyns

KU Leuven, BE

Site contamination is a global concern because of the potential risks for human health and ecosystem quality. In Europe alone there are 340 000 potentially contaminated sites and this number is forecasted to increase even more by 2025. The huge amount of contaminated sites that will have to be remediated in the coming years has increased the attention for the secondary environmental impacts (i.e. the environmental impacts caused by the site remediation activities themselves) of the remediation. These secondary environmental impacts are also an aspect of the more holistic 'sustainable remediation' framework.

Every contaminated site has its own specific characteristics and the large range of potential contaminants, as well as the recent focus on sustainable remediation, resulted in new developments, and stimulated technological innovations. The increased availability and efficiency of techniques makes the final choice of remediation alternative increasingly complicated. Life Cycle Assessment (LCA) can support site owners and remediation companies in the choice between remediation alternatives, taking into account their secondary environmental impacts. LCA as such has also been used on several case studies to compare the secondary environmental impact of different alternatives but has been critiqued for being too complicated, time consuming, and data demanding.

This paper shows how, by following the ISO 14 000, 14 040 and 14 044 guidelines initially drafted for the development of a consequential LCA, an attributional study of the environmental impacts of a site remediation case study can be done more efficiently. The case study used for this purpose entails the soil and groundwater remediation of a tar, poly-aromatic hydrocarbons (PAH) and cyanide contamination of a school ground by a former gas plant. The remediation alternative chosen in this case study, after a cost and preliminary soil analysis, is excavation with off-site thermal treatment of the contaminated soil. The attributional LCIA is based on the data from the site remediation project, and modeled by using the Ecoinvent 3 database in SimaPro 8.2.0.0.

Secondly a societal Cost-Benefit Analysis (CBA) is performed on the same case study using the same data sources. The outcome of this 'traditional' CBA is critically compared to the outcome of different monetization methods, namely Stepwise 2006, Eco-cost, Ecovalue and Benefit transfer method which use the outcome of an LCA to calculate the monetary value of the environmental impact. This comparison uncovers and evaluates those elements that are not covered in the monetization methods but are essential for a monetary valuation. The usefulness of the different valuation methods in the context of site remediation is also assessed in order to come to an improved method for the monetization of environmental and health effects of site remediation.

A framework for remediation sustainability and socio-economic appraisal and a case study at a mega site in China

Deyi Hou; Yinan Song

Tsinghua University, CN

Sustainable remediation is a new movement in the remediation industry that has drawn much attention globally from both industrial practitioners and regulators in the last decade. However, there are many challenges for remediation professionals to incorporate sustainable remediation in real practice, especially for developing countries like China where the remediation industry is still in its infancy. The primary author is leading a task force to write China's first national technical standard on green and sustainable remediation. The task force consists of three top research institutes and two leading remediation companies in China. The proposed framework and the case study is part of the efforts in formulating the sustainable remediation technical standard for China.

The remediation market in China is only emerging but it has been growing exponentially over the last several years. It is expected to become one of the largest remediation markets in the World. A report by the Ministry of Environmental Protection in 2014 suggested that 16.1 percent of the nation's land has soil contamination. The government has realized the seriousness of land contamination, and vowed to give a high priority to remediation on the agenda. Due to the large scale of the issue and limited resource available, both policy makers and researchers have realized the importance of optimizing the allocation of resources in remediation. To this end, sustainable remediation can play an important role.

This presentation intends to discuss a framework that is proposed to assess the environmental, social, and economic sustainability in contaminated site remediation. The framework is specifically designed for the technological and social-economic context in China. The framework is applied to a mega-site in Southern China, where over one million cubic meters of contaminated soil are remediated by a variety of remediation technologies. Sustainability appraisal results as well as lessons learned will be shared in the presentation.

ThS 4c.2: Managing large scale industrial pollution

Towards a precautionary and sustainable approach in the management of industrial sites based on the Industrial Emissions Directive (IED)

Joerg Frauenstein

Umweltbundesamt, DE

Activities of industrial installations might cause serious pollution in soil and groundwater. Due to experiences with historic contaminated sites it is obvious how complex and expensive remediation measures of contaminated sites are. Therefore remediation requirements have to be reduced through a strict implementation of precautionary principles. Best Available Techniques References (BREF) and their advancements increase the standard of technical installations. As long as installations will be operated in line with existing regulations, the occurrence of soil and groundwater pollution are almost barred.

However, the avoidance of any contamination is much more sustainable approach than any sustainable remediation after site closure.

The IED took up this approach and highlighted this issue by introducing two new elements.

First a Baseline Report is required. The report should provide evidence and should provide reference for a possible obligation to return the site to the baseline situation. The operator of an installation must submit a baseline report together with the permit application documents, whenever relevant hazardous substances are present. Those documents have to compile all relevant data about substances and mixtures which are used, produced or released within the installation. With the final closure of an installation the competent authorities is obliged to compare the status describes in the baseline report with the current situation of the site.

Secondly, the competent authority has to decide about further obligations to the operator, in case of significant pollution within soil and groundwater. Then the operator has to bring back the site of installation to baseline conditions. However technical feasibility of such measures may be taken into account. In Germany an interdisciplinary working group was initiated in order to develop within guidance documents criteria and implementation rules for competent authorities, service providers and operators how to proceed in line with IED.

Beside the need for an overall methodology these IED requirements are peppered with a couple of challenges not really solved so far. The analytical detection and verification, the assessment, the appraisal of a significance of pollution especially for multicomponent installations are still a playing field of challenges for practical solutions.

The presentation will focus first on experiences and challenges concerning the practical implementation of the baseline report procedure in Germany. Further on a concept will be presented, how authorities should implement and assess the significant increase of pollution of soil and groundwater and about criteria and requirements to return the site to the baseline situation.

There are also highly demanding challenges in re-use of former industrial sites with historic contamination. The setup of practical and legally admissible criteria are important for the practical implementation. They will provide an essential step towards a more sustainable use of industrial and commercial sites and for the prevention and mitigation of new contaminated sites.

Innovative assessment of impacts from industrial activities on the groundwater body quality for improved regional groundwater management

Corinne Merly¹; Laurent Cadilhac²; Marc Moulin¹; Clément Doney¹; Romain Chartier³; Guy Fourniguet¹

¹ BRGM; ² AERMC; ³ DREAL, FR

Groundwater Directive 2006/118/EC (Daughter to Water Framework Directive 2000/60/EC) establishes specific measures in order to prevent and control groundwater pollution. It specifically requires to assess plumes originating from punctual sources such as those due to industrial activities, in order to check if they do not spread and degrade the chemical state of the groundwater bodies. In this context, BRGM (French Geological Survey) supported by the AERMC (Water Agency on the Mediterranean Rhone River basin) has developed an innovative methodology to assess the impact of industrial activities on the quality of groundwater body. This methodology has been tested and applied on the whole Rhone River basin which covers one quarter of France, five regions and thirty counties. The assessment methodology includes three phases: 1) Inventory of industrial pressures and identification of targeted industrial areas; 2) Assessment of groundwater quality body with respect to industrial contaminants; 3) Assessment of industrial pressures and their impact on the groundwater body. These phases result in technical factsheet on each targeted industrial zone and a proposition for groundwater quality status of each groundwater body of concern. Overall, 57 targeted industrial areas were selected and studied. The assessment of groundwater quality in these zones enabled to identify compounds or groups of compounds causing groundwater degradation. Sixty-five percentage of studied areas were impacted with contaminants (those being by order of importance metals, hydrocarbons, HVOCs and BTEX) originating from around 420 sites. An impact rate (None /local / wide) was attributed for each site / contaminant couple. This "pressure/impact" method enabled to combine industrial data and groundwater data and to give an unprecedented assessment of groundwater quality at the regional scale (contaminated land being mostly managed at the site level in France). It processed numerous groundwater data. The deployment of this innovative methodology at the Mediterranean Rhone River basin scale required a strong engagement with numerous stakeholders (local authorities, regional water agencies, etc.), which in turn fed in the project by providing data and their points of views on the regional-scale project results. The outcomes of this project were used by the AERMC to report groundwater state and quality (with respect to impact from punctual pressures) in compliance with the groundwater directive. The findings enabled to define priority areas where further innovative methodology on regional groundwater body management - encompassing eg multi-sources management, less stringent groundwater objective setting - is currently being developed.

Phytoscreening as a tool to delineate Cl-VOCs plumes and prioritize pollution management efforts for large scale and multisource sites

Sébastien Kaskassian¹; Loïc Yung²; Mathilde Ecoellan¹; Michel Chalot²

¹ Tauw France; ² Université de Bourgogne Franche-Comté, FR

The root system of trees explores the first meters of soil to take up water and dissolved minerals. During these processes, trees can also extract contaminants that are present in the subsurface either in the aqueous phase, dissolved species in pore water and groundwater, or in the gaseous phase, VOCs vapors that are solubilized in the pore water before entering the root system. The USGS has demonstrated that the uptake of subsurface contaminants by trees can be used as a proxy for pollution delineation, especially for chlorinated solvents (Schumacher et al., 2004). Sampling and analyzing protocols are available and robust (Vroblesky, 2008). Further research (Balouet and Chalot, 2015) showed that phytoscreening can be extended to BTEX, some PAHs and metals for soil and groundwater pollution characterization.

The potentially contaminated zone of the experimentation site covers about 30 hectares and is located on top of a shallow sandy alluvial aquifer. Trichloroethylene (TCE) has been used between the 40s and the 90s as a degreasing agent of reaction tanks. For safety reasons, the production was located in small buildings scattered throughout the site. The site operator has evaluated the presence of 24 potential TCE sources. The groundwater table is 2 to 4 m deep and trees are abundant, mostly oak, pine, poplar, acacia, and plane trees. Groundwater monitoring shows concentrations of TCE and metabolites, cis-dichloroethylene (Cis-DCE) and vinyl chloride, up to 140,000 µg/l in the shallow aquifer and indicates pollution transfer to the deeper aquifer. Due to the number of potential sources and the size of the site, phytoscreening was seen as a cost effective strategy to evaluate the Cl-VOCs presence in the subsurface and to help in the decision making about where to further investigate soil pollution.

In April 2016, a small-scale tree survey was implemented to demonstrate the applicability of phytoscreening: 39 trees were sampled over a 2 hectare zone where groundwater pollution was delineated in the shallow aquifer by the means of 20 micro-wells. The 'TCE+Cis-DCE' plume delineated by phytoscreening showed good agreement with the groundwater plume. A 30m grid resolution seemed acceptable to delineate multi-source plumes at a larger scale. In September, a strategy was designed throughout the entire zone: groundwater sampling of 25 monitoring wells, phytoscreening of 185 trees (both oak and poplar trees) with specific QA/QC protocols (blank and duplicate samples, temperature monitoring from field to the lab, etc.), and mapping by interpolating all available data (38 wells and 224 trees from different surveys). Out of the 24 potential sources, this second study revealed 8 plumes with elevated concentrations and 9 zones with no apparent pollution. The remaining zones showed indication of pollution with either lower concentrations or higher uncertainty.

For large scale multi-source sites, combining phytoscreening and groundwater sampling proved to be an efficient strategy to optimize pollution assessment in the subsurface and to plan and prioritize further characterization or remediation.

Industrial site in the east of France: an innovative technical proposal for managing a complex problem

Laurent JAY¹; Thierry Delloye²; Maxence Vermersch³; Christophe Bourdin¹

¹ GRS Valtech; ² SOLVAY; ³ MAVESA Environnement, FR

Context:

The industrial site is on a site where there was a thriving industrial and chemical activity for more than 115 years, on approximately 10 hectares of land. The main productions were dedicated to organic intermediates for pharmaceuticals, veterinary products, cosmetics, crop protection, etc.

With the activity closing down in 2007, the site is currently being refurbished for industrial or logistics usage. Like any industrial activity, and despite the environmental prevention and protection measures deployed throughout the history of the site's activity, the land has suffered historic soil pollution.

An innovative technical proposal for managing a complex problem

For treating the various site zones impacted by the site's industrial activity, GRS Valtech recommended the implementation of soil treatment via SVTE (Soil Venting Thermal Extraction).

GRS Valtech has a European patent pending for this process. SVTE processing consists in heating the soil in the contaminated zones to a temperature causing the vaporisation pressure of the pollutants to rise sufficiently so as to facilitate their extraction by venting. Under the effect of the heat produced in this way, the pollutants are turned into gas which is then captured in a series of intermediate extraction wells to be treated by means of various processes (condensation, catalysis, photo-oxidation, scrubbing, activated carbon, etc.) depending on their nature, their initial concentrations, the time scales and the volumes of materials in place to be processed.

The strong points of this process reside in:

- Limiting noise pollution (no excavation and landscaping work) and nuisance odours
- Shorter processing duration than for traditional in-situ techniques
- No earthmoving, limiting the potential risk of traffic accidents
- Favourable environmental credentials (no transporting material off-site)

As part of the industrial site refurbishment project in the east of France, in order to best optimise the processing of the soil via SVTE, GRS Valtech instituted a pilot zone to the west of the site. Here, on an area of 270 m², 103 heating wells and 37 extraction wells were deployed. The processing was conducted per sector with 37 heating points simultaneously, for an approximate duration of 2 months. The global duration of the processing was around 8 months (excluding the preparation, installation and installation dismantling periods).

Over all the zones to be processed, situated to the east of the site, in addition to the pilot zone, 685 heating wells and 264 extraction wells have been deployed over an area of 2170 m².

The processing is again conducted per sector, with 99 heating points installed simultaneously for an approximate duration of 2 months heating per sector for a global processing duration estimated at 14 months (excluding preparation, installation and installation dismantling periods).

The project began in June 2015 and is scheduled for completion in late 2017.

Null-space Monte Carlo particle tracking to assess groundwater PCE (tetrachloroethylene) diffuse pollution in North-eastern Milan Urban Area

Loris Colombo¹; Luca Alberti¹; Giovanni Formentin²

¹ Politecnico di Milano; ² Tethys srl, IT

The Italian Law 152/2006 adopted the EU Water Framework Directive which entrusts the Regions with the task of identifying areas subjected to groundwater diffuse pollution and to assess their level of contamination. In urban areas, the sources of groundwater contamination can be classified into two different categories: point sources (PS), which are identified areas releasing plumes of high/very high concentrations (hot-spots) and multiple-point sources (MPS) constituted by a series of unidentifiable small sources clustered in a large area, generating diffuse contamination. The latter category predominates in European FUAs and cannot be managed with standard remediation techniques such as those conceived for large/medium contaminated sites, mainly because of the difficulty to identify the many different source areas releasing small contaminant mass. Consequently, the standard techniques are not economically sustainable and often fail to provide results in an acceptable time frame. Due to the European relevance of the topic, the EU project AMIIGA (Interreg. Central 2016-19) has recently ongoing with the aim to set up a common methodology to assess multiple point diffuse groundwater contamination in highly undetermined settings.

Due to the uncertainty related to the exact position and intensity of MPS, a numerical model (MODFLOW) was implemented in a pilot area in the North-Eastern sector of the Milan. The proposed methodology allows to consider the uncertainty linked to the contaminant mass released by unknown sources in groundwater. Moreover, it provides the means to identify the areas not directly interested by plumes and mainly connected with a diffuse contamination. Using the inverse calibration code PEST, a model was calibrated representing the hydraulic head surveyed in May 2014.

This was then used as input to a statistical process based on the Null-Space Monte Carlo (NSMC) method, which allows to generate unlimited sets of hydraulic conductivity fields, all respecting the measured head targets. Considering the effect of hydraulic conductivity heterogeneity in the spread of PCE, using MODPATH and placing the particle starting points where a PCE measurement is available, a backward run was done, by considering only those targets with concentration higher than 10 µg/l (higher than drinking water threshold Italian law for PCE). 400 backward runs were performed starting by a stochastic set generated by the NSMC procedure and minimizing the objective function (composed by the head targets in monitoring wells). Collecting the particle positions in each cell for the 400 realisations and dividing the analysis for unconfined/confined Aquifers, results highlighted the cells crossed by a high number of particles, which are an indication of potential sources position of PCE to be verified by field survey.

The new assessment method, incorporating probability into the forecast, was investigated to support Public Authorities in programming investigation aimed to locate areas where unidentifiable small contamination sources are clustered. Mathematical models within a probabilistic framework prove a powerful tool for planning of groundwater management.

ThS 4c.3: Strategies for managing large scale pollution

The Act on Environment and Planning - instruments for local integrated soil management

Michiel Gadella

Rijkswaterstraat, NL

The Act on Environment and Planning

Legislation in The Netherlands consists of dozens of laws and hundreds of regulations for land use, residential areas, infrastructure, the environment, nature and water. Each has its own starting points, procedures and requirements. This makes the legislation too complex for the people who have to work with it.

The Dutch Government wants to simplify the laws on the environment and planning and combine them in a single Environment & Planning Act (E&P Act). The A&P Act will replace 23 laws, including the Soil Protection Act.

The aim of the E&P Act is to make it easier to start up projects, for example, the construction of housing on former business parks. The instruments introduced by the A&P Act will provide municipalities the democratic tools for stakeholder participation and multidiscipline integrated decisions on spatial and environmental developments.

Dealing with Soil contamination

Incorporation of the Soil Protection Act in The E&P Act will result in the loss of specific instruments for dealing with contaminated sites. An important precondition for transferring the Soil Protection Act into the integrated E&P Act is the Dutch goal to remediate all urgent sites before 2020. When all urgent sites are remediated, legislation on the inventory, selection and remediation of urgent sites can be withdrawn. Soil contamination will however still be an issue but will be just one of the aspects that have to be taken into account when an initiative for a development is taken.

In the E&P Act the initiator – for example the developer of a housing project – and not the contaminated site will be the focus point of the regulations. The aim is that remediation of contaminated sites is fully integrated in the development of brownfields and residential areas. General rules for dealing with contaminated soils in building projects will make a development more predictable in advance. Municipalities will be granted the opportunity to deviate from these general rules in order to further stimulate development or protect the environment.

Instruments for local integrated soil management

One of the key designing principles of the E&P Act is the principle of decentralisation. Decisions on spatial planning and the environment are best made at the level of the municipalities. In order to operationalise this designing principle the E&P Act introduces two key-instruments for municipalities: The municipal vision and the municipal plan on environment and planning. In the vision the municipality describes in close collaboration with stakeholders which ambitions the municipality has on different societal goals, for example on climate adaptation or on redevelopment of brownfields. In the plan the municipality sets down the local legislation which is needed for implementing the vision.

The full article and presentation will provide an outline of the soil regulations in the E&P Act, will address the progress on the remediation of urgent sites and will emphasize on the opportunities for municipalities to operationalise the contribution of the soil-water system for the societal goals in their municipal vision and plan.

COCOON: Consortium for a Coherent European Landfill Management Strategy

Jan Frank Mars¹; Fons van de Sande

¹ Rijkswaterstaat, NL

Since the onset of the Industrial Revolution Europe has been disposing waste in landfills. Historically, these 150,000,500,000 EU landfills were developed without any consideration of their potential neither to pollute nor to valorise. Enhanced Landfill Management and Mining (ELFM²) can provide for a substantial part of the EU's material, energy and land needs, while avoiding environmental and health problems. Production of secondary raw materials, as well as land recovery will be increased while future environmental hazards can be avoided. The Netherlands participate in the Interreg project COCOON to develop, integrate and improve relevant policy instruments for ELFM².

Objectives for the Netherlands:

- Policy will be formulated to determine the location of the landfill sites, categorise them and research the possible environmental risks of the sites. Potential environmental risks, especially risks for the groundwater bodies, will be addressed. Control measures and monitoring is needed to prevent leaching from former landfill sites. Our goal: In 2020 all groundwater contaminated sites have to be remediated or in control;
- The Ministry of Infrastructure and the Environment developed policy instruments such as the programme VANG (from waste to useful materials). With this project we can participate with the Circular Economy Package of the EU, which includes revised legislative proposals on waste to stimulate Europe's transition towards a circular economy. With the Circular Economy it is stimulated to re-use rare raw-materials. Our goal: To obtain a reduction of waste dump of 50% in 2022 relative to 2012 ;
- Space is limited in the Netherlands, therefore landfill management policy instruments are needed to stimulate release of space, social development and protection of the environment. Our goal: We will start a pilot about landfill rehabilitation;
- What legal and financial instruments are needed for a good business case in a circular economy? Our goal: Evaluation and update of the aftercare paragraph of the Environmental Protection Act, the regulations for soil- and groundwater protection in the Dutch landfill directive (Stortbesluit);
- For the operational landfill sites and for future landfilling sites, innovative landfill management will be stimulated and monitored for a period of 10 years. Our goal: Reduce negative environmental effects and a reduction of costs.

Sharing knowledge:

For the Netherlands one of the main investment priorities is promoting a resource-efficient economy by investing in innovative technologies enhancing energy efficiency and the increased use of renewable energy sources. Innovations by top sectors for smart specialization in high-tech systems and materials are essential. For this project central government, provinces, local public authorities, knowledge institutes, companies and public (the quadruple helix) uses its growth potential via cross-overs.

The presentation:

How does the quadruple helix enlarge sectoral thinking? How are innovations stimulated and implemented into actual policies? How do cross-overs work in practice? And what can we learn from our audience?

Monitoring, risk assessment and remediation of pulp and paper fiberbanks and fiber-rich sediments in the Northern Sweden

Lijana Gottby¹; Johan Norrlin¹; Sarah Josefsson¹; Olof Larsson¹; Lovisa Zillén Snowball¹; Anneli Persson²; Linnea Melin³; Anna Löfholm⁴; Karin Jönsson⁵; Emelie Haglund⁵; Veronica Lundgren⁶; Anna-Karin Johansson⁶

¹ The Geological Survey of Sweden (SGU); ² County Administrative Board of Norrbotten; ³ County Administrative Board of Västerbotten; ⁴ County Administrative Board of Jämtland; ⁵ County Administrative Board of Västernorrland; ⁶ County Administrative Board, SE

Pulp and paper fibers were discharged to the aquatic environment mainly by these industries up until the 1970's in Sweden. Anthropogenic fiberbanks and fiber-rich sediments are present, especially along the coast of northern Sweden as well as inland waterbodies such as lakes and rivers. These organic-rich sediments are oxygen-poor and thus unfavorable for biota. In addition they may contain high levels of toxic pollutants that could spread and which might negatively affect the surrounding aquatic environment.

17 study sites in northern Sweden were selected and investigated in a three-year project financed by the Swedish Agency for Marine and Water Management. Eleven of these sites were located on the coast and six in lakes and rivers. The project was collaboration between five northern administrative counties and the Geological Survey of Sweden (SGU).

The project goals:

- 1) To identify levels of environmental contaminants, and the material and chemical properties of the paper and paperboard fiberbanks and fiber-rich sediment.
- 2) To classify risk level of the identified fiberbanks with a new methodology for inventory and classification of contaminated sediments.
- 3) To present a proposal for action plan including discussion on remediation alternatives for a number of fiberbank pilot- by each county.

SGU carried out the monitoring and assessment of contaminated sediments using a combination of advanced hydroacoustic measurements and sediment sampling in areas where the distribution of fibre-containing sediments on the bottom surface could be interpreted. In total, an area of 80 km² was surveyed and eleven fiberbanks were found in eight of the investigated areas. The fibre banks cover a total surface of approximately 1 km². In addition, fiber-rich sediments with a total area of approximately 12.5 km² were defined.

In total 147 sediment samples were analyzed for their contamination levels by number of organic pollutants such as for example dioxins, DDT, PAH, PCB and metals. The results from chemical analysis showed high levels of both groups of pollutants in several of the investigated areas. Different areas had different pollution-patterns that could be explained by historical information from pollution sources such as paper industry in the areas of investigation.

The outcome of the project has increased the knowledge of fiber-containing sediments in northern Sweden in the form of monitoring data on the areas of fiberbanks and fiber-rich sediments and levels of contaminations at the investigated waterbodies near the large scale industrial pollution with historical and ongoing pollution from large scale industrial pollutants.

Combined with the first practical application of a risk classification model for sediment, the project has taken a step forward in the long-term work of dealing with contaminated sediments. In addition, the knowledge of how fibers are spread and deposited has increased. These experiences will be of value when continuing the inventories of contaminated sediments, risk assessment and discussions for alternatives for risk reduction in the future for use policy makers at the governmental level, by regional authorities and by industry.

Assessment and Strategic Management of Australia's Longest PFOS Groundwater Plume

Rachael Casson

AECOM Australia, AU

Background

The Army Aviation Centre Oakey (AACO or Base) occupies an area of approximately 850 hectares and is located on alluvial floodplains on the northern side of the town of Oakey in Queensland Australia. Land use in Oakey and surrounds is dominated by agricultural activities. Military operations have variably impacted soil, groundwater, surface water and sediment at the AACO. The use of Aqueous Film Forming Foam (AFFF) may have contributed to a 4-5 km long plume of dissolved phase perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in the heavily-utilised groundwater resource residing in the Oakey Creek Alluvium (OCA) aquifer. The OCA is a sub-aquifer of the Australian Great Artesian Basin (GAB), which is one of the largest groundwater basins in the world.

Activities

Groundwater use on Base has been discontinued and a precautionary recommendation against drinking groundwater applies across potentially affected properties in the Investigation Area. Concerns have arisen in the community regarding potential health effects and economic impacts associated with the identified PFOS and PFOA impact.

Defence has undertaken proactive management actions at Oakey in response to the discovery of PFOS/PFOA impact. In particular the development of strategic management initiatives to guide Defence's management of the impact sourced from the Base and the management of the associated health, community, and environmental impacts in the immediate, short, medium and long term. These strategic initiatives provide an overarching clear strategy on a multitude of issues which are supplementary to contamination. The initiatives specifically: Identifies a pathway toward maintaining legislative compliance; Ensures management actions are prioritised to address identified levels of risk; Ensures management actions are co-ordinated and undertaken in a logical sequence; Allows Defence to plan its budget commitments over the short to long term; Provides consistent messaging; and can be used for internal and external communication.

Results/Lessons Learned

Staged and multi-disciplinary assessment has been conducted to inform management decisions and includes, AFFF concentrate, soil, sediment, surface water, groundwater, concrete, animal and plant testing, ecological assessment, human health risk assessment, hydraulic and solute transport modelling. Implemented management activities include: installation of spent AFFF solution recovery tanks; treatment of Base pool water; construction of a purpose built training ground and implementation of a policy of 'no AFFF use' during training; verbal and precautionary advice to "Do Not Drink Groundwater Sourced from within the Investigation Area"; Cleaning of residential water tanks and swimming pools (including replacing filters) and provision of clean water for domestic purposes in instances where there is no other available source; stakeholder engagement; and source zone control and water treatment pilot trials. Lastly, Decision Trees have been developed to inform decision makers as to who qualifies for the provision of alternate water supply, tank and pool cleaning.

Land use effect on nitrate storage and transport through unconfined Chalk aquifer

Géraldine Picot-Colbeaux¹; Dominique Thiéry¹; Nicolas Devau¹; Josse Marine²; Nicolas Surdyk¹; Hubert Péru³; Marie Pettenati¹; Marc Parmentier¹; Laurent André¹

¹ BRGM; ² SIEP du Santerre; ³ AGROSOL, FR

Chalk aquifer is the main water resource for domestic water supply in many parts in northern France. In this region, groundwater is frequently affected by quality problems concerning nitrates. Often close to or above the drinking water standards, nitrate content in groundwater is mainly due to historical agriculture practices, combined with aquifer recharge through the vadose zone. The complexity of processes occurring into such an environment leads to combine a lot of knowledge in agronomy, geochemistry and hydrogeology in order to understand, model and predict the spatiotemporal evolution of nitrate content and provide a decision support tool for the water producers and stakeholders. To succeed in this challenge, conceptual and numerical models representing accurately the Chalk aquifer specificity will be developed, including a multidisciplinary approach to simulate storage and transport from the ground surface to the underlying groundwater. This involves a new agronomic module "MONICA" (MOdelling Nitrates transfert taking into account Crops and Agricultural practices), a soil-crop model calculating the nitrogen mass balance in arable soil, integrated in the 3D transient groundwater numerical code "MARTHE". This approach integrating existing multi-disciplinary tools is a real challenge. It enables to decrease the number of calibration parameters by selecting the relevant equations and simplifying them without altering the signal. The numerical development is applied on a 2D vertical cross-section in the vadose zone representing experimental nitrate vertical measurements in soil profiles (0-22 m depth) in the Somme region (France). The experiment results highlight the land use management effect on nitrate evolution into the vadose zone (e.g. forest instead of crops). Simulations constrained by climate forcing, land use and nitrogen inputs over several decades reproduce the nitrate spatial and temporal distribution. This approach will be ultimately used to model in 3D the drinking water catchment area. It will be calibrated using nitrate contents time series of nitrate content measured in the domestic water pumping well available since 1995 (field in northern France – Avre Basin region). This numerical tool will help the decision-making in all activities in relation with water uses.

ThS 5a.2: Brownfield regeneration

Sustainable redevelopment of a complex industrial real estate portfolio – a holistic approach

Dirk Nuyens¹; Patrick Charbonnier²

¹ ERM France; ² ArcelorMittal Real Estate, FR

Optimizing the real estate portfolio and managing the environmental liabilities are key business drivers in the current economic situation. ArcelorMittal's portfolio is a rather complex one, it covers various countries with each of them having their specific local regulatory setting (and implementation) for cleaning-up the historical subsoil impacts. Both active manufacturing sites (including steel and coke plants, ...) and mining operations, and additionally mothballed brownfield sites (having had decades of heavy industrial activities) awaiting redevelopment make part of the portfolio. In order to apply a coherent approach across its real estate portfolio both in provisioning and cleaning-up and/or redevelopment ArcelorMittal has developed a holistic strategy to pro-actively manage its assets.

The backbone of ArcelorMittal's holistic portfolio management strategy consists of the following basic principles that are currently deployed on its real estate projects:

- The development of a detailed Site Conceptual Model is a crucial phase, it should be based on reliable historical information, a good understanding of the (hydro)geological conditions, a clear definition of the (potential) receptors, the subsoil impacts and the exposure pathways
- Sustainable redevelopment should always be at the core of any project, when doing site characterization, delineation and risk assessment works, or when looking into subsoil impacts that require remedial measures (both active and passive) or the application of usage/deed restrictions ;
- Residual impacts should be able to remain in place as long as they do not trigger any (potential) risk for human health and environment both through exposure to receptors or leaching into the environment;
- Clean-up strategies should be applied within the BATNEEC (Best Available Technologies Not Entailing Excessive Costs) principle, and the reuse of impacted materials (incl. dismantling) within a specific redevelopment project should get priority;
- Synergies should be created with the redevelopment project and this includes all works related to decommissioning, dismantling and demolition of former industrial facilities;
- Financial modelling and provisioning should be done at any stage of the project. The use of probabilistic modeling with Monte-Carlo should be considered over single-point estimates as it captures better the uncertainties related to the subsoil conditions and to project definitions during the lifecycle of the redevelopment/clean-up projects. This modeling needs to be refined during the lifecycle of the redevelopment project as environmental liabilities and real estate value might change during due course;
- Finally it is key to approach the stakeholder engagement in a pro-active way in order to obtain and maintain the 'license to remediate/redevelop'.

Some selected case studies will be presented at the AquaConsoil 2017 conference to illustrate ArcelorMittal's holistic approach for pro-active portfolio management discussed above in more detail.

A Conceptual Site Model for the Sustainability of Brownfield Regeneration for Soft Reuse: A Case Study of Port Sunlight River Park

Paul Bardos¹; Xiaonuo Li; Euan Hall; Sarah Williams; Andy Cundy; Weiping Chen

¹ University of Brighton, Brighton, UK, r3 Environmental Technology Ltd., GB

The aim of this project has been to understand the economic, environmental and social benefits of transforming a brownfield site into a public open space and managing it long term. Port Sunlight River Park, a 28-hectare park on the Wirral, is being used as the case study for this research. Port Sunlight River Park (PSRP), a 28-hectare park on the Wirral, was transformed, by the Land Trust, from a former landfill at Bromborough Dock into a public green open space with £3.4m allocated for the site restoration, park creation and ongoing management. The park, which opened in 2014, provides visitors with a scenic waterfront and a variety of walks whilst a section of wetland to the north of the site, along with River Mersey mud flats is already an important site for large populations of water birds and is a site of special protection. To understand the links between PSRP and overall wider benefits bringing together environmental, societal and economic considerations, a conceptual model for sustainability assessment based on SuRF-UK framework was developed to identify the services / benefits delivered by land regeneration for a park compared with a possible baseline situation of no Land Trust involvement and the land fill continuing to be managed in a basic way by the waste management company responsible for it.

The project was a co-operation between University of Brighton and the Chinese Academy of Sciences who supplied a student on a one year secondment who carried out the research over 2016.

We carried out a comprehensive qualitative sustainability assessment against the base line using the SuRF-UK methodology. We then extended this assessment to look at individual sustainability linkages to build a more explicit site conceptual model for sustainability which could be more readily valued. We have reviewed a wide range of possible valuation techniques and assigned these to individual linkages on the basis of best fit. However, we have not carried out quantitative evaluations as, while the baseline scenario is sufficient for a qualitative assessment, there would be significant difficulties in collecting the necessary evidence to support quantitative assessments for a number of linkages. Nonetheless we have provided Land Trust with a qualitative understanding that is rigorous and wide ranging and shows a wide range of sustainability compared with Land Trust not having intervened. Our work complements existing social return on investment studies Land Trust have carried out for the site, and identifies how a more robust and wide ranging sustainability assessment could be made and valued in the future.

Assessing the Age, Location, and Vapor Intrusion Potential of VOC Sources Beneath Large Buildings

Craig Cox

Cox-Colvin & Associates, Inc., US

The ability of the environmental professional to accurately assess the age, location, and vapor intrusion potential of VOC sources beneath large buildings is constrained by the time and cost of installing typical sub-slab vapor points, collecting and analyzing soil-gas samples by standard methods, and obtaining a site's history of VOC use from site personnel having first-hand knowledge. Recent advancements in the vapor intrusion field have significantly streamlined and improved the assessment process. Through the use these new advances, the environmental professional can complete a thorough and accurate assessment of sub-slab vapor conditions in less time and at a lower cost. Information generated by an accurate assessment can then be leveraged using GIS applications to increase the understanding of a VOC source's age and the potential release mechanism.

The presentation will discuss: the historical production and use of chlorinated solvents; standard disposal practices prior to the adoption of environmental regulations; reasons why interviews with site personnel (if available) may cause the environmental professional to focus on the wrong areas; reasons why streamlined methods are cost effective means of improving data quality, data density, and the understanding of vapor intrusion potential. In addition, the presentation will demonstrate how GIS methods can help the environmental professional develop a more accurate understanding of the age, location, and release mechanisms that resulted in the VOC sources.

The discussion presents three case studies of large former manufacturing facilities (up to 22,000 square meters) that had been active as early as 1880. At least one of the sites had a long documented history of chlorinated solvent use. In each case, the use of high quality, rapidly obtained, active sub-slab soil gas measurements obtained from narrowly spaced grid systems (7 to 10 meters between points) provided information necessary to locate VOC sources. Information obtained from the grid sampling was also used to estimate the potential age, strength, lateral variability, and potential for vapor intrusion. In one case, using the methods presented, a dense non-aqueous phase liquid (DNAPL) associated with releases in the 1950s was identified at a depth of 5 meters beneath the building slab.

Field activities associated with the assessments, which are typically completed within a week or less, can result in datasets consisting of as many as 200 separate sub-slab soil gas locations. Screening data obtained using common hand-held instruments allows these assessments to proceed very efficiently and cost effectively. The results of the screening assessments help to focus subsequent investigations. Evaluating the results of screening data and analytical data in a GIS application helps to bracket age of the releases, locate preferential pathways for soil gas migration, and design vapor mitigation systems.

Embedding Sustainability During the Implementation of Remedial Projects

Cecile Rao¹, Paulo Valle²

¹ Consultant, ERM Belgium; ² Technical Director, ERM EMEA, BE

Nowadays sustainability is highly ranked on the global trendy topics billboard. However, despite of multiple efforts the implementation of sustainability-driven approaches during management of contaminated sites remains limited, often still seen as an additional cost rather than a favorable outcome.

Step by step, ERM is embedding sustainability in the implementation of Contaminated Site Management (CSM) projects, aiming for a balance between the works to be performed, the regulatory drivers, and the potential achievable sustainable outcomes.

This paper will present two sustainability assessments that were performed by ERM during the implementation of remediation projects performed in Belgium. With the support of specific monitoring tools, Health and Safety (H&S) observations and CO₂ impacts have been continuously monitored, assessed and discussed on a weekly basis throughout the remedial works. During the process, the monitoring tools as well as the remedial works were revised and adjusted where possible.

These dynamic sustainability assessments allowed to characterize the magnitude and distribution of the project impacts during the execution of the works, and to identify specific key factors which could improve environmental and social factors during project execution.

On a broadened horizon, communicating results and findings is crucial to increase the general understanding of the benefits of implementing sustainable approaches. ERM will continue to replicate these assessments on the execution of new projects, starting from planning and design stages.

Our goal is to support the development of diversified tools (to cover new techniques, well-being, communication, etc.) in order to increase stakeholders engagement on sustainability aspects. All together these contribute to further embed sustainability in a practical and balanced manner in CSM projects.

Ground gas risk assessment and mitigation in new buildings: practical application in a UK context.

Hannah Lewis

Ramboll Environ, GB

Following several high profile landfill gas explosions in the UK and US in the 1980s (including the 1986 Loscoe incident in Derbyshire), ground gas monitoring, assessment and mitigation have increasingly been considered an important aspect of contaminated land management and remediation in the UK.

It is well accepted that the commercial landfilling of waste can generate significant amounts of ground gas. However other human activities, such as deposition of made ground and infilling of features (such as ditches and ponds) with organic material can also create ground gas sources. Hazardous gases including, but not limited to, carbon dioxide and methane are produced by the natural degradation of organic matter. Methane is flammable, and if present at high concentrations in the presence of oxygen can represent a fire or explosion risk. Carbon dioxide can accumulate in properties and can cause asphyxiation and other physiological effects. It is not only the degradation of organic waste that can result in hazardous gases; soil and groundwater contaminated with hydrocarbons and solvents, can pose a risk to humans through volatilisation or as a result of degradation. The presence of former coal mine workings may present a risk, and some hazardous gases, such as radon, may be present naturally.

When assessing ground gas risks to a building, the hazardous gas concentration, the gas flow rate, and the sensitivity of the building are all taken into consideration. The assessment of risks from gas is based on the source-pathway-receptor approach, and in order to mitigate a ground gas risk, migration and exposure pathways must be broken. Whilst this can involve source removal, the focus of this presentation is on the installation of physical barriers.

Within the UK regulatory framework, substantial guidance has been published on the monitoring, assessment and mitigation of ground gases. The presentation will include practical examples of:

- Monitoring (including sampling spacing, frequency and methodology)
- Assessment (including a simplified semi quantitative assessment)
- Mitigation Design (selection of appropriate gas mitigation measures, taking into consideration the use of the site and its sensitivity)
- Implementation and Verification (including the competence of installers of gas protection measures, and the type and extent of verification inspection)

This presentation will provide an overview of the UK approach to the risk management of ground gas in buildings, and will consider how the approaches differ across countries.

ThS 5a.3: Regeneration of brownfields and agronomy

Combining soil construction engineering and agronomy to value derelict industrial wastelands

Robin Dagois¹; Geoffroy Séré¹; Apolline Auclerc¹; Damien Blaudez²; Frédéric Darboux³; Noële Enjelvin⁴; Lucas Gossiaux⁵; Sophie Guimont⁵; Jean-Louis Morel¹; Frédéric Rees⁶; Marie-Odile Simonnot⁷; Christophe Schwartz¹

¹ Laboratoire Sols et Environnement; ² Laboratoire Interdisciplinaire des Environnements Continentaux - LIEC; ³ Biogéochimie des Écosystèmes Forestiers / Laboratoire Sols et Environnement; ⁴ Groupement d'Intérêt Scientifique sur les Friches Industrielles; FR

Since several decades, the outbreak of large areas of derelict wastelands has challenged researchers and stakeholders to develop innovative reclamation processes. Among them, land management, via soil construction, has gathered particular interest to bring value of impacted - and potentially contaminated - surfaces. Not only, soil construction gives the freedom to re-create fresh and efficient agro-eco- systems, but it can also be used to provide economic value to the damaged ecosystems. Moreover, soil construction can be managed by implementing unwanted industrial by-products into the process. To experiment these valorization procedures, several team from the Lorver research program associated to manage a large scale study on a former industrial site via (i) soil construction with industrial by-products and (ii) agricultural practices on the freshly constructed soils. The main objective is to understand the evolution of a diverse set of indicators (pedogenesis, agronomy, mesofauna colonization and surface structure) to validate the conversion of recently associated materials into fully functioning agro-systems.

For this, two plots (1 and 1.5 ha) were set up in august 2016 on the former coking plant site of Homécourt (GISFI experimental facility) dedicated to fiber (hemp, nettles) and wood economic valorization (with a first culture set in spring 2017). The soils consist of association of industrial by-products materials (paper mill sludge, river sediments, bioremediated soils and compost) to mimic natural/agricultural soil structure, chemistry and functions. To assess the effect of time on these newly constructed Technosols, high frequency sampling and analysis was performed in the top soil consisting in agronomic and geochemical characterization and surface structure analysis (Landscape Function Analysis). Early results show that constructed soil depicts similar properties as agricultural standards: slightly alkaline pH (8); quite sufficient N and C content for organism's activity (1-2 g kg⁻¹ and 15-30 g kg⁻¹ respectively) supported by an intermediate value of cationic exchange capacity (10 – 12 cmol+ kg⁻¹). Content in CaCO₃ (> 100 g kg⁻¹) and in exchangeable cations (K: 0.7 – 1.5; Ca ech: 13 – 18 and Na: 0.4 – 0.7 cmol+ kg⁻¹) will be further tools to assess pedogenesis fluctuations. LFA shows a progressive increase in soil stability (linked with more resistant soil aggregates and a progressive crop cover) but stagnation in infiltration over the first three months (August – November). Soil mesofauna (springtail) colonization is non-existent during the studied time period. These results will serve as a strong reference and "initial state" for the upcoming monitoring of this large scale device. Overall, they will support the possibility to convert former industrial sites into fully functioning agricultural landscapes.

Sustainable management of brownfield sites: the LORVER project

Sophie Guimont¹; Marie-Odile Simonnot; Geoffroy Séré; Lucas Gossiaux; Jean-Louis Morel

¹Valterra Depollution Rehabilitation, FR

In the context of circular economy, degraded sites and organic and industrial wastes can be considered as resources. In the absence of short-term development project, former industrial sites may turn into abandoned land. These areas could be used to grow non-edible biomass for industrial purpose. However, these soils that have generally been cleaned up have a low fertility. The construction of new Technosols, using urban wastes and industrial by-products has proved pertinent for the restoration of derelict lands and waste recycling (Séré et al., 2008; Rokia et al., 2014). These soils are able to supply with many ecosystem services, especially provisioning and regulating services (Morel et al. 2015).

The LORVER research project aims at demonstrating the interest of growing biomass on constructed Technosols, in order to produce energy, fibres and possibly metal products. This project involves a consortium of 4 companies and 5 labs of the Lorraine region (France). The main challenge of the program is to develop ecosystemic service chains leading to sustainable redevelopment of brownfields while allowing industrial use crop productions and its promotion.

The objective of the present contribution is to give an overview of the LORVER project. This project is organised in 5 work packages. The first one focuses on identifying resources (sites, amounts of wastes and industrial by-products) as well as regulation issues. The second one is dedicated to pedological engineering for soil construction. The third one deals with plant cultivation. The fourth one aims at producing energy and biochar by pyrolysis, fibres and metal compounds. The last one is devoted to the environmental assessment and the techno-economic study of the LORVER chain.

Industrial wastelands and usable waste deposits have been identified in the Lorraine region. Large experimental plots of 2 ha of constructed soils have been implemented on the site of the GISFI scientific group, former steel making plant. Technosols of one meter thick composed with bioremediated industrial soil, papermill sludge, dredging sediments and sewage sludge compost were set up. Besides, cultivation of energy crops and hemp has been investigated on constructed soils as well as cultivation of nettle and hyperaccumulator plants. Energy and biochar production by pyrolysis has been investigated from the lab to the pilot scale, as well as fibre production.

Moreover, the impact of the LORVER chain on the environment has been studied, e.g. its impact on biodiversity. To finish, a life cycle assessment has provided clear conclusions on the effects of the chain and has provided the conditions at which this approach is pertinent.

Rokia et al. 2014, *Waste Management* 34:2155-2162

Séré et al. 2008, *J Soils Sediments* 8:130-136.

Morel et al. 2015, *J Soils Sediments* 8:1659-1666

An effective method for regenerating and upgrading the use of a large surplus contaminated land area

Fouad Abo

GHD Pty Ltd, AU

Background/Objectives

Few hundreds hectares of a surplus brownfield area were impacted by long term (>100 years) use for soil and grass filtration treatment of sewage.

The area is becoming a surplus due to advanced sewer treatment technologies. It now encroached residential area, and hence, capitalising on a higher value land use, the owner is proposing to assess higher potential uses of the land (e.g. recreational, residential, eco-tourism, etc.).

This study looked at different methods of generating a high value future land reuse(s). The review of the soil and groundwater contamination data indicated that the most effective method is to use human health and ecological risk assessment (HHERA) as a tool to assess whether the existing soil contamination in the land presents an unacceptable risk to potential sensitive receivers and, if so, what control measures (including remediation) would lead to generating a higher value of this brown field area including conserving its ecological and historical values.

Key chemicals of concern identified included:

- Dioxins & furans exceeding the Human Health criteria (presented as Toxic Equivalent to 2378-TCDD);
- Metals (including cadmium, chromium (total), chromium (hexavalent), copper, mercury, lead, and zinc); and
- Dieldrin, DDT, PBDE (fire retardants), and PFCs (PFOS, PFOA).

Soil properties were also characterised to assess bioavailability and phyto-availability.

Approach/Activities

Based on a comprehensive contaminants fate and behaviour, linked with soil characteristics and exposure scenario, a risk based approach was decided upon as the approach to assess the potential of generating a high value land uses. Of particular importance for selecting this approach was the significance of the land area and the potentially huge cost and ecological disturbance of an area of internationally ecological significance.

Community perception of risk and expectation of future land uses were considered as part of the risk method to generate and upgrade the surplus contaminated land and a CSM was developed.

Results/Lessons Learned

Despite the real complexity and recalcitrant nature of the contaminants of concern, the approach used resulted on safely risking out any potential exposure to the contaminants mentioned above. This was a very successful approach which not only saved potentially millions of \$ on remediation cost and avoided any potential disturbance to the ecologically sensitive receiving environment. Even more importantly generate a high value future land use of this surplus brown field area, therefore the return on investment was huge for both the owner and the community at large.

Using exposure equations, exposure factor; chemical-specific toxicity, exposure duration, frequency, aging, soil properties it was estimated the risk was acceptable for higher value future land uses.

The innovative and integrating scientific knowledge, in the context of site specific will be discussed in detail and shared.

A study of abiotic, biotic and functional parameters of six derelict soils in the north-east of France - towards a potential use of derelict soils as a resource.

Quentin Vincent¹; Apolline Auclerc; Thierry Beguiristain; Corinne Leyval

¹ University of Lorraine, FR

The intensification and closure of industrial activities led to large surfaces of derelict lands. The derelict soils remain unused because they have often a low fertility and could be contaminated. However, soils are limited resources, and derelict soils might be considered for potential re-use, with or without remediation and restoration phases, such as for non-food biomass production. Since soil biodiversity and biological activity play a key role in ecosystem functioning, their study may be an indication for a potential use. The objective of our study was to characterize the taxonomic and functional belowground biodiversity (microflora, fauna, flora) of derelict soils and to link their physico-chemical and biological parameters.

Six derelict soils - three constructed soils and three industrial wastelands - located in north-east of France were sampled using a gridline strategy. Firstly, they were characterized for their physico-chemical properties. The abiotic parameters of the studied soils were measured through fertility and contamination proxies. Then, three main biotic components were quantified (abundance and diversity) - microflora (bacteria and fungi), fauna (collembola and macro-invertebrates) and flora - at the same time and in a same square. Finally a functional approach was carried out through decomposition function (percentage of meso- and macro-decomposers, mineralization capacity, enzyme activities and percentage of polycyclic aromatic hydrocarbon degrading bacteria).

In order to compare the co-structure of abiotic and biotic parameters for the 6 derelict soils and find relationships between abiotic and biotic parameters, a co-inertia analysis was done. A second co-inertia analysis based on abiotic and functional parameters was carried out too. We noticed that biodiversity levels in the derelict soils were rather high but depended on the considered biotic component. Several biotic parameters should then be considered to characterize soils for potential reuse. According to the multivariate analysis, the biotic parameters were more linked to fertility proxies than to soil contamination proxies. Similarly, the functional parameters were significantly linked with abiotic parameters. For instance, we found that the compost amended constructed soils that had the highest fertility level showed the highest decomposition level, and the contaminated constructed soil with the highest pollutant concentration had the lowest decomposition level.

Our study showed then that derelict soils could provide ecosystem services such as biodiversity reserve and decomposition process. Considering biotic and functional soil parameters, such as biodiversity and the potential decomposition processes, could help to identify the derelict soils that could support the biomass production ecosystem service.

Management of soil geochemical backgrounds and threshold levels in areas affected by brownfields and diffuse anthropogenic pollution.

José Luis R. Gallego¹; Alicia Fernández-Braña; Carlos Boente; Elías Afif; Nerea García; Arturo Colina; Eduardo Rodríguez-Valdés

¹ University of Oviedo, ES

There are several methods of gathering information to carry out an in-depth study of the impact of potential toxic elements (PTE) accumulation by anthropogenic sources. In this context, and in order to regulate the management of contaminated land, many countries have derived threshold levels usually named as soil screening values (SSVs), soil screening levels (SSLs), or RBSSLs (risk-based soil screening levels) taking into account geochemical backgrounds sometimes supplemented with risk-based data, i.e. toxicological calculations. Usual methodologies for the investigation of geochemical backgrounds tend to consider only soils of natural or uncultivated pasturelands, which are supposed to be virtually pollution-free. For instance, SSLs were defined for the region of Asturias (Northern Spain, approx. 10.000 km²) in 2014 based on the geochemical backgrounds obtained in pristine areas of the territory.

One of the main industrial locations within Asturias is Langreo, which is nowadays a shrinking city, whereas in the past it had a successful economy associated with heavy industry and mining. In fact, as a result of partial industrial abandonment, it is suffering effects of depopulation and rising unemployment, together with the affection of the environmental quality. In this context, the surface occupied with abandoned industrial areas is considerable, thereby conditioning the urban planning of the city, implying a problem of soil sealing, and generating human health risks given that some of these lands are heavily polluted (site-specific releases). At the same time, both natural and urban soils in this territory have been subjected to an increase in PTEs concentrations as a result of the atmospheric emissions of industry and mining for more than a century (diffuse anthropogenic pollution).

We hypothesized that the use of the regional SSL as defined above, can affect the quality of soil studies to be done in industrial areas such as Langreo, for example in terms of the appearance of a number of "false positives" wherever soil affected by atmospheric emissions (diffuse pollution) are sampled. Therefore this work has been scheduled to obtain specific SSLs for the Langreo municipality (approx. 82 km²), in order to establish a comparison with the regional SSLs, to distinguish between geogenic enrichment and anthropogenic pollution, and also to identify significant changes when data of specific polluted brownfields are evaluated at the light of one (local) or another (regional) table of SSLs.

The study has been accomplished by means of the analysis of 150 soil samples taken all along the municipality after a careful design based on the geomorphology of the area, a brownfields inventory, and an equilibrated distribution between urban and non-urban soils. Initially, the identification of outliers was valuable to identify sources of pollution and specific areas to be further analyzed in risk assessment studies. Furthermore, univariate and multivariate statistics together with geochemical mapping have revealed significant differences between the behavior of some PTEs at regional and local level, mainly Pb, Zn and Hg.

ThS 5b.1: Recovery of nutrients and other valuable resources

Sustainable management of Nitrogen in landfills

Hans Groot; Nanne Hoekstra

Deltares, NL

On October 6th, 2015 the Dutch Government formally agreed to the start of the Sustainable Landfill program Introduction Sustainable Landfill Management. This program aims to find a sustainable alternative for the long term management of landfills using measures to substantially reduce the emission potential to soil and (ground)water like pre-treatment, immobilization, aeration, recirculation, solubility control, percolation/flushing and biodegradation. This should result in a reduction in aftercare cost because there is no need to install a top liner after closure of the landfill.

It is expected that sustainable landfills will meet the standards to be set under the European Groundwater Directive, possibly with the exception of Cl^- , NH_4^+ , and SO_4^{2-} . Specially the emission potential of NH_4^+ poses a problem for the successful execution of the concept. There is yet insufficient knowledge of the behavior of Nitrogen in waste material and of the interaction of Nitrogen and Carbon. Therefore the potential emission of Nitrogen to the groundwater is acknowledged as being a limitation for the successful execution of the Sustainable Landfill concept.

This initiated the research project "Sustainable management of Nitrogen in landfills", a project performed by Deltares in cooperation with the Technical University Delft and Oonkay, funded by the Sustainable Landfill Foundation and Dutch Government (TKI).

Goal of the research project is to research the dominant physical, chemical and biological processes of Nitrogen and Carbon in the waste material of landfills. This is important for determining the risks of potential emission of Nitrogen via leachate. Knowing these processes we are able to design measures to reduce Nitrogen emissions from landfills to the groundwater.

In our presentation we will show you the available research results.

Electrokinetic enhanced in-situ leaching of waste repositories: Metal speciation and transient behaviour of metals.

Claudia Peppicelli¹; Peter John Cleall¹; Michael Harbottle¹; Devin Sapsford

¹ Cardiff University, GB

Waste repositories can be seen not only as a potential source of contamination, but also representing a potential source of valuable resources, such as base and precious metals. This paper reports a preliminary experimental programme on the application of electrokinetic processing to three different waste materials: two mine tailings and a metallurgical dust.

The electrokinetic process involves application of a low voltage between two electrodes set in the ground to induce an electric field. The acidic environment established by the electrolysis of water enhances the dissolution or desorption of metals from soil particles which then migrate by electromigration and electroosmosis.

The study focuses its attention on the interaction and the effect that the electrokinetic process has on metals associated with different geochemical fractions identified by a 5-step sequential extraction scheme (SSE). The partitioning of metals can be determined between the different geochemical fractions identified as follows: (i) exchangeable, (ii) carbonate, (iii/iv) easily/ moderately reducible (oxides), (v) oxidisable (sulphides), and (vi) residual.

The mineralogical and geochemical characterization of the three materials allows classification of them as: an acidic pyrite-rich mine tailings (WM); a circumneutral sulphidic mine tailings (MT) and an alkaline metallurgical dust rich in Zn-Fe oxides (FD).

The department of Pb and Zn between the various SSE fractions is of particular interest for these materials. In the WM material both Pb and Zn are primarily associated with the residual fraction, remaining Pb is enriched in the reducible fraction. Zn is largely associated with sulphides and the exchangeable fractions. MT is characterized by Pb equally distributed amongst the different fractions, while the Zn is almost entirely present in association with sulphides in the oxidisable fraction. Thus, the elements associated with pyrite and other sulphides are susceptible to mobilisation induced by oxidation and those related to oxyhydroxides will become accessible under low pH conditions. Regarding FD, Pb is mainly enriched in the carbonate fraction, while Zn is mostly present in the residual fraction, with remaining Zn equally associated between carbonates and oxyhydroxides. In this case the high buffer capacity and the alkalinity of the material presents a major obstacle to the mobilisation of the metals, which even when mobilised will tend to easily re-precipitate.

After 4 weeks, with the application of a constant voltage of 10 Volts across the specimens, the SSE applied to the two mine tailings shows an internal redistribution of Pb and Zn amongst the SSE fractions (i) – (iv) with an increase towards the most mobile fractions. The FD material shows no significant redistribution of those elements between SSE fractions.

Change in pH and redox conditions are identified as being critical factors and the three different starting conditions allow investigation of the influence that they have on the mobilization of metals by electrokinetic processing.

Agromining for the recovery of nickel from soils

Marie-Odile Simonnot¹; Baptiste Laubie; Mathilde Guilpain; Vivian Houzelot; Claire Hazotte; Guillaume Echevarria; Jean-Louis Morel

¹ Université de Lorraine, FR

Hyperaccumulator plants are able to extract and accumulate metals (or elements) from soils. There is an incentive to recover these metals as products to partially mitigate the cost of disposing the contaminated biomass from soil remediation projects. Moreover, recovering metals from secondary sources (e.g. polluted soils, serpentine soils, mine tailings) has become an essential challenge.

Agromining aims at growing hyperaccumulator plants in order to reach high yields of metals and recover metals by pyro or hydrometallurgy. It has been mainly developed for nickel (Ni) since i) more than 400 Ni hyperaccumulators have been identified, ii) large areas covered by serpentine soils or mine tailings are available worldwide and iii) processes have been designed and upscaled to obtain Ni metal or Ni- based compounds (salts, oxide, catalysts).

The objective of this contribution is to present two types of hydrometallurgical processes to recover Ni from the biomass of a Ni hyperaccumulator, *Alyssum murale*, containing ca 1 wt% of Ni. It has been demonstrated that yields of 110 kg of Ni per ha can be reached by growing this plant, with appropriate agronomic practices.

The first approach consists of burning the dry plants to produce ashes and energy. Ashes contain 15-20 wt % of Ni, which is far higher than any Ni ore. They also contain potassium, calcium and magnesium as major cations. Ni can be recovered from ashes, after ash washing, acid leaching and several precipitation steps, in order to produce Ni salts or oxide. These processes have been designed at the lab scale and up-scaled to the pilot scale. Details will be presented on the operating conditions and Ni mass balance along the process. The re-use of the by-products has been also investigated, as well as the overall environmental impacts of the agromining chain.

The second approach consists of extracting Ni directly from the dry plant, using water as a solvent. The challenge is to recover Ni from the leach liquor, which is a multicomponent solution containing dissolved organic matter to which Ni is strongly bound. An original method has been developed using a complexing resin, selective of Ni.

The presentation will end up with a comparison of both approaches, to show the advantages and drawbacks of recovering Ni after combustion or directly from the dry plant.

Soil management in a circular economy

Anton M. Breure¹; Linda Maring²; Johannes Lijzen¹

¹ RIVM; ² Deltares, NL

The European Community introduced a strategy for circular economy ('Closing the loop', http://ec.europa.eu/environment/circular-economy/index_en.htm) in December 2015. The main aims of the strategy are to maintain the future provision of natural resources by their efficient use, including decrease of resource use, reuse of waste materials and substitution of scarce resources by resources that are easily available and recyclable.

This strategy has important interfaces with the EU 2020 strategy ("land as a resource"), EU Biodiversity strategy, the EU Soil strategy, and European policy on agriculture.

Role of the soil in:

Provisioning of resources

The origin of resources is mainly the soil that serves as a reservoir for minerals, fossil fuels and groundwater. Soil is a factor in the production of biological resources (such as wood, crops or fibers). One of the substitution routes for mineral resources and fossil fuels is the use of biobased resources, originating from agriculture or organic waste from other sources. The multiple possibilities for their use can also generate competition and create pressure on land-use. In the circular economy framework land itself is seen as a resource.

Reduction of resource use

Ways to reduce the use of mineral resources and fossil fuels, next to the design of resource-efficient products, lie in the use of ecosystem services such as geo-energy, purifying capacity of soils, soil fertility and water storage capacity. In addition, efficient spatial planning of urban and rural areas, connecting surface and subsoil application of space contributes to a lower resource use.

Waste phase of products and resources:

Extraction of minerals and fossil fuels also has great regional and environmental impacts on land and soil. Moreover, much of the waste produced during use of products and at the end of the life cycle, ends up in the soil. The reuse of waste materials has implication for the quality of residual waste and soil quality. The use of organic waste in biobased materials has consequences for the amount and quality of organic waste to be used in agriculture for maintenance and improvement of soil fertility.

Natural cycles

Soil plays an important role in the water cycle, as well as in the nutrient cycles (nitrogen, carbon, sulphur and phosphorus), by biological, chemical and physical processes in the soil. It contains an important part of the freshwater stock and large amounts of fossil fuels, constituents of the carbon cycle. The biogeochemical cycles in the soil play a crucial role in the renewables flow. The water and mineral cycles are of major importance also, for soil fertility, climate regulation and the quality of our "habitat".

Concluding

Natural resources are part of our natural capital, as is land and the soil-water system. Circular economy provides a framework for asset management of natural capital, including land and soil, mineral and biobased resources, fossil fuels, water and biodiversity.

In our presentation, we will describe how a circular economy approach may be used as a tool for sustainable land and soil management and we will provide some examples of its application.

Thermodynamic and kinetic studies on adsorption of chromium (VI) by the olive pomace of the region of Beni Mellal

Aziz Menichi

University Hassan II - Casablanca, MA

Most liquid effluents from tanneries contain chromium. In its form chromium (VI), it shows toxicity of 500 times higher than that of chromium (III) [1]. Therefore, to avoid the harmful impact on public health, the elimination of the metal in the source is a major concern of the industrial world. In addition, the interest is focused on efficient methods of application at the lowest cost.

In the present work we have focused on the removal of chromium (VI) by adsorption onto olive pomace lignocellulosic (OPLC) prepared with olive pomace crude (OPC) of the region of Beni Mellal. [2]. The important parameters influencing the power of adsorption of (OPLC) namely the concentration of adsorbent, the pH, and the temperature of the midst were examined in a static reactor.

The kinetic study was performed using the equations of the pseudo first order and pseudo second order as well as a modeling of isotherms by applying known models such as Langmuir, Freundlich, Temkin and Dubinin Radushkevich.

The results of this work showed that the prepared material can be used as an effective adsorbent for the treatment of wastewater because of its high properties of adsorption.

ThS 5c.3: Reuse and upgrading of water and soil products I

Advanced monitoring-modelling communication tool for optimising Soil Aquifer Treatment (SAT) system design & operation

*Marie Pettenati*¹; *Géraldine Picot-Colbeaux*¹; *Anne Togola*¹; *Benjamin Lopez*; *Nicolas Devau*¹; *Loïc Thomas*²; *Axel Aurouet*²; *Matthieu Baisset*³

¹ BRGM; ² Géo-Hyd; ³ IMAGEAU, FR

Non-conventional water source for Managed Aquifer Recharge (MAR) containing chemicals, both endogenous and anthropogenic, have the potential to enter the aquifer environment from infiltration surface systems. Pre-treatment is necessary to enhance system performance and efficiency, to remove critical contaminants (pathogens...) from the source water, to ensure the long term system performance and to meet regulatory demands, particularly in the view of new target uses as indirect potable reuse (IPR). When MAR includes Soil-Aquifer-Treatment (SAT), it becomes a method to enhance groundwater quality and not only groundwater quantity. Some of the advantages of MAR include floodwater mitigation, control of saltwater intrusion, storage of water to reduce pumping and piping costs, temporary regulation of groundwater abstraction, and water quality improvements (Asano, 2007). The technology has also gained increasing attention as natural water treatment and water reuse application, for irrigation (Lazarova et al., 2011, Kazner et al., 2012) and, increasingly for IPR (Grützmacher et al., 2013). Potential drawbacks and obstacles to large-scale implementation are (1) decrease of system performance due to clogging of the infiltration system (Pavelic et al., 2007) (2) unforeseeable long-term behaviour due to low-kinetics geochemical processes (Goren et al., 2012), (3) residual micropollutants, pathogens and antibiotic-resistant bacteria and genes (Pal et al., 2010) after treatment, (4) regulatory constraints related to potential impact of the qualitative status of groundwater bodies. The use of subsoil natural systems (soil and aquifer) for water treatment requires a stringent monitoring and modelling to detect and foresee any adverse effects and risks for the concerned water bodies (e.g. contaminant flow beyond the confined injection-pumping perimeter). In the context of H2020 AquaNES project, 13 combined natural-engineered treatment systems (cNES) demonstration sites in Europe, India and Israel covering a representative range of regional, climatic, and hydrogeological conditions are studied as sustainable adaptations to issues such as water scarcity, excess water in cities and micro-pollutants in the water cycle. One of these demonstration sites is located in France and concerns a coastal shallow sand aquifer threatened by salinization. The wastewater treatment plant infiltrates secondary effluent in a reed bed then through sand dune aquifer. The water is then used for golf irrigation. At this MAR/SAT site, the investigated scale is the groundwater body. On site, online Subsurface Monitoring Device (SMD) combined with water monitoring and laboratory analysis will be able to assess availability of groundwater resource regarding MAR and saline intrusion. Based on this innovative monitoring, hydrodynamic, reactive transport and fate modelling, extending previous work (Pettenati, 2012, Thiéry, 2010), will be provided in order to predict the geochemical and hydrodynamic processes. We demonstrate the performance of an advanced monitoring-modelling communication tool to assess and optimize the management of cNES sites and their future implementation.

The fate of emerging pollutants: prediction of physico-chemical properties and modelling of degradation experiments

*Philippe Blanc*¹; *Aourel Mauffret*²; *Nicolas Devau*; *Benjamin Lopez*; *Géraldine Picot-Colbeaux*; *Nicole Baran*; *Anne Togola*; *Marie Pettenati*

¹ BRGM; ² IFREMER, FR

Water quality and societal wellbeing are currently threatened by emerging pollutants (CEC) and the presence of organic micro-pollutants (e.g., pharmaceuticals) in wastewater effluent and receiving waters is already demonstrated (Kasprzyk-Hordern et al., 2009). The fate in the environment (transfer in solution, sorption onto solid matrixes and (bio)degradation) of these new molecules remains an open question for a large part of them. As a contribution to this issue, this work proposes a methodology to model the behavior of CEC, namely diazepam, sulfamethoxazole, carbamazepin and metoprolol in degradation tests (type OCDE 308). The resulting model is not limited to these substances and it is meant to extent to a larger panel of molecules.

Our model considers the sorption onto organic substrates. For neutral and anionic molecules (sulfamethoxazole, carbamazepine), sorption is modelled using the partition coefficient KOC, depending on the molecule pKa and the solution pH (Franco et al., 2009). KOW and pKa values are predicted using QSAR models from the literature and KOC is deduced from the relations developed by Franco et al. (2009). For cationic molecules (metoprolol), the exchange model proposed by Droge and Goss (2012) is implemented in our model. The diffusion of the organics into the organic substrate is modelled using a dual kinetic expression. The biodegradation uses the Michaëlis-Menten/Monod approach. Co-metabolism is implemented only for readily degradable molecules, using soil or sediment organic matter as a co-substrate and oxygen as the electron donor. The parameters for organic matter degradation are obtained from the study by Pettenati et al. (2012).

Our general model is implemented in the geochemical code PhreeQC-2 code (Parkhurst & Appelo, 1999), using the Thermoddem database (Blanc et al., 2012). It is applied to the degradation tests conducted by Löffler et al. (2005) and Ramil et al. (2010). For each test the model requires the fitting of 3 parameters only to reproduce the evolution of both the adsorption and the biodegradation with the reaction time. The methodology has then been applied to 15 molecules in order to obtain empirical relations between parameters allowing predictions over a larger set of molecules.

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Mineralogical and chemical characterization of phosphogypsum before pretreatment and valorization

Denise Blanc¹; Sara Bisone; Mathieu Gautier; Vincent Chatain

¹ DEEP - INSA LYON, FR

Phosphogypsum (PG) is the byproduct of the production of phosphoric acid and phosphate fertilizers from Phosphoric rocks, mostly from apatite group $\text{Ca}_5(\text{PO}_4)_3[\text{F},\text{OH},\text{Cl}]$. The most widely used process, the dihydrate (DH), consists of an acid digestion with sulfuric acid at high temperature.

The DH process generates among 5 tons of PG for every ton of phosphoric acid produced. Even though reclaim of this waste has been widely studied, most of the phosphogypsum produced worldwide is still stockpiled. As a substitute of natural gypsum, PG has been recycled in building materials in the composition of cement and concrete, to produce plaster and plasterboards or as a road base material. The presence of phosphate, fluorine and metals imposes some technical limits to its reuse, thereby a pretreatment is usually recommended.

Before any pretreatment selection, a knowledge of PG characteristics is required. Little is known about impurities distribution and behavior in disposed PG, hence it is difficult to evaluate the feasibility of a reuse scenario of gypstacks. This study focused on the characterization of a PG stack with the aim of estimating the pertinence of the valorization of this waste. In order to evaluate the effect of depth on phosphate and fluorine solubility, three sections of a core sample of 13.5 m were studied. A mineralogical study, leaching behavior tests, and geochemical modeling with Phreeqc were performed.

X-ray diffraction (XRD) and differential thermogravimetric analysis (TGA-DTA) showed a relatively pure gypsum phase (around 95% of the dried matter). Crystallinity was comparable for the three samples and no mineralogical difference with depth could be observed with these techniques. Beside this mineralogical similarity, residual acidity varies considerably, clearly showing an evolution of the PG with.

The existence of a trend with depth was confirmed by leaching tests. Leachates of deeper samples showed a higher concentration in major anions (F^- , PO_4^{2-} , Cl^- and SO_4^{2-}) and in most of the analyzed cations (Fe, Cr, Cu, Na, Si, Zn). Results pointed out that the solubility did not strictly depend on total content. In addition to pH, dissolution and precipitation of minor phases may be one of the causes of the solubility differences with depth. The study of acid-base neutralization capacity of PG allowed determining base consumption for the three samples. At a later stage, investigations on elements solubility as a function of pH provided evidences on the effect of neutralization on metals, fluorine and phosphates availability.

Modeling batch leaching tests corroborated the identification of phases controlling solubilisation. Mineral assemblage chose for the model fitted the solubility of elements analyzed and acid-base behavior of the PG. Then, model was used to simulate pretreatment effectiveness on acidity neutralization and impurities leaching.

In conclusion, disposed PG characteristics not only depend on production process used, but also on the evolution and ageing of the gypstack. This study supports the use of a multiple approach to determine PG behavior and pretreatment feasibility, in the interest of evaluating reclaim scenarios.

Pollutants retention in deposit layers of vertical flow constructed wetlands treating domestic wastewater

Mathieu Gautier¹; Manon Kania; Boram Kim; Philippe Michel; Rémy Gourdon

¹ DEEP - INSA LYON, FR

Protection of natural ecosystems from anthropic activities is a major issue in sustainable development. Wastewaters and other liquid effluents generated by communities must therefore be treated so that water can be discharged to the environment in a safe manner. Constructed wetlands are considered amongst the technologies best adapted to household wastewater or stormwater treatment. Their development has been considerable since the end of the 90s, making them today the main water treatment process used at small community scale (more than 3000 plants installed in France in 2015). In the case of vertical-flow constructed wetlands (VFCW) which are predominant in France, the suspended matter contained in the effluents to be treated leads to the formation of an organic surface sludge layer. This sedimentary layer could be considered as an anthroposol where pedogenesis is occurring in interaction with the substratum below. Despite its strong role in the treatment performance, few studies have yet been published on the processes occurring within this layer.

VFCW have been mainly developed to treat nitrogen and organic matter from wastewater. Phosphorus (P) removal later became an important issue since its uncontrolled discharge into water bodies may result in their eutrophication, and P is at the same time a non-renewable resource of great value as a fertilizer component. While agriculture demands P inputs, wastewaters are a good source of phosphorus if properly treated. A diversity of organic and metallic pollutants are however carried out in wastewater streams and may accumulate in these sediments via complexation or adsorption mechanisms onto particulate organic matter (OM), and / or mineral phases such as Fe-, Mn or Al-oxides, including clays. These retention mechanisms have positive results when considering the treatment performance of the effluent, but also bear potential risks of adverse effects in case of malfunctioning (i.e. flooding) or improper land application after dredging.

The present study investigated both qualitative and quantitative retention of contaminants within the surface deposit layer. A focus was made on the nature of the bearing phases involved in adsorption/desorption phenomena, and on the time course evolution of sludge organic matter. Samples were taken from several French VFCW plants that had been in operation for a few months up to 11 years. Complementary analytical methods were used at the laboratory scale to investigate the composition and reactivity of the sludge material.

The results of this study firstly revealed the accumulation of nutrients (e.g., N, P), metals (e.g., Cu, Zn), micropollutants (e.g., econazole, ciprofloxacin) and surfactants (e.g., LAS). Some correlations were established between the nature of the pollutants and the particularities of the territory, showing that the deposit could be used as an indicator. Then chemical fractionations performed on P and metals gave us important information on the pollutant-bearing phases and the risks of release. For example the phosphorus seems to be released in small quantity only after long period of flooded showing the strong retention in this deposit.

Removal of emerging contaminants during artificial recharge through a reactive barrier: Evaluation of processes

Cristina Valhondo¹; Lurdes Martinez-Landa²; Jesús Carrera; Carlos Ayora

¹ CSIC; ² Technical University of Catalonia, ES

The demand for quality water has increased with the population growth and the availability of fresh water in arid and semiarid regions is likely to decrease because of climate change. Therefore the development of sustainable, high-efficiency, low cost technologies for water treatment is urgent.

Artificial recharge of aquifers with impaired water is a low-energy and low-cost water recycling technology which allows to improve the recharge water quality and to increase groundwater resources. One of the major concerns with artificial recharge using impaired water is the potential contamination of the aquifer with organic chemicals present in the infiltrating water, including organic emerging compounds (EOCs). EOCs, such as pharmaceutical residues, personal care products, and industrial chemicals, are increasingly identify in the environment although most of them remain unregulated.

The main processes involved in the EOCs elimination during their pass through the soil are sorption and biodegradation. We designed a reactive barrier to favor these two processes. The reactive barrier comprised sand, which provides structure to the barrier, vegetal compost, which releases dissolved organic carbon into the infiltrated water, favoring a broad range of redox conditions underneath, and very small fraction of clay and iron oxides, which increase the sorption sites for cationic and anionic EOCs, respectively.

The tests of the reactive barrier on the field yielded to positive results. First order degradation rates, to quantify biotransformation, and retardation coefficients, to quantify adsorption, of several EOCs were estimated using a flow and transport numerical model (with flow and conservative parameters previously calibrated). The degradation rates of each compound was estimated for three zones defining according to the redox state. The results point out that the fastest degradation occurred in the reactive barrier and that the estimated revalues were similar or higher than those reported in column and/or field experiments for most of the compounds. These results suggest the efficiency of the reactive barrier enhancing the removal of EOCs.

ThS 5c.4: Reuse and upgrading of water and soil products II

Beneficial use of sediments to reverse land subsidence

Bruna Oliveira¹; Martijn Smit; Tim Grotenhuis; Huub Rijnaarts

¹ Wageningen University, NL

Land subsidence is occurring in many low lying and delta areas worldwide. Land subsidence is mostly a consequence of long term geological effects and anthropogenic interference such as drainage which results in shrinkage due to the loss of volume occupied by the water and rearrangement of the particles (Oleszczuk et al. 2003), and in organic matter oxidation (Sanei et al. 2005).

The dense networks of waterways needed to regulate the water level in lowlands and Delta areas is perpetuating the subsidence and is becoming increasingly costly (Querner et al. 2012). Periodical dredging of the waterways is generally performed to maintain their nautical and hydrological functions and improve water quality. A beneficial use of non-contaminated dredged sediments is to spread these on the land adjacent to the waterway, as naturally occurs in floodplains. This might be a solution to reverse land subsidence by rising the land surface level (Harmsen 2007) especially considering that in some areas the sediments and water flow are restrained, by dams and ponds, which limits natural restoration through sediment accumulation (Kolker et al. 2011). Furthermore, since the sediments mostly originate from erosion of soils in the same water basin, and therefore the characteristics of the sediments are often identical to the soils in the adjacent lands, the impacts on the ecosystem of using sediments locally should be minimal when compared to relocation outside the water basin or import of sediments (Salomons 2008).

Both scientific literature and European policies favour the beneficial use of sediments to reverse land subsidence. The stakeholders involved in dredging and sediment management, and the general public should be involved in the planning of the water basins to increase the acceptance and feasibility of beneficial uses of dredged sediments .

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Environmental assessment of two sediments reused in road engineering: feedback after one year of monitoring through the Sedimed project

*Flore Rebischung*¹; *Aurélien Ustache*¹; *Erwan Tessier*²; *Alain Pieters*³

¹ INERIS; ² NEO-SUD; ³ Envisan France, FR

Road engineering is one way for sediments to be reused and enter the circular economy, instead of being stored in landfill. The so-called "Guide Setra" constitutes the French framework for reusing alternative materials in road engineering, including three kinds of road structures: coated (with an impervious layer), covered (with at least 30 cm of natural material) or uncoated and uncovered.

The Sedimed project investigated those three options, settling lysimeters (uncoated and uncovered) and building experimental road (coated) and landforms (covered), incorporating two sediments from the Toulon bay (QN and QC). Leachates were collected and sampled on these three experimental structures, and pollutants (12 metals – As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn –, 3 anions – Cl⁻, F⁻, SO₄²⁻ –, 16 PAH and 3 emerging pollutants detected in the sediments – DBT, TBT and DEHP), were analyzed on every sample, enabling the draw of the total released quantity of each pollutant on a L/S basis (ratio between the volume of water that percolated through the structure and the mass of sediment in the structure).

The total content of organic pollutants of QN would normally disqualify this sediment for road engineering, according to the "Guide Setra". Yet, only considering the potential impact on groundwater, the released quantities of pollutants are far from very protecting thresholds.

For both QN and QC, the anions content (Cl⁻ and SO₄²⁻) exceeded the "Guide Setra" thresholds for some structures, indicating that the control of these parameters and the reduction of their global content during the lagooning period might be triggering the reusing options for marine sediments.

Those new data and knowledge might contribute to the definition of a specific framework for reusing sediments in road engineering.

Beneficial Reuse of Sand from the Lower Fox River Sediment Remediation Project

Neil Geevers¹; Terri Blackmar²; Richard Feeney²; Ron Dielhof¹

¹ Boskalis Environmental; ² Tetra Tech, US

The Lower Fox River sediment remediation project in Wisconsin includes dredging, capping and covering of PCB-impacted sediment at specified locations over a 13 mile (21 km) stretch of the river. One key objective of the sediment processing facility is to minimize waste disposed at the landfill by beneficial reuse of the separated coarse fractions (sand) and by dewatering the fine (contaminated) fraction of the dredged sediments.

The project contractor team is comprised of Tetra Tech as prime contractor for the engineering design and construction, J.F. Brennan Company as dredging & capping subcontractor, and Stuyvesant Projects Realization Inc. (SPRI) as desanding & dewatering subcontractor. SPRI is one of the USA operating companies of Boskalis Environmental. Together with its Dutch sister company Boskalis Dolman bv, which supports SPRI with engineering and equipment services, these companies have more than 30 years of directly relevant experience in the management of 15 million tons of contaminated sediments/soils in the USA, Canada, The Netherlands and other European countries. Both companies are part of Royal Boskalis Westminster N.V., a leading global services provider operating in the dredging, maritime infrastructure and maritime services sectors.

The presentation will explain how beneficial reuse offsite of recovered sand from the seven years of operation to date (2009-2015) has been successfully implemented; the first such application on a full scale sediment remediation project in the USA.

The primary reasons for separating sand include: 1) avoid unnecessary transportation & disposal (T&D) cost; 2) produce a product that can possibly be beneficially reused, thereby conserving valuable landfill space; and, 3) prevent additional wear and tear on downstream processing equipment.

Various beneficial reuse opportunities were identified and evaluated, and a major local infrastructure (highway construction) project provided the perfect fit. The process of achieving regulatory approval for beneficial reuse included Tetra Tech's preparation of a "Low Hazard Waste Exemption Request", along with the required public meeting, project logistics, and commercial arrangements. All potential beneficial reuse applications required approval by the Wisconsin Department of Natural Resources (WDNR), the state environmental agency. Sand sampling program parameters, chemical testing criteria, and project-specific allowable contaminant concentrations will be presented.

The "Integrated Approach" used to perform this sediment remediation project emphasizes the seamless integration of all aspects of the work by each of the performing partners. This includes the Client, the regulatory agencies, local stakeholders, and all of the contractors performing the various aspects of the work (e.g., dredging, desanding, dewatering, water treatment, beneficial reuse, and transportation & disposal).

Using cement industry wastes for improving soil properties and crop performance in Egypt

Mahmoud Morsy

Faculty of Agriculture ,Minia University, EG

The reuse of some industrial wastes or by-products is beneficial to prevent or at least to reduce the environmental pollution. One of these wastes is Cement Kiln Dust (CKD). The CKD is beneficial as a raw material, construction material, absorbent, and improving the sandy soil properties. Pot experiment using a sandy soil cultivated with corn was set up to study the efficiency of using the CKD as a soil amendment. The tested CKD was applied to the sandy soil at six rates (0, 5, 10, 15, 20, and 25 Mg ha⁻¹). Application of the CKD at the rate of 25 Mg ha⁻¹ to the sandy soil increased the plant height, fresh and dry weight of the corn shoots, and water use efficiency by the corn plants, but it decreased the water consumptive use by the corn plants. In general, application of the CKD decreases the lost water by leaching, rationalizes the irrigation water use, and enhances the corn growth. It could be recommended to use the CKD at the rate of 20 Mg ha⁻¹ as an amendment for the sandy soils under the conditions of El-Minia Governorate, Egypt.

Key words: Sandy soil, cement kiln dust, amendment, and corn.

Contaminated sediments, a matter best buried!

Gerben van den Berg

TenCate Geosynthetics, NL

This paper concerns three case studies involving the use of geotextile tubes to transform contaminated sediments into qualified construction material in an economical and environmental manner. The first case study involves the use of geotextile tubes to dewater and consolidate contaminated harbour sediments to be encapsulated and turned into the foundation of a modern sports infrastructure. Here, the distance between the port in question (Port-la-Forêt in France) and the sports facility was overcome entirely by the pumping force of the dredge and a booster. In this effective way costly transport to a landfill could be avoided completely. The filled tubes pleasingly blend in to the landscape. The second case study involves dredging of contaminated sediment from the river IJssel in the city of Zutphen in the Netherlands. The industrial harbour of De Mars had been neglected for the previous 40 years. Fully loaded ships could only enter the harbour at high tide. The innovative geotextile tube solution allowed the dredged contaminated sediment to be put to beneficial use as riverbank restoration material. In relation to this project the subject of carbon footprint is presented in comparison with the conventional methods and the favourable geotextile concept. Lastly we present the case of EmbraPort, Brazil. This, the biggest new build port infrastructure in Latin America in the past four years, clearly illustrates the decisive and practical impact geotextile tubes can have when it comes down to realizing a harbour extension and solving a sedimentation problem at the same time.

ThS 6a.2: Ecosystems Services based subsurface management

Towards societal benefits by soil services

Margot De Cleen; N.J. Molenaar

Ministry of Infrastructure and the Environment, NL

How to get soil services on the political agenda? Information on the political context, definition of the soils services concept, identification of ingredients for transition, discussion about your contribution: these are the ingredients of this session organized by members of the MAES Soil group and the Common Forum working group "Soil as a resource".

The services provided by soils are vital for Europeans! The EU strategy Europe 2020 addresses several societal challenges which the EU wants to achieve smartly, competitively, sustainably and inclusively. Many of these challenges can only be met by sufficient good land and soil availability. However, land and soil availability is under pressure as it is needed for a range of uses such as supporting houses, food and biomass production, biodiversity, water management, leisure and other cultural aspects.

Society at large is not sufficiently aware of the importance and relevance of soil services for meeting societal challenges, such as food security, climate change adaptation and mitigation, energy transition and safe and clean drinking water. Often this leads to significant damage and loss of economic and societal benefits. The risks and costs from an ongoing degradation of ecosystems and their services are neither properly integrated into our economic and social systems nor our decision-making processes. In this context, related knowledge instruments, such as ecosystem accounting, need to be developed. To address societal challenges the multiple-use of land, soil and its services is needed. This needs to be done in a sustainable way to secure these benefits for present and future generations.

Because land is often owned by private parties and used by different stakeholders, solving societal challenges asks for cooperation between public and private parties. For societal benefits, agreements should be made to use this land in such a way that not only the landowners' needs are met, but also societal expectations can be fulfilled. Due to the different interests on how land shall be used, an integrated approach is desired. Therefore, the challenge for policy makers is to develop instruments to better balance private and societal interests. A transition is needed from protection against soil threats towards a sustainable use and a land management in which various stakeholders do participate.

Aim of this session

In this session we start the discussion with you on how to contribute to the transition needed, based on a narrative showing the importance of well-functioning soil services for society. Basis are the results of the MAES Soil group and the agenda of the Common Forum Working group "Soil as a resource" will. We want

- To show the global and European political context;
- To clarify the concept of soil services;
- To address the approaches of soil threats versus sustainable use and management;
- To introduce the tragedy of the commons and instruments to come to multipurpose land use and value creation.
- To identify ingredients to come to a transition including the role of authorities, industries and other stakeholders, society and knowledge institutions.

Ecosystem benefits generated by environmental interventions: a case study

Giorgia Quadri; Alessia Cavalli; Elisa Bizzotto; Fabio Colombo

Ramboll, IT

The presentation will discuss the economic assessment of ecosystem services improvement generated by a set of “environmental interventions” proposed for an area in North Italy that was historically exposed to an industrial contamination.

This territory includes both fluvial and terrestrial ecosystems, located near a river flowing in lake bay, with presence of several Natura 2000 sites.

The interventions proposed are composed by 14 actions, divided in 4 main categories related to the environmental issues characterizing the territory of interest. All these interventions were designed to meet the requirements of the Habitats (92/43/EEC), Birds (2009/147/EC), Floods (2007/60/EC) and Water Framework Directives (2000/60/EC):

- Category 1 - measures to protect water resources;
- Category 2 - measures to protect the fish and wildlife: repopulation and protection of riparian habitats;
- Category 3: improvements aimed at increasing the natural, recreational and social values;
- Category 4: measures aimed at reducing the flood risk.

After identifying the most significant ES and the benefits they generate for each proposed action, their positive impacts were estimated in monetary terms.

The expected benefits were estimated identifying the Ecosystem Services (ESs) improvements, associated to the interventions. These improvements were estimated through the application of monetary quantification techniques (as listed REMEDE 2008, EFTEC 2013).

The main approaches used to quantify the economic benefits were the method of market values, the method of avoided costs, and the method of Benefit Transfer (BT) due to the impossibility to conduct a direct specific survey for certain ESs. BT allows the use of outcomes from other scientific studies, appropriately selected from the literature and adapted to the case in question.

In conclusion, the generated economic benefits were estimated to be more than double of the initial investment for the interventions realization.

The role of urban soil ecosystems as the basis for healthy urban gardening

Anton M. Breure; Dienneke Schram; Liesbet Dirven-van Breemen; Frank Swartjes; Piet Otte

National Institute for Public Health and the Environment (RIVM), NL

The Snowman project Urban Soils studied the role and function of urban soil and the potential of urban gardening to contribute to health and wellbeing. Based on an extensive literature study, we developed a framework for the relationships between soil ecosystem services, ecosystem health and human health. The effects of urban gardening on determinants of human health were described.

The performance of ecosystem services is a prerequisite for realization of urban gardening and its contribution to individual and community health.

Regarding the use of urban soils, both health benefits and health risks need to be taken into account. Often, a site's history provides clues to the presence of contaminants in soil such as lead, copper and cadmium. To date, no specific European policy on urban gardening practices exists. Risk management policy is usually established by local authorities within a national framework.

Literature suggests that health benefits of urban soil use for gardening result from stress reduction, increased physical activity, increased consumption of vegetables and fruit, and more social contacts, particularly in the elderly. In addition to effects on an individual level, it may affect neighborhood characteristics favorable to community health, such as social cohesion.

Incidentally, effects on violence rates, inclusion of vulnerable or minority groups, and improvement of the physical and ecological quality of the area are described. However these effects were not always observed. Urban gardening provides the opportunity to alter and self-manage the environment; important determinants of human health and well-being. However, the positive effects may have been overestimated: it is likely that urban gardening attracts people selectively. In addition, we have to take into account the possibility that only studies showing positive relationships between urban agriculture and health have been published, in contrast to studies showing negative or no relations.

Indicators were defined to quantify ecosystem services, effects on individual health and community health. Indicators for ecosystem services of green space include retention and provisioning of nutrients, soil structure, and pest control. Urban gardens may contribute to consumption of locally produced food, which reduces the environmental burden of food distribution. From an ecological perspective, sustainable gardening practices are preferred. Relevant indicators for individual health are: perceived stress reduction, perceived health, amount of daily physical activity, social contacts, and frequency of consumption of vegetables and fruit. Over-arching indicators are the perceived health and the presence and location of unsealed soils (i.e. in use for urban gardening or for distinguishing different types of green infrastructure) in cities. The results of the study suggest that urban gardening can contribute to health and to governmental environmental agendas. It could be used to address a range of health policies like healthy aging, obesity in children, or reduction of socio-economic health disparities.

The Protection Value of the Soil Ecosystem

Pär-Erik Back¹; Sofie Hermansson¹; Lars Rosén²; Yevheniya Volchko²; Karin Wiberg³; Malin Fransson⁴; Anja Enell¹

¹ Swedish Geotechnical Institute; ² Chalmers University of Technology; ³ Swedish University of Agricultural Sciences; ⁴ Swedish Transport Administration, SE

The driving force for remediation at contaminated sites in Sweden is often the protection of the soil ecosystem. There is yet no commonly agreed methodology for site-specific ecological risk assessment (ERA) and there are few examples of site-specific ERA applied on real cases. When preparing for an ERA, there is a need for consensus on how the soil ecosystem should be valued. Is it worth protection, and if so, why? Such questions are answered differently by authorities and other stakeholders throughout Sweden. The aim of this study was therefore to conceptually clarify what is meant by the protection value of the soil ecosystem, and to describe what it consists of. The derivation of the protection value is based on environmental ethics and the Swedish environmental legislation (the Swedish Environmental Code).

Different environmental ethic views would probably lead to different valuations. People with an anthropocentric view would value the soil ecosystem solely for the goods and services it can provide to humans; for example food, clean groundwater etc. These values are called instrumental values, often expressed as ecosystem services (ESS). On the other hand, people with an ecocentric view would argue that the soil has value beyond what it provides humans, i.e. a value of its own, or a so called intrinsic value. According to our interpretation of the Swedish Environmental Code, this law combines two ethic views: inter-generational anthropocentrism and weak ecocentrism. This implies that nature has a value in the goods and services it provides to present and future human generations, and that both humans and nature are ascribed intrinsic values. Therefore, the protection value of the soil can be expressed as a combination of three types of value: (1) the intrinsic value of the soil, (2) ESS provided by the soil, and (3) benefits to the whole ecosystem provided by the soil. The intrinsic value of the soil is especially important to consider where humans have limited use of the soil environment. Regarding the ESS, the time perspective is particularly important to take into account; some ESS may not exist today, but may arise in the future, depending on land use.

In the guidelines developed by the Swedish EPA on risk assessment, generic protection levels are given based on two kinds of land use: sensitive land use (residential areas) and less sensitive land use (industrial areas). The reason for the use of different levels of protection, when applying our model, is that the instrumental values differ for the two kinds of land use. In other words, it is assumed that in residential areas the sum of the instrumental values (ESS etc.) is higher than in areas used for industrial purposes. An important aspect is that the intrinsic value may be the same, i.e. a decision to change the land use does not affect the intrinsic value of the soil.

To conclude, in order to fulfil the intentions of the Swedish Environmental Code, both the soil's intrinsic value and its instrumental values must be taken into account. It must be noted though that this does not automatically mean that such values always are strong or high, but they should be considered.

Paving the path with soil functions for developing tools to sustainable soil management

Michiel Rutgers¹; Liesbet Dirven-van Breemen; Ton Schouten; Anton M. Breure; Rachel Creamer

¹ National Institute for Public Health and the Environment RIVM, NL

Society requires vital soils for life support functions, such as: efficient production of strong crops, production of drinking water, climate control, water safety, nature's habitat, nutrient cycling, building platform, and recreational, educational and spiritual values. These functions are often coproduced in a bundle of soil-related ecosystem services: in one defined location each service has a specific spatial and temporal scale. This perception defines the scene for the contribution of soil information and science to furnish a framework for quantification and assessment of soil functions. Soil policy makers, land managers, farmers, water boards, government and society need insights in the performance of soil functions and its responses to soil management, to make land use more sustainable.

In this contribution, we will demonstrate how soil information can be used to quantify and assess soil functions. In the EU H2020-project LANDMARK a generalized soil function framework was defined based on two subsequent steps. The first step comprises the quantification of a soil attribute, i.e. a characteristic of the soil system, which can be measured, modeled or estimated with best professional judgment. The second step consists of application of utility functions to quantify a soil function, through combining weighted attributes in a multi-criteria approach. In this respect, a soil function is an overarching aspect of the soil system, which is valued by the end users: i.e. society (e.g. climate functions), or (groups of) persons (e.g. food production, water safety) which have specific interests or needs from the soil system.

The approach will be furnished with data and models from the nation-wide soil-monitoring network in the Netherlands, with chemical, physical and biological soil indicators. The network consists of a random-stratified grid design with about 400 sites. The network was deployed since 1997, and many sites were analyzed three times in a six year cycle. This allowed us to model the soil characteristics at the scale of the Netherlands, and to produce maps of soil functions. The maps are freely available from the Atlas Natural Capital (www.atlasnatuurlijkkapitaal.nl).

ThS 6a.4: Subsurface engineering to optimize diverse use options

Soil Sealing by Enhanced Aluminium and organic matter Leaching (SoSEAL): a novel geo-engineering technique for in situ soil permeability reduction

Susanne Laumann¹; Jiani Zhou²; Frank Volkering³; Dick van den Heuvel⁴; Richard Rijkers⁵; Jauk Stroo⁶; Timo Heimovaara²

¹ Tauw bv, Delft University of Technology; ² Delft University of Technology; ³ Tauw bv; ⁴ Heijmans bv; ⁵ Movares Nederland bv; ⁶ De Vries & vd Wiel bv, NL

The utilization of natural processes for engineering purposes has been widely discussed in recent years since they might enable the development of cost-effective, robust and sustainable engineering technologies. We hereby propose a novel geoenvironmental tool for in situ permeability reduction which is inspired by podzolization. Podzolization is a soil formation process where the mobilization and subsequent leaching of aluminium, iron and organic matter (OM) in the topsoil is followed by their precipitation at greater depth. The accumulation of Al/Fe-OM precipitates results in the formation of an almost impermeable soil layer. In such way induced in situ permeability reduction is interesting for several engineering questions, including contaminant containment, dike stabilization, and sealing of leaking water bodies.

The first pilot demonstration of the SoSEAL concept (Al-OM flocculation for permeability reduction) was performed at a dike stretch along the river Lek, near Schoonhoven, The Netherlands. At the site a highly permeable sand layer is located at a depth between 7 to 13 m below ground surface (bgs). Reducing its permeability will increase the stability of the dike. The aim of the pilot was to create a circular low-permeability-zone in the sand layer via separate injections of Al and OM solutions. Before the start of the pilot a COMSOL based 3D reactive transport model was used (1) to design the injection strategy, (2) to simulate the solute transport, the geochemical reactions and their effect on the permeability at the site, and (3) to predict the possible outcome of the pilot implementation.

Implementation took place between July and October 2016. In total 20 injection wells were placed in a circle. At each injection point two wells were installed with filter screens at a depth of respectively 7-8 m bgs (shallow) and 8-12 m bgs (deep). Eight monitoring wells were installed surrounding the circle of injection wells while one extraction well was placed in the centre. Injection of aluminium chloride and OM was performed over two weeks with a total injection volume of 12.5 m³ of both components in the deep injection wells and 5 m³ in the shallow wells. During injection, groundwater was extracted from the central well to control the groundwater streamlines and therefore facilitate mixing of the two separately injected fluids. The eight monitoring wells surrounding the injection circle and the extraction well were equipped with pressure and electric conductivity sensors. Monitoring of the whole processes during the injection consisted of groundwater sampling from the monitoring wells, the extraction well and the tanks containing the reaction fluids, and electrical resistivity tomography (ERT) measurements. At this moment additional measurements are performed to evaluate the effect of the injection on the permeability within the circle. Results will be presented at the conference.

Groundwater energy: policies, integrated technologies & management

Tim Grotenhuis¹; John Flyvbjerg²; Nanne Hoekstra³

¹ Wageningen University, NL; ² The Capital Region of Denmark, DK; ³ Deltares, NL

In the transition to sustainable energy systems the demand for space heating and cooling is of crucial importance, as it requires 50% of all the energy we use. Subsurface storage of heat utilizes abundantly available heat with demand at another time (e.g. summer-winter, or day/night). Aquifer Thermal Energy Storage (ATES), also called 'Groundwater Energy', provides a cost-effective solution: heat and cold can be stored for six months or more.

Storing thermal energy in aquifers and acquiring heat and/or cold from extracted groundwater is in the Netherlands a popular sustainable energy technology, because of its cost-efficiency, delivering on average approximately 60% less CO₂-emissions and substantial savings (ROI < 5 – 10 years) compared to sole use of fossil energy. In the pan-European Climate-KIC project Europe-wide Use of Sustainable Energy from aquifers (E-USE(aq)) we showed before that in the rest of Europe, socio-economical, legislative and some technological barriers prevent widespread application so far, but that these can be overcome.

ATES can function as stand-alone technology, be integrated in energy grids with other cooling/heating technologies, combined with sustainable power production or with reuse of surplus heat and cold from e.g. industrial plants. ATES systems may offer, especially in combination with cooling, very cost-effective solutions with savings up to a factor 4 compared to conventional systems.

Currently, in Europe scarce awareness on ATES systems as well as regulatory and knowledge barriers hamper the wide adoption of such systems. In this session technical specialists are connected with decision makers in an interactive discussion about a wide range of solutions for these difficulties including policy contributions.

At the start of the session Sara Picone (ASTER, It) will present a short overview on how barriers are overcome in demonstration projects of different ATES applications from the EU project E-USE(aq) which aims at boosting market application of ATES in Europe.

Five hot topics will be addressed in three minute pitches, each pitch will result in a statement about how to realize Europe-wide implementation of Groundwater Energy.

The statements of the pitches will be the basis for discussions by an international panel of experts in which the audience can participate, led by Ruud Cino (Ministry Economic Affairs, NL).

The topics of the pitches are:

- 1) Optimal use of subsurface space with ATES requires 'smart energy grids'. (Martin Bloemendal, TUD/KWR, NL)
- 2) The use of ATES to stimulate biodegradation of VOCI contaminated groundwater. (Zhuobiao Ni, SYSU, China)
- 3) The dilemma on water scarcity and development of sustainable technologies (Dynamic Closed Loop (DCL) for heating and cooling. (Alicia Andreu Gallego, Instituto de Tecnología Cerámica, Spain)
- 4) New generation solar cells to improve electricity production plus production of heat: PVT cells (Nicholas Simmons, Naked Energy, UK)
- 5) Creation of attractive business cases for groundwater energy (Matteo Mazzoni, Nomisma Energia, It)

In the international panel (John Flyvbjerg (Capital region of Denmark, DK), Johan Ceenaeme (Ovam, B), Wouter Gevaers (Arcadis, B), Attilio Raimondi (Emilia-Romagna Region, Energy Service, It)) opposite opinions of a variety of stakeholders will discuss the changes and hick-ups for societal implementation of the proposed technologies. The chair of this special session will stimulate interaction with the public.

ATES-PLUS: combining underground energy storage and cleanup of contaminated groundwater using a new bioremediation concept

Maurice Henssen¹; Erik de Vries¹; Arjan de Vries²; Eric van Griensven²; Andre Tennekes³

¹ Bioclear; ² Brabant Water; ³ T&K Service, NL

In the Netherlands, underground energy storage using open Aquifer Thermal Energy Storage (ATES) plays a significant role in the increase of sustainable energy and therefore these systems are frequently being used. Especially for cooling, ATES is by far the most effective available technique in urban areas. ATES is also easier to incorporate in urban areas, compared to wind and solar energy, especially in industrial or commercial zones with high buildings.

However, due to (historic) industrial activities in urban areas, groundwater is often contaminated. ATES systems may cause unwanted spreading of these groundwater contaminations, may lead to legal complications and increasing cost for the cleanup of these contaminations. Therefore, ATES systems are often not permitted in urban contaminated areas. This can be overcome if ATES systems have a remediating effect. This was the incentive for Bioclear to define a new concept called ATES-PLUS. A concept in which specific bacteria are introduced in the subsurface, using the ATES system to spread the organisms. These bacteria feed on the contaminations, thus cleaning the groundwater.

Normal bioremediation often imply the injection of organic substances into the groundwater to enhance bacterial growth and degradation of contamination. This is unwanted in ATES, since organic additions will lead to both bacterial growth and redox shift in groundwater, both of which in turn will cause precipitation and well clogging.

However, only microorganism infiltration by itself does not lead to well clogging. ATES-PLUS consists of a bioreactor system cultivating high concentration anaerobic bacteria that are injected using the ATES wells, thereby leaving the redox condition in the groundwater unchanged, but leading to a significant contamination breakdown. As ATES systems are built to be used for decades, this results in an effective combination. Laboratory results (2014) showed very good removal of dichloroethene (c-DCE) and vinylchloride (VC) in iron reducing and sulphate reducing soil/groundwater systems, without addition of significant carbon sources. A first pilot project at Paleiskwartier in 's Hertogenbosch was conducted. A onetime injection of bacteria led to a dechlorination shift of 5% within 4-6 months. A second pilot test started September 2016 in Apeldoorn. Spreading of the injected organisms, soil/groundwater ratios of the bacteria, activity of cells and dechlorination rates are monitored. Results of this promising technology will be presented. ATES-PLUS can be of importance to various municipalities around Europe, leading to effective use of sustainable energy concepts combined with quality improvement of the contaminated subsurface.

This project has been scored number 1 by the Dutch Ministry of Infrastructure and Environment, Department Rijkswaterstaat and is supported financially by the Ministry to perform two pilot studies and a full scale application. The project is carried out by the municipalities of 's Hertogenbosch, Apeldoorn and Tilburg, Province of Noord-Brabant, Bioclear, Brabant Water, T&K Service, IF Technology, Wageningen University, Hydreco and AVANS.

Progress in Sustainable Land Management Worldwide

Barbara Maco¹; Nicola Harries; Hans Slenders; Francois Beaudoin; Jonathon Smith; Laurent Bakker; Claudio Albano; James Henderson; Yasuhide Furukawa; Alfonso Rodriguez; Colin Chen; Mengfang Chen; Renelle Watson

¹ WACTOR & WICK LLP, GB

Background

Over the last 20 years' management of historically contaminated land has largely been based on prevention of unacceptable risks to human health and the environment, to ensure a site is 'fit for use'. In the last 10 -15 years, additional interest has been shown to include sustainability as a decision-making criterion. The sustainable approach considers the environmental, social, and economic consequences of risk management activities themselves, and also the opportunities for accelerated site reuse with wider benefits for the local community beyond achievement of risk-reduction goals alone.

Approach/Activities

Sustainable remediation has now become an area of development globally with public and private sector organisations becoming involved in many projects and networks intended to improve remediation practice and make it more sustainable.

Sustainable Remediation Forum (SuRF) initiatives are now well established in UK, USA, Canada, Australia, New Zealand, Netherlands, Italy, Taiwan, Brazil, Japan, Columbia, with further interest in China and Scandinavian Countries. The more mature networks are now looking holistically at sustainable land management, considering climate change and the resilience of communities to deal with this. With the Network for Industrially Contaminated Land in Europe (NICOLE) also being involved, these networks have been meeting quarterly for the last four years to share knowledge, work collaboratively and provide support to the newer networks with information made available through www.claire.co.uk/surfinternational More recently these networks have formed an alliance known as International Sustainable Remediation Alliance, the aim is to reach out to external global stakeholders with similar agendas and look to work collaboratively and to help promote the work of the different SuRFs including capacity building through on-site and on-line global events. A focused effort has been offered by different SuRFs, in collaboration with other international bodies to plan and lead the organization of a number of International Sustainable Remediation (SustRem) Conferences around the Globe.

Results/Lessons Learned

With a remarkable degree of consensus across many programmes the purpose of this workshop session is to provide a brief global round up of progress of the different initiatives, how thoughts are developing on sustainable land management concepts, how climate change and resilience of communities is being considered. The workshop will review common themes and points of divergence and encourage open dialogue throughout the session.

ThS 6b.1: Water and Subsurface management in the context of climate change

High groundwater table in a Danish town - Challenges and opportunities in a climate adaptation perspective

Anja Melvej¹; Henrik Larsen¹; Rolf Johnsen¹; Anders Juhl Kallesøe²; Thomas Gad³; Benny Nielsen⁴; Jesper Bjergsted Pedersen⁵

¹ Central Denmark Region; ² GEUS; ³ Herning Municipality; ⁴ Herning Water Utility; ⁵ Aarhus University, DK

Background: Central Denmark Region (CDR) has in the In a 3½ year European project "Top-Soil" a number of pilots that will be involved in understanding the challenges and find relevant measures and solutions to the climate change affects at the hydrological cycle. For more details see paper 678, topic 6b.

One of these pilots is located in the town Sundsin Herning municipality (DK). In Sunds the groundwater table is very close to the surface and subsequently reacts rapidly in response to increasing rainfall. Due to renovation, in this case sealing, of the sewage pipe system and extra precipitation in future climate, the town and adjacent fields is likely to be flooded by rising groundwater and already at present state basements are flooded during winter periods.

The challenge is new in Denmark and the responsibility of the challenge is at present at household level. Rising groundwater tables are not a task the local authorities are responsible for. The municipality and the local water company are responsible of securing clean drinking water and discharge of rain and sewage water. The stakeholders involved in this pilot all have different interests; the water utility company wants to avoid the huge amount of excess water within their sewer system and the municipality wants to secure the citizens of the town against flooded basements etc.

Aim: The aim of this pilot is to enhanced comprehension of the challenges connected to a strong control of the groundwater table. With all the different stakeholder interests it is essential to have a common understanding of the problems based on a joint dataset. Data from the different stakeholders will be included in a common geological- and later groundwater model. The model will form the basis of all investigations and assessment of potential solutions.

The quality of the excess water differs. In some areas, the quality is of high standards while in others the quality of the water is poor due to pollutants. Handling the climate adaptation in relation to groundwater flooding will be investigated by new geophysical methods and by introducing knowledge from other Interreg partners with expertise within this field. 10 drillings have been carried out to investigate groundwater levels and quality parameters. Further we have planned to investigate the surface-water quality within the pilot. The investigations should contribute to the assessment of different applicable solutions to avoid flooding. The quality of the water will indicate the possible use of the water.

Presentation: At the conference, the pilot Sunds will be presented with focus on the geological and hydrological survey and further the groundwater quality and how this can be utilized when various solutions for the area are assessed.

Third river of Zwolle, the use of the deep groundwater system in the urban area of Zwolle for climate adaptation and water retention

Andreas van Rooijen¹; Renate Postma¹; Koen Weytingh²; Reinder Slager³

¹ City of Zwolle; ² Toekomststerk; ³ 3Dimensions, NL

Water system thinking

Breezicht, a subarea at the outskirts of Zwolle, will be developed over the coming years. Located in one of the lowest parts of the IJssel/Vechtdelta, climate resilience is an important challenge.

Traditionally, when designing the water system, we think in a horizontal manner: drainage of excess water or intake of new water is achieved via ditches, ponds, and optionally, using a pumping station. For Breezicht however, this thinking process has been reversed. We do not think horizontally, but vertically; we are going to involve the subsoil and the deeper groundwater system in the system.

At its core, the alternative concept is simple. The green-blue structure to be constructed is used for the drainage and partly for the storage of rain. The excess rainwater is led to a deep (former) sand extraction lake, via the green-blue structure. This lake cuts through the shallow water separations and connects the phreatic groundwater body to the deeper aquifer. This allows the water to be slowly infiltrated and drained via the groundwater.

Because the water level is lower than the ground level, the water can flow down under gravity (via waterways) to the lake. The water level of the lake will rise temporarily, which causes the water to gradually infiltrate into the subsoil until the water level of the lake is equal to the 'natural level in the subsoil' again.

In times of drought, the principle works the other way: evaporation lowers the level of the surface water, and of lake as well. Groundwater from the subsoil will flow toward the lake to restore the level to its natural state.

Advantages

This system offers various advantages. The infiltrated water will be discharged via the deeper groundwater (the third river) and no longer needs to be removed by the water authority. Dewatering via this principle mainly creates a dampening effect over time.

The water is introduced into the lake, infiltrates the aquifer, and basically becomes part of the third river.

This way, the same rainwater will not reach the pumping stations within a few days, but after a period of weeks to months. This dampening effect has the advantage that the surface water system does not need to deal with peak discharges as much. This is beneficial in light of climate change and the expected increase in frequency of heavy showers.

The greater the difference between the level in the lake and the water level in the subsoil, the faster the water infiltrates or vice versa. Once the water level has dropped, the drainage will slow down and the water level will drop more slowly on the way back to the natural level. As if the subsoil 'thinks' about the optimal combination of retention, storage, and discharge.

In times of drought, when the system works in reverse, there is no need to let in extraneous water; instead, the system replenishes itself.

This way, the storage capacity of the green-blue structure in combination with the lake will be so great that the expected future showers can be stored. In addition, there will be a lot of green (larger trees) present in the district in the long run, which reduces the chance of heat stress in the dry period.

Video: <https://vimeo.com/193367218>

Dependence of green infrastructure on groundwater quality and quantity for effective ecosystem services delivery

Suzanne van der Meulen¹; Reinder Brolsma; Sophie Moinier; Frans Van de Ven

¹ Deltares, NL

Utrecht is one of the four biggest cities in the Netherlands and the city has strong ambitions to optimize the city for healthy urban living and climate resilience. There is growing awareness that green (including blue) infrastructure can play an important role in this respect. The effectiveness of green infrastructure for services such as heat stress reduction and runoff mitigation depends on availability of groundwater and soil conditions. For example, the cooling effect of vegetation is reduced in case of drought stress during summer months.

In this presentation, we demonstrate a method for analysis of groundwater availability and demand for ecosystem services provision by urban green infrastructure. The method has been applied in the city of Utrecht; the analysis is targeted at the ecosystem services temperature regulation (cooling), stormwater runoff mitigation, air quality regulation, noise reduction, recreation, increasing general wellbeing and water quality improvement.

Besides the current situation (2015), demand and supply have been analysed for different climate (2030 and 2050) and land use scenarios. The analysis shows that the cooling potential of vegetation in the research area is strongly limited by drought stress during summer months. Based on model simulations, the effectiveness of measures to improve the availability of water to vegetation and its effect on ecosystem services provision has been determined. This results in practical recommendations to city planners for optimizing the potential of green infrastructure.

Sustainable management of soils is a benefit for all

Rachelle Verburg¹; David Thelen; Paul Van den Elsen; Hans Slenders

¹ Arcadis Netherlands, NL

In the Netherlands remedial obligations towards historically contaminated sites are almost accomplished. In 2019 a new integral environmental law - the "Omgevingswet" - will be implemented. For soil and groundwater this means that the main focus is on continuity of services that our soils provide in, and on facilitating the sustainable use of our soils. Also the "Omgevingswet" strives for a more local way of decision making. This highlights that the role of the Dutch government is receding, taking more the role of a facilitator that stimulates the preferred outcome of the decision making processes instead of prescribing standard measures and deciding how to get there.

In Dutch society an arising awareness of the necessity of sustainable soil management is visible. Several triggers lead to a more prominent positioning of sustainable use, like the necessity of protection of our drinking water reservoirs, continuity in food and feed production and preservation of valuable nature and ecosystem services. The sense of urgency can be clearly demonstrated by capitalization of the potential losses due to poor soil management. A broad variety of parties (both public and private companies, as well as decentral governments) are working on answers for socially relevant problems which in principle can be united by sustainable soil management:

- Investors and banks with an interest in farmland stimulate sustainable land management due to the risk of value reduction of their investments caused by exhaustion of soils and decreasing yields. Some Dutch investors own several thousands of hectares of farmland with a value of several billions of euro's. A decrease in the value of farmland can have substantial financial consequences.
 - Drinking water companies increasingly cope with the fact that natural purification of soils is no longer in balance with the growing amounts of contaminants near drinking water stations. At the moment 140.000 kg medicine residues and 17.000 kg agrochemicals are discharged in the Netherlands on a yearly basis. For drinking water this means that 80% of the surface water exceeds the standards for agrochemicals and 25% of the groundwater supplies are threatened. On a yearly basis this results in extra costs of several billions for additional treatment in water purification plants.
 - Production companies that rely on soil harvesting have a clear benefit in guarding soil fertility (and preventing exhaustion) for durability of their production process, strategic and economic position.

Due to diversity of interests in above mentioned topics and the declaration that benefits and burdens often are not evenly distributed between the involved parties, accurate stakeholder management is an imported key element for a sustainable outcome. And with the receding role of the government the initiative for joint efforts will more and more be taken by private parties.

This presentation clarifies the sense of urgency of sustainable soil management, using factual statistics and capitalization of (potential) losses. Furthermore, the importance of stakeholder management and a roadmap to sustainable outcomes will be illustrated using several cases and examples.

Managing groundwater in changing climate to support regional development

Hanna Zydor; Victor Sposito; Robert Faggian

Deakin University, AU

Australia is the driest inhabited continent on Earth and groundwater is critical to sustaining agriculture and many settlements (accounting for 30% of consumption). However, groundwater remains a poorly understood resource; a situation that will be exacerbated by climate change and the associated uncertainty it brings.

Water in Australia is a public resource and its management was centralised through the establishment of National Water Commission (NWC) and Intergovernmental Agreement on a National Water Initiative (NWI) in 2004. Based on this agreement all Australian governments (Local, State and Federal) committed to a more unified approach to water management that included a system of water rights and water trading. In general, this system has worked well for surface water but a general lack of understanding of groundwater systems has resulted in over-allocation and over-exploitation of aquifers. According to the Victorian Auditor General, the State Government does not know if groundwater is being used sustainably and this is due to inadequate data and monitoring systems and inefficient implementation of management plans.

The issue of climate change makes ground water management much more complex. Our research on an economically important, groundwater-dependant region in southwest Victoria indicates that while climatic conditions will become warmer and drier, the future climate will actually favour the expansion of agriculture. This will create new economic-development imperatives for the region and therefore increase the risk of groundwater over-exploitation. This paper reports on the development of methods to assess groundwater volumes, coupled with crop yield models, across a region that is subject to rapid development and land-use transformation under climate change. The methods developed in this case study will be generalised for application in any ground water-dependant agricultural region.

To ensure that the opportunities associated with climate change are capitalised on sustainably, new groundwater assessment and monitoring approaches are required that can inform water policy and management in the context of imperfect data and information.

ThS 6c.1: Spatial assessment of soil and water quality using big data and GIS

Spatial interpolation of big data on urban soil contamination - Autocorrelation of data from the City of Copenhagen

Nemanja Milosevic¹; Peter Engelund¹; Martin Jakobsen²; Kristoffer Stensbo-Smidt³; Marcos António Vaz Salles³

¹ MOE; ² The City of Copenhagen; ³ The University of Copenhagen, DK

Big data are typically characterized by big volume, big velocity or big variety. In case of urban soil contamination it is mostly the variety that poses a challenge in data management and interpretation. It results from complex urban field conditions and a lack of standards for investigation (usage of various methods for soil sampling, chemical analysis and interpretation of results). Regarding volume, the number of contaminated sites globally is estimated to 5-10 million, most of them in urban areas [1]. Moreover, growing datasets are a commonplace in public offices for urban soil contamination, where management and risk assessment of contaminated soil are monitored and often financed. The public offices are challenged in having a good overview of past and ongoing activities and collected and missing data in their jurisdiction areas.

We hypothesize that 1) soil contamination can be inferred from nearby sites, given that a number of contamination processes exhibit spatial autocorrelation; 2) techniques that exploit spatial autocorrelation can be either improved or better tuned by the use of machine learning approaches. Thus we develop a spatial interpolation for data obtained with existing geochemical analytical methods, which includes algorithm development and data visualization in a geographic information system (GIS) [2].

We use kriging as the basis for our approach, but extend it to include critical new functionality. By using machine learning methods, the algorithm can automatically learn its parameters, thus achieving optimal performance on scales from single parcels to entire cities. Critically, the algorithm will be able to improve itself by observing new data from other cities or countries.

As soil measurements are never evenly distributed across a city, the algorithm can transfer information from, for instance, local geology, hydrogeological conditions, historical land use or properties of relevant chemical compounds to help infer contamination citywide. By using an active learning approach from machine learning, the algorithm can suggest locations for new measurements that will benefit the interpolation the most. The interpolation is visualized using a GIS heat map, which is also showing the interpolation accuracy at all locations.

The decision making process using the developed approach is conditioned by an agreed cut-off decision value for interpolation accuracy. The agreed values, however, make the approach useful both in areas with low and high interpolation accuracies. The main advantage is that the approach is developed without traditional confinement to borders of individual contaminated sites but upon multiple sites with shared contamination sources and pathways.

[1]: CRC Care, Fact Sheet 1 – Contamination, <http://www.crccare.com/publications/fact-sheets-and-brochures/fact-sheets-and-brochures>

[2]: GANDALF: Untargeted Fingerprinting Analysis and GIS Visualization of Contaminants, www.plen.ku.dk/gandalf

Compositional data analysis of geochemical soil data

Jennifer McKinley

Queen's University Belfast, FR

Baseline mapping and the calculation of threshold values are often used to assess the quality of land based on land use categories such as residential or industrial sites. A threshold is often set to differentiate between concentrations of the element that naturally occur in the soil and concentrations that result from diffuse anthropogenic sources. Regional geochemistry soil databases are increasingly being used to determine these baseline environmental assessments. The key question raised in this presentation is whether the use of a single component baseline or threshold geochemical map can provide an accurate interpretation on its own. Implicit is the thought that single component geochemical maps represent absolute abundances. However, because of the compositional nature of the data due to the closed or constant sum problem, univariate geochemical maps cannot be compared directly with one another. As a result, any interpretation based on them is vulnerable to spurious correlation problems. This presentation examines what this means for baseline quality documentation and risk evaluation. Despite the limitation of relative abundances, individual raw geochemical maps are deemed fundamental to several applications of geochemical maps including environmental assessments. However, element toxicity is related to its bioavailable concentration, which is lowered if its source is mixed with another source. This may be more adequately dealt with if a single component map is not interpreted in isolation to determine baseline and threshold assessments. A range of alternative compositionally compliant representations based on log-ratio and log-contrast approaches are explored to supplement the classical single component maps for environmental assessment. Case study examples are shown based on the Tellus soil geochemical dataset covering Northern Ireland, UK.

An Urban Geochemical Database for Contaminated Land Management

Jean-François Brunet¹; H el ene Roussel²; Etienne Taffoureau¹

¹ BRGM; ² ADEME, FR

In February 2007, new approaches of management were proposed by the French Ministry for Sustainable Development to the various actors involved in “(potentially) contaminated land management”.

They describe the stages of management of a (potentially) contaminated site: the diagnosis identifies and locates pollution, the management plan sets objectives of rehabilitation, the residual risks assessment verifies the accuracy of the selected management option, the Media Quality Assessment (MQA) (Interpretation de l'Etat des Milieux, IEM) verifies the impacts out of the site.

During these approaches, the interpretation of the data collected from the field necessarily causes the comparison of the analyses and measurements with reference values. Thus, the approach of MQA is based on the risk management policy conducted by the public authorities for the French population. It results in comparing the state of the investigated mediums with:

- Natural environment close to the zone of investigation;
- Regulatory management values set by the public authorities.

Indeed, the public authorities fix sanitary values which regulate air quality as well as water and food. Therefore, these values naturally serve as references. However, the soil is not the object of a specific regulation and no regulatory reference value exists in France for this medium.

A soil is considered free from pollution since its characteristics are coherent with the local natural geochemical background. This is why, the approach results in comparing the state of the investigated soil with the state of the natural soils close to the zone of investigation. With this intention, the knowledge of the natural geochemical background, in particular of the local geochemical anomalies, is essential. Moreover, the characterization of pollution is important to distinguish if it implies the site or not.

However, the industrial sites are more often gathered in industrial and urban areas where an anthropic geochemical background is superimposed to the natural geochemical background. It then becomes necessary to compare data collected on the investigated site with this anthropized pedological and geochemical background.

In order to support the various actors implied in the management of (potentially) contaminated land, it was thus proposed to carry out a database of analyses of soils from urban and industrialized environment on the whole French territory. The project “Diagnoses of the soils in the places hosting children or teenagers” implemented by the French ministry for Sustainable development, was the occasion of launching an operation of sampling and analyses of urban soils at the level of the national territory. The collection of analyses during this operation constitutes the heart of the project “Geochemical Database on Urban Soils and Subsoils (BDSolU) conducted by BRGM and funded by ADEME.

Soils analyzes include inorganic trace elements, mercury, cyanides, phenol index, HC C10-C40, PAH, PCB and PCDD/PCDF...

This presentation points out the building of the database and describes the difficulties encountered.

Geochemical mapping and urban allotment garden soil management

Béatrice Béchet¹; Cécile Le Guern²; Liliane Jean-Soro¹; Thierry Lebeau³

¹ IFSTTAR -IRSTV; ² BRGM; ³ Université de Nantes, FR

Urban Allotment Gardens (UAG) are expanding worldwide, especially in large cities. A large program towards UAGs has been launched since a few years in the city of Nantes (France). A soil quality assessment was conducted in 26 gardens on the city-territory. As eight of the gardens showed soil contamination problems, detected by a light screening (4 or 5 samples per garden), a diagnostic on the entire in surface of these gardens was conducted to help stakeholders in decision-making on the soil management.

Environmental pressures (pollution, gardener's practices, geogenic contamination) result often in potentially harmful trace elements in garden soils. The objective of the study was to assess the spatial variability of trace element distribution in UAGs at garden scale, to evaluate abnormal values under environmental pressures, and to assess the portable X-ray fluorescence screening method as a useful tool in soil management. The sampling and measurement strategy was based on a preliminary study of the environmental and historical context (including geology and historical land use) and on in-situ heterogeneity tests. On site measurements of trace elements content in soils were carried out during dry periods using a portable X-ray fluorescence analyser. Additional ICP-MS analyses were used to check the accuracy of the results. Finally, the spatial distribution of trace elements in soils was mapped and used to discuss the management options with the stakeholders.

Each garden showed a specific spatial distribution of trace elements, linked to its environmental context but mainly to the land-use evolution. The contamination zones account for 10 % to more than half of the surfaces of the gardens, Pb and As being mostly present. At first, the analysis of geological maps and land-use evolution of sites allowed a more efficient screening strategy (definition of zones which the same characteristics). Aerial photographs were useful to detect potential impact from the environment of the garden, refillings of the zones and the development of the UAGs. PXRf measurements of trace elements concentrations combined with description of soil profiles allowed a better interpretation in terms of land-use changes and impact of parent materials. The PXRf screening method and mapping were very helpful for hot spot detection or delineation. But even if the spatial distribution and origin of trace elements were well described at garden scale, the source of trace elements has to be validated through additional methods in three study-cases (former market gardening).

The method used was proved to be a cost-effective solution for soil management at garden scale because it could also be used to discriminate between zones with and without cultivation restrictions. The soil management solutions were adapted to the contamination levels: excavation and refilling, addition of non-contaminated soil, change in use (orchard, collective green space). Moreover, an innovative phytoremediation solution is currently carried out in one of the gardens.

Strategic planning of sustainable soil management

Joan Krogh¹; Benja Johannesen²

¹ NIRAS A/S; ² Vordingborg Kommune, DK

Background:

Urbanization in form of development projects of brownfield areas and in the land zone as well as sewer and cable work results in large amounts of soil to be relocated each year. The soil is transported many kilometres away from its origin and replaced by uncontaminated gravel materials derived from mining pits. Traditional soil handling is expensive and the environmental impact is negative; i.e. increase in greenhouse gases, CO₂ emissions, and transport through densely populated urban areas cause traffic congestion thereby having a negative impact on traffic safety.

A more efficient and sustainable soil management can take place at two levels:

1. An overall strategic level that is initiated by the local authorities.

The strategic soil management can provide new opportunities for local reuse and provide strategic guidance for managing soil within the municipality. It is implemented through district plans and environmental permits.

2. In the individual projects.

The sooner soil management is incorporated into the project, the more options and alternative solutions can be created and be available at various stages of the project. The handling of the soil is controlled through soil management plans, partly at the strategic level, partly through the details of the project; i.e. the number of soil samples, soil handling sites and supervision (described in soil handling plans).

Aim:

In the municipality Vordingborg a vision of using clean and slightly contaminated soil from construction projects in the area have led to development of a strategy for reusing the soil locally that includes the entire municipality. The municipality is located in South Zealand and the nearest soil handling site is located far away. Consequently, the project aims at creating practical and flexible opportunities for the local contractors to handle the soil locally and thus save money by considering soil as a resource and not a waste product. The strategic solutions provided by the municipality helps the contractors to a more successful planning of the individual projects and thereby help the municipality to execute its own projects.

The development of an overall strategy of sustainable soil management also aims at strengthen the branding of Vordingborg Municipality and ensure good competition for the local contractors.

Conclusion:

As part of the development of the strategy, a number of project ideas have been recognized and listed in a 'Possibility Catalog'. The implementation of the selected project ideas are over the next 12 years expected to result in 600,000 m³ of soil reused locally, a reduction in cost of 24 mio. DKK, a reduction in transportation of 3,5 mio. kilometers and 2,900 tons of CO₂-eq or 75% of the emissions associated with traditional soil handling.

ThS 6c.2: Assessment of sustainable use of the subsurface resources

Tools for sustainable development with the subsurface

Thom Maas¹; Linda Maring²

¹ Rijkswaterstaat; ² Deltares, NL

Better cooperation between urban developers and sub-surface specialists in early phases accelerates (re)development processes and contributes to more sustainable strategies. This asks for approaches that integrate technical, economic and social aspects. Tools can add to this. There is a multitude of tools available to guide sustainable development both in urban planning as well as in subsoil projects. Although there is a multitude of tools, they cannot always be found and are therefore underused. And if a list of tools can be obtained, there is a risk to get lost.

When do we use tools?

Tools have been developed in different regulatory contexts and with different concepts/ideas of sustainability and for different tasks in the phases of redevelopment and may focus on one or multiple aspects of sustainability and on different phases of redevelopment.

Tools can ease the process of structuring and analysing data. They can combine and visualize different sources of information, give meaning and add to understanding and support of stakeholders; assess impacts, costs or sustainability of alternative strategies; can indicate and support the exchange examples and experiences, etcetera.

There is a need for tools that are focused on specific tasks on specific moments in a (re)development project. Tools need to be used for the task that they were developed for to be effective and give meaningful input. An important boundary condition for the use of tools is that they should ease our work. The costs and benefits of using them must be in balance. For application of any tool the user needs to: be allowed to (managerial approval, e.g. for the time spent), be able to (necessary resources: data, information, knowledge, stakeholder), and want to (to add something extra or special to a project, the right questions need to be asked and the people need to be enthusiastic about it).

How to find the right tool

To improve the use of existing tools and find the right tools for the right task, RWS and Deltares have developed an online navigator with over 275 tools that are focused on subsurface / groundwater / urban (re)development

The users of the navigator are guided by a faceted search system. The search system is funnelled as follows:

- What for? Starting point is a (societal) challenge or issue such as climate adaptation or remediation
- What? For each challenge, tasks are defined such as using the subsurface or assess effects
- How? The type of instrument is given, divided in reading (eg a manual), calculating, showing (eg GIS tools) or doing (quickscan, workshop)
- When? The entry "phase" is not used yet because most tools are for the initiative / plan phase (and not realisation, evaluation and maintenance phase) and is not distinguishing sufficiently. The entry can be added in a later phase.

Concluding

There are many useful tools that contribute to the integration of spatial (re)development and the role of the subsurface, but in many cases they are rarely used. To support users to find tools for their specific tasks, contributes to better utilization. By using tools, and exchanging user experiences and examples, they can be improved and kept up to date.

GeoEkoKalkyl – development of a tool for integrating constructability and ecosystem services in municipal planning

Christel Carlsson¹; Bo Lind¹; Jim Hedfors¹; Ola Wik¹; Annika Åberg¹; Ann-Mari Fransson²; Yevheniya Volchko³

¹ Swedish Geotechnical Institute; ² Swedish University of Agricultural Sciences; ³ Chalmers University of Technology, SE

Soil is a vital natural resource which provides us with important environmental, economic and social functions. Soil properties and quality is a prerequisite for the promotion of a number of ecosystem services in urban areas, such as maintaining a green infrastructure (e.g. water and nutrient supply, climate control, recreation, biodiversity) as well as buffer and filter capacity (sorption of contaminants, regulation of storm water). The soil is also the subbase for buildings and constructions. Often there is a conflict between the need for new housing and the need for maintaining ecosystem services. With the current migration and urbanisation, there is a high risk that many ecosystem services in urban areas will be lost. Thus, it is important to value soil in a resource efficient and sustainable way, including both geotechnical and ecological aspects.

A project with the purpose to develop a GIS-based planning tool GeoEkoKalkyl will be presented. The tool will be designed to help identify, document and visualize the ecosystem services and the construction costs for land development. The tool will be based on an existing tool, Geokalkyl, which calculate the costs for ground reinforcement, excavation work and landscape modulation for instance in municipal planning. GeoEkoKalkyl will consist of an upgraded version of this tool, with a new feature linking geotechnical soil quality with different ecosystem services. Within the project different soil quality indicators are identified or developed from a minimum data set of soil parameters. The soil quality indexes are then used separately or in combination to describe and classify the soil quality needed to meet a range of ecosystem services. Project relevant ecosystem services are for instance maintaining green infrastructure (i.e. secure water and nutrient sources, climate regulation, recreation and biodiversity), buffering and filter capacity (i.e. regulation of surface water and sorption of pollutants). GeoEkoKalkyl will enable analysis and evaluation of how soil conditions affect both costs for land development and access to or loss of ecosystem services in construction. The results from the calculations in GeoEkoKalkyl will be presented in 2D or 3D maps, or as Excel matrices, and can be used as a basis for discussion and decisions in municipal planning. The tool is developed in close cooperation with stakeholders and will be tested in two case studies in the municipals of Malmö and Västerås.

Strategic Environmental Assessment (SEA) for the Spatial Vision for the Subsurface in the Netherlands (STRONG)

Martijn Gerritsen¹; Ivo van der Sommen²; Mark in 't Veld¹

¹ Tauw bv; ² Ministry of infrastructure and the Environment, NL

In November 2016 the Dutch ministry of Infrastructure and Environment published a draft of the National Strategic Spatial Plan for the subsurface (STRONG: STRuctuurvisie ONderGrond). The plan focuses on activities in the deep subsurface which are considered to be of national interest or which fall under the jurisdiction of the central government (mining act). This includes the management of groundwater resources for the preparation of drinking water, the exploration and exploitation of gas and oil reserves (including shale gas), geothermal energy, mining of rock salt and storage in the deep subsurface.

STRONG will provide a framework for spatial planning of the subsurface and for the emission of mining and environmental permits. The framework is based on a comprehensive approach of both the sustainable use of the subsurface and land use planning on a region scale.

Tauw provided the Strategic Environmental Assessment (SEA) for STRONG in corporation with different scientific institutes in the Netherlands. The SEA was not just used to assess the environmental impact of the final plan but was also used in the process of policy making by providing insight into the environmental effects of different policy scenario's. In our presentation we will present and discuss the working process and the final results of the SEA. We will explicate on the most important steps in the working process:

1. Scoping of the relevant environmental effects: a wide range of environmental effects is considered but the focus in STRONG, being a national wide plan, is on the environmental impacts on a regional scale. Local effects will have to be addressed in the environmental impact assessment for individual subsurface projects. For each relevant effect we made a systematic cause-effect analysis. This has led to a qualitative risk assessment based on expert judgment.
2. Spatial scoping: both the feasibility of mining activities and the likelihood of environmental impacts depend on the conditions in the subsurface. For each activity considered, maps are drawn to zoom in on the regions where environmental effect are most likely to occur
3. Development of scenario's: four scenario's are drawn up to investigate the far edges of the way in which the use of the subsurface could develop . These scenario's are not meant to be the actual policy options, but serve to provide insight in the range of opportunities and bottlenecks connected to the extent to which the subsurface is used
4. Elaboration of the scenario's: by combining the results of the first three steps, the potential environmental impacts of each of the scenario's is assessed and compared to a baseline scenario. The scenario's are compared and similarities and differences in the environmental impacts are analyzed on a regional scale
5. Assessment of the draft Strategic Spatial Plan: based on the information already gathered, an assessment is made of the environmental effect of the (policy) choices in the draft Strategic Spatial Plan for the subsurface

Asset Management to support urban land and subsurface management

Linda Maring¹; Maaike Blauw¹; Elmer de Boer²; Douwe Jonkers³; Jasper Lackin⁴; Joost Martens⁵; Coen Teeuw⁴; Kees de Vette⁵; Albert de Vries⁶

¹ Deltares; ² RWS; ³ Ministry of infrastructure and the Environment; ⁴ Witteveen+Bos; ⁵ Municipality Rotterdam; ⁶ Municipality Utrecht, NL

Challenges in urban areas increase by demographic and climate change. People in urban areas expect a healthy and safe environment. Municipalities implemented a system of various "assets", built over centuries, such as sewers, street lights and parks. Asset management is the transparency of trade-offs between performance, cost and risks throughout the entire lifecycle of these assets.

To enable liveable and adaptive urban areas different strategies are needed. One of the strategies is to make better use of subsurface space and its functions. What is present and possible under our feet, is in many cases unknown. Many projects in cities result unintentionally in the loss of subsurface functions. As a result, opportunities are missed or damage occurs. Using asset management when looking at the subsurface, visualizes its value and importance for the functioning of the city, now and in the future.

Asset Management of the Subsurface (AMS) can be used 1) to use the subsurface in a sustainable way within urban spatial planning (using its benefits, avoiding problems) and 2) to manage and maintain the subsurface and its functions.

AMS is based on "traditional" asset management methods, but next to manmade assets in the subsurface (e.g. underground parking garage), it also considers the (ecosystem) services as provided by the subsurface, including groundwater. These services (e.g. water storage) represent a value and therefore can be considered as "assets".

The basis for AMS is, similar to asset management, the balance between the performance of functions, risks and costs. As the subsurface is a slow-responding system, aspects such as irreversibility and scarcity of subsurface functions are important. In addition, multifunctional use of space adds value.

- Performance: which subsurface functions are potentially present and which functions are desired for an area? Possibilities and challenges are mapped; using area knowledge, subsurface data, information and models. Switching between scales (from area to project, from current situation to future) is an important aspect.
- Risks: risks for projects and land use functions due to subsurface characteristics and (unexpected) loss of the performance of subsoil functions are assessed. The interactions between the soil-water system and urban, anthropogenic system are examined to assess the effects of interferences.
- Costs and value: costs and value related to employment and maintenance of subsurface functions are assessed to be used in the processes of making alliances and decision making. Subsurface is a slow-responding system. Aspects such as irreversibility and scarcity of subsurface functions are important. Multifunctional use of space adds value.

Above aspects can both be assessed as quick scan or in an extended quantitative way, dependent on the objectives and project phase.

For AMS, four main adjustments on asset management are needed:

1. From maintaining objects to maintaining functions. The municipality is responsible for maintaining and managing essential functions for the public. These functions can be obtained both by deploying anthropogenic or natural assets. Consideration of long term performance, risks, costs and benefits supports decisions on how to provide specific functions: with natural solutions, civil engineering or a mix.
2. Consider the system: the subsurface is a system containing different assets (Anthropogenic assets: such as cables and pipes and natural assets: such as groundwater with temperature buffering capacity to be used for soil energy (ecosystem services)). These assets can coexist, compete for underground space, or interfere, leading to positive or negative effects. Therefore knowledge about this system is essential.

3. Private versus public asset management: Normally assets are managed by a public or private entity that is directly responsible for and affected by its performance. This is not the case when using the subsurface. While the government owns the subsurface in public areas, other entities benefit from using it. Also privately owned land in urban areas influences the ability of local authorities to fully employ subsurface functions. It is a challenge to allocate the costs and benefits of the subsurface. This requires good interaction with stakeholders.
4. From lifecycle to land (management) cycle: where assets have a specific life time and are considered from construction to disposal, many subsurface functions are “just there” for “eternity”. They should be considered using a land (management) cycle in which they perform their role. This has strong links with the above points. By continuously applying AMS, information on the subsurface and its functions and the AMS mode of operation can be improved.

The work described on AMS was performed by a Community of Practice. The CoP AMO consists of Municipalities of Utrecht and Rotterdam, Ministry of Infrastructure and the Environment, RWS, Witteveen+Bos and Deltares. Conclusion is that AMS contributes to:

1. Structure: due to decentralization in The Netherlands, responsibility for subsurface management is shifted to local authorities. AMS provides a structured way to support this.
2. Value: AMS contributes to preventing and reducing costs and cashing benefits.
3. Decision-making: Mapping values, risks and costs supports decision-making management of the subsurface.
4. Communication: asset management provides a language to improve communication between different policy fields and management layers.

AMS provides a method which allows for well-considered decision-making, based on the right information by balancing performance, risks, costs and value.

Sustainable brownfield restoration in Parc de l'Alba-Barcelona Synchrotron park

Jordi Boronat Rodriguez¹; Consol Pérez²; Xavier Rubio²; Vicenç Martí³; Irene Jubany⁴

¹ MediTerra Consultors Ambientals, SL; ² Consorci Urbanístic Del Centre Direccional De Cerdanyola Del Vallès; ³ Technical University of Catalonia; ⁴ Fundacio CTM Centre Tecnologic, ES

This is an example of how the development of an extensive degraded area can be done using urban planning tools in a sustainable way with the objective of balancing economic viability, nature conservation and improvement of ecological systems and biodiversity, and the enhancement of the quality of life in surrounding communities.

Parc de l'Alba (Barcelona Synchrotron Park- BSP) occupies an area of 400 Ha, 20 km to the north of Barcelona (Catalonia). The area has been occupied by different types of industrial activities mainly ceramic and related industries and former clay pits extractions that have been transformed into landfills.

An urban plan has been developed for this area where new businesses (including the Synchrotron) and residential areas (4,600 apartments) will share common spaces with rain feed crops, watercourses and woods. Recreational areas will include a large preserved ecological connector with 140 hectares assigned to natural areas connected to Collserola Natural Park, the main green lung of the Barcelona metropolitan area.

Before developing the current urban planning for the area, several studies have been carried out to delimit and characterize the quality of the soil and groundwater in brownfield areas and propose the alternatives of restoration and future uses to make them compatibles with the urban developing planning.

Some of the key redevelopment projects include the restoration of an industrial landfill of 18 ha (Can Planas). In a preliminary urban plan, a residential area had been designed for this landfill but after remediation alternative assessments, and based on risk based assessment, it was decided to develop the area into an urban recreational park. Remediation activities will consist on the installation of a capping layer, hydraulic barriers and gas extraction. The uses onsite will be limited avoiding any construction on top of the new capping layer. Furthermore, a controlled landfill of non-hazardous waste with methane gas problems is now being closed and compatible uses of this area are being assessed. Another example is former clay pits (Arids Catalunya) that were filled with different types of waste in the past (including asbestos waste) that have been restored, by means of containment measures and control of water runoff, into a recreational area and are part of the green corridor. Moreover, approximately 39 Ha of industrial land (occupied by ceramic and associated activities) have been dismantled and transformed in green areas.

The BSP action program designed to support its Green Infrastructure is structured in 5 strategic axes including Restoration and improvement of the ecological connectivity (including restoration of soils degraded by former activities), implementation of nature-based solutions, Ecological management of green spaces and pending building areas or Support for agriculture.

All these actions have been incorporated in the Urban Planning by means of accurate development measures and management regulations, and the concrete actions to implement the restoration of brownfields in order to make them compatible with the new suitable uses.

Posters

Topic 1: Assessment and monitoring of soil, water and sediment quality

1a. Adaptive monitoring based on real time data, model driven

New guidance on the use of remote telemetry in the monitoring and sampling of environmental media

Jake Hurst; Jon Coulson; Roy Dennis; Katy Baker

Arcadis UK, GB

Recent years have seen an increased focus on the importance of compliance with new or evolving environmental protection legislation, leading to ever greater collection of environmental data to help inform robust decision-making and monitor compliance. A natural progression has been the development of new methods and techniques that can be used to gather such information in the safest and most cost effective manner. This includes collection of data using remote systems with the information transmitted back to the user without need to repeatedly visit a site. However, knowledge and understanding of available techniques and technologies for undertaking remote telemetry environmental monitoring is not widespread. New technical guidance, commissioned by the Energy Institute and developed with the intention of raising awareness of the applicability and value of remote telemetry technologies in environmental monitoring and sampling, will be introduced.

Within the guidance, telemetry has been defined as “The automatic measurement and transmission of data, typically employed to collect information from remote or inaccessible locations”, whereas remote monitoring has been defined as “A process by which automatic measurements are made remotely. Data may be transmitted via a telemetry system but could also be stored electronically and collected manually at the data gathering location”.

The guidance recognizes that while there are many potential advantages in employing remote telemetry monitoring or sampling to obtain environmental data, there are a number of important criteria that should be evaluated before any system is employed, such that the advantages and potential disadvantages and risks can be considered prior to implementation.

A number of technologies for collecting, storing and transmitting will be introduced, to demonstrate the breadth of currently available technologies – and where research is still ongoing to develop new technologies. A flowchart developed to guide users through the key questions to ask when selecting or designing a remote telemetry monitoring or sampling system will be explained, alongside presentation of matrices which enable the reader to compare and contrast different techniques for collecting data in the field, storing and transmitting the data. Case studies, demonstrating how the guidance can be used to determine an optimum solution where remote telemetry monitoring or sampling is desired, will be explored.

High-resolution site characterization based land redevelopment in Switzerland

Eugen Martac

Fugro Consult GmbH, DE

With its unmatched mix of flourishing economic, tourism and residential regions, the four-countries region of Lake Constance is one of the "hot spots" of Europe for investors and developers. The 44,000 m² area of a former textile company is in a prime location directly on Lake Constance. The subsoil of the site was, however, partially contaminated with chemicals (CKW and BTEX). Currently, the whole area is under a complex urban development action. As preliminary step, Fugro Consult GmbH was commissioned to carry out a high-resolution site characterization. The scope of work included Membrane Interface Probe (MIP) soundings down to approx. 15 m bgl to be validated by depth oriented soil and groundwater samples. The high resolution site characterization aimed to identify the contaminated hot spots as prerequisite for a successful site remediation. Over 100 Direct Push MIP soundings delivered the necessary information for a reliable 3D contaminant delineation. Validation of the MIP probing was insured by more than 50 liner respectively 10 groundwater depth oriented samples. The site investigation was performed in an adaptive manner during several phases following a functional and spatial conditioning. The individual profiles were spatially combined within horizontal 2D distributions of the maximum over the entire depth measured detector signals, vertical 2D cross sections of lithology and contamination and 3D block diagrams.

Models of the spatial distribution of contamination and lithology were constructed for the areas of interest and were continuously updated during the investigations. Using these models, the architecture, volume and size of the contamination body were mapped and estimated. These data allowed the site manager to make a well-founded decision on the dimensioning and implementation of the remediation technology and work.

1b. Sensors and sampling

Characterization of a former and reactive industrial landfill via non-intrusive investigations and core sampling

Ariane Ancel¹; Amiel Boullemant²

¹ Ramboll Environ; ² Rio Tinto, FR

A minerals processing site located in southwestern France operated for almost a century a wide range of industrial products – mainly magnesium – with waste materials deposited onsite. In 2005, this 16ha site was remediated with two former industrial platforms and three landfills. Shortly thereafter, liabilities were transferred to a new company with a poor data transfer. Within a decade, it became apparent that one landfill was still chemically active, causing gas emissions, fissures and potential slope instability. On-going reactivity at the site triggered a suite of environmental investigations to obtain a better understanding of chemical reactions and the associated risk for human and local ecosystems.

Environmental investigations involved a three-step approach. Initially, a documentary study was carried out to gather all relevant information and assess existing gaps in data. The second step involved non-intrusive investigations designed to evaluate occupational risk for the planned third stage involving detailed sampling and analysis of the waste materials.

- A preliminary field sampling campaign was conducted based on the review of existing data : gas emissions were measured by using an in-house gas chamber device at 5 points of the fissures present on the top of the landfill. The monitored compounds and their sampling and analytical methods were:

Compound-Sampling method (in-house gas chamber device plus)- Analytical method:

Amines - Impinger - IC NIOSH 3509

Ammonia - Impinger - IC NF X 43-303

NO & NO₂ - Tube ORBO/76 - IC OSHA ID 182

Cyanides - Quartz membrane NaOH soaked - IC Metropol 027

Acetylene - Canister - GC FID US EPA TO-14

H₂ - Direct by ImpulseXP

- Difference in surface temperatures was evaluated by a drone-mounted thermal IR instrument.
- subsurface temperature and hydraulic properties, in particular waste material permeability, were measured using Cone Penetration Testing (CPT) and HPT (Hydraulic Profiling Tool) technologies.

Finally, a comprehensive field campaign was conducted via 4 core drill holes over the entire thickness of the landfill (up to 20m) to measure gaseous emissions, water content, and temperature under remote control and specific HSE procedures. Each core was then divided into sub-samples based on lithology/appearance. Core, sub-samples were analyzed for particle size distribution, major by XRF, nitrogen, trace elements by ICP-MS, and mineralogy (XRD, X-RAY, SEM-RAMAN).

Both acetylene and ammonia were measured in atmospheric emissions while high concentrations of ammonia, hydrogen cyanide and dihydrogen in the working atmosphere were measured during coring. Eight major groups were identified from analysis of the mineralogical data with a further four major geochemical/mineralogical associations found.

Inadequate characterization of waste materials deposited during an initial remediation phase has resulted in an on-going environmental liability. Underestimation of wastes chemical reactivity in a mineral processing landfill site led to an unstable rehabilitation ten years later. An international characterization study of the waste materials allowed identification of remediation options.

Groundwater sampling, purge or no purge that is the question

Valérie Guérin¹; Alexandre Boisson; Jean-Pierre Vergnes; Fabrice Quiot

¹ BRGM, FR

There are uncertainties about to what extent the water in the well is representative of the water in the aquifer. So usually, for groundwater sampling a purging step is considered. This purging step used to consider a number of volumes purged (from 3 to 5 times the well's volume) or more recently the stabilization of the physicochemical measures before the sampling itself. This purging step is nowadays done with flow rates less important than they used to be, due to the emergence of the low flow procedure (Puls and Barcelona, 1996) and the availability of new pumps.

This purge step presents several constraints (Robin et Gillham 1987), among which the time (and thus cost) and the treatment/ elimination of the water purged. In France, a new standard will be published in 2017, it states that in some conditions the purge can be avoided.

Moreover some questions remain on the spatial representativeness of the water sampled regarding the protocol used for the purge step (flow rate, position of the pump in the well screen interval). Considering also that in many wells there are very small differences in loads within the aquifer that can generate ambient fluxes in wells (Zinn and Konikow, 2007) which may have an impact on the results of the deployment of passive samplers compared to classic sampling

Or the representativeness of the sample taken is of paramount importance because it has a direct influence on the interpretation of the quality of the water and / or the pollution present. It is therefore necessary to know precisely which part of the aquifer is considered and how to proceed (purge or not).

A project financed by the French Ministry of Environment between two public research bodies (BRGM and INERIS) has the objective to state the influence of the purge on the sampling representativeness.

To answer those questions, three means will be used: a questionnaire to know the position in other EU countries, on-site measurements campaigns for different hydrogeological contexts of the influence of some parameter (no purge, purge at different flow rate, at different positions in the well) and modelling of flows in and near the well for different scenarios (including the modelling of real cases) stating origin of the pumped water.

This study will allow to evaluate the interest and the consequences of the purging processes during the realization of qualitative samples of water and will allow the production of guidelines for different cases.

Column Experiments to Determine Infiltration and Adsorption Characteristics of 1,4-Dioxane in Soil for the Development of Effective Field Screening Tool and Investigation Methods

Ray Hidaka; Makoto Nakashima

Kokusai Kogyo Co.,Ltd., JP

Japan will implement and enforce a new Environmental Quality Standard regarding soil contamination with 1,4-Dioxane (DXA) on 1st of April, 2017. The new EQS for soil leachate will be set to 0.05mg/L. It will be added as a listed hazardous substance to the already implemented 11 Volatile Organic Compounds (VOC) list in the Japanese Soil Contamination Countermeasure Law (JSCC Law).

However, the application of the currently required investigation methods for DXA is considered difficult because of differences in the physical characteristics of DXA compared to the other hazardous substances specified in the JSCC Law. Hence, the development of suitable, efficient and effective methods and techniques for sampling and analysis in order to grasp the extent of contamination with DXA are under progress.

In order to develop a method for sampling and analysis, physical characteristics regarding migration and distribution of DXA in soil have to be understood. In this study the physical and chemical properties of DXA in soil and groundwater environments have been investigated

This study presents partial results from the first year, in which batch distribution experiments as well as three soil column experiments were conducted regarding DXA. These experiments were conducted in order to understand the physico-chemical characteristics of DXA in soil and groundwater.

In this study, the adsorption characteristics of DXA on soil during infiltration of surface water into the unsaturated soil, as well as flow through saturated soil were investigated for two soil types (Toyora sand and organic soil) in column experiments. The infiltration and breakthrough curves were modeled with Hydrus1D for further analysis.

The soil column for infiltration into the unsaturated soil showed that DXA will dissolve in infiltrating rain water and percolate with it until the capillary fringe; however, in the case that no rain water infiltrates into the unsaturated zone, the concentration of DXA remains high within the soil matrix. Hence, it is likely that the concentration of DXA remains high within the unsaturated soil matrix at locations where rain water infiltration does not occur, such as below solid structures. DXA may be mobilized after demolition of those structures through infiltrating rain water. This behavior also has implications for the drilling technics used for soil sampling; only dry drilling technics are suitable to receive soil samples for DXA analysis. Breakthrough curves of DXA contaminated water through saturated columns filled with two soil types (Toyora sand and organic soil) respectively, showed a slight retention and tailing of the DXA breakthrough curve in the column filled with organic soil compared to the Toyora sand column.

The content of this research was partly funded by the Environmental Research and Technology Development Fund (5-1503) of the Japanese Ministry of the Environment.

Suspended Particulate Matter Collection Methods affect the Quantification of Polycyclic Aromatic Compounds (PACs) in the River System

Laurence Mansuy-Huault¹; Catherine Lorgeoux; Emmanuelle Montargès-Pelletier; Fayez Abuhelou; Delphine Cattelain; Valéry Collin; Allan Bauer; Hussein Kanbar; Renaud Gley; Fabien Thomas

¹ LIEC - CNRS/Université de Lorraine, FR

PACs enter the river systems through gas exchange at the air-water interface for the most volatile compounds, or associated to soot particles for the high molecular weight PACs, through atmospheric deposition and run-off or leaching of terrestrial surfaces. Eventually, these compounds are partitioned between the dissolved and the particulate phases in the water column, depending on their physical-chemical properties and the hydrological conditions in the river. The suspended particulate matter (SPM) plays a major role in the transport and fate of micropollutants in rivers and numerous studies focus on their characterization. Therefore, the process of sampling collection is a crucial prerequisite to ensure the quality of the analyses and the conclusions that can be drawn from their study.

In this study, we compared the influence of two different separation methods, filtration (FT) and continuous flow centrifugation (CFC) on the concentration and the distribution of polycyclic aromatic compounds (PACs) in suspended particulate matter (SPM). SPM samples were separated with FT and CFC from the waters of an industrial river during five sampling campaigns over a year and a half, allowing to cover different hydrological contexts. Samples were analyzed to determine the concentration of PACs including 17 polycyclic aromatic hydrocarbons (PAHs), 11 oxygenated PACs (O-PACs) and 5 nitrogen PACs (N-PACs). Results showed a clear difference between the two collection methods. In half of the sampling campaigns, PAC concentrations were differed from a factor 2 to 8 for PAHs and from 2 to 10 for O-PACs for filter-separated SPM. Furthermore, the molecular distributions of PACs were also affected by the sampling method. SPM collected by filtration were enriched in 2-3 ring PACs and showed diagnostic molecular ratios assigned to petrogenic and/or coal tar contribution whereas SPM collected by field centrifugation had PAC distributions dominated by medium to high molecular weight compounds characteristic of diffuse atmospheric contribution by combustion processes. These differences could be explained by the eventual retention of colloidal matter and fine-grained particles on glass-fiber filters. This highly divided matter appeared as very reactive phases particularly enriched in low molecular PACs. These differences between filtration and field-centrifugation were not observed systematically and were rather enhanced by high water flow conditions and high SPM loadings. Thus, according to the sampling method, evaluation of PAC distributions between dissolved phase and suspended matter can be appreciably different.

Contaminant mass flux measurement in groundwater with passive samplers – A field application

Julien Michel¹; Goedele Verreydt²; Fabrice Richez¹

¹ INERIS, FR; ² Universiteit Antwerpen, NL

In France and more generally speaking in Europe, passive sampling is an emerging method to measure groundwater quality and as a consequence to monitor contaminated sites. Contaminant mass flux measurement in groundwater can be of great interest for the management of contaminated sites because it can better define pollution sources and plumes and therefore improve practically all aspects of site characterization and remediation. For example, it can allow a better definition of contaminant transfer pathways, a better calculation of natural attenuation rates or a more efficient design of remediation techniques. In some countries like in Switzerland, the remediation urgency is already evaluated thanks to contaminant mass flux. So far, contaminant mass flux evaluation in groundwater is not as precise as it could be, because they are calculated from concentrations measured in snapshot groundwater samples and generic Darcy velocities and therefore do not account for possible concentration and groundwater flux variations over time and space. Passive samplers for contaminant mass flux such as passive flux meters (PFMs) can therefore be an interesting alternative to improve contaminant mass flux determination in groundwater. To date, this kind of passive sampler is not used in Europe and feedback is needed in order to promote their use and encourage consultants to use them.

In this context, this work aimed at evaluating PFMs to measure contaminant mass flux in groundwater at a site contaminated with chlorinated solvents. On site, 6 monitoring wells were equipped with PFMs at different depths. 2 phases of exposure were carried out and PFMs were exposed during 3 months in each phase. The tests on site consisted in comparing the concentrations in groundwater given by the PFMs (average concentrations over the exposure time) to the average concentrations calculated from snapshot samples obtained with the conventional sampling method before the installation and after the retrieval of the PFMs, that is to say well purging prior to groundwater sampling with a pump. Concentrations coming from the PFMs were as well compared with an integrative sampler (ceramic dosimeter) having a constant sampling rate and giving average concentrations over the exposure time. Contaminant mass flux benefit was as well evaluated.

Chlorinated solvent concentrations in groundwater snapshot samples taken before and after passive sampler exposure showed little variation. Therefore, concentrations given by the ceramic dosimeters were consistent with the ones obtained from the conventional sampling method. Nevertheless, PFMs showed a vertical distribution of the contamination and significantly higher concentrations were measured at some depths. These results showed that concentrations could be underestimated with the conventional sampling technique, leading to an underestimation of the risk for Human and Environment. PFMs offered complementary information because they allowed multi-level sampling in the wells and took into account variations in time and space, which could be of great value and seems very promising for contaminated sites characterization and remediation improvement.

Investigation on fibrous sediments in Sweden, an overview on objectives, geophysical method and results.

Johan Norrlin¹; Lijana Gottby; Johan Nyberg; Anna Apler; Olof Larsson; Sarah Josefsson; Lovisa Zillén

¹ The Geological Survey of Sweden (SGU), SE

In many regions in Sweden the forest industry was, and partly still is, very important. Unfortunately, the manufacturing of different types of wooden products, such as paper pulp and particle board, caused large amounts of fibrous material to be discharged with the wastewater in the late 19th and most of the 20th century. The fibers accumulated in calm aquatic environments in the near vicinity of the factories or further downstream in the catchment area. In addition, various chemicals were used or produced in the processes, and therefore, in many locations, the fiber sediments contain large amounts of contaminants and are considered as environmental risks. Several natural and anthropogenic processes cause or might cause a spreading of hazardous contaminants from these sediments to the aquatic environment.

To get an overview of the spatial extent of fiber sediments in Sweden, the Swedish Environmental Protection Agency and the Swedish Agency for Marine and Water Management have financed surveys for inventories of this type of sediments. This overview is a necessary basis for further assessment, monitoring and remediation of these contaminated sites. These activities conform to the EU Marine Strategy Framework Directive, especially the environmental descriptor number eight (i.e. concentrations of contaminants are at levels not giving rise to pollution effects).

In collaboration with the county of Västernorrland, which is situated at the northern part of the Bothnian Sea, the Geological Survey of Sweden has developed a method for inventory of fibrous sediments. It is based on a combination of hydro acoustic (geophysical) measurements and sediment sampling. The method has now been applied in all counties in northern Sweden to investigate expected fiber sediment areas, mostly in coastal areas but also in lakes and rivers. It is clear that these marinegeological tools, normally used in conventional bottom floor mapping, can be used to facilitate the mapping of contaminated fibrous sediments.

So far, a total of 39 sites, have been investigated, covering a total area of c. 170 km². 44 fiberbanks, consisting almost entirely of cellulose fibers, have been identified and estimated to cover a total area of c. 2.5 km². In addition, fibre-rich sediments, i.e. natural sediments displaying a pronounced content of fibers and/or wood chips and bark chips, have also been mapped and estimated to cover a total area of c. 26 km². Further work on these depositions, in terms of e.g. risk classification and priorities for remediation, will need to be carried out by regional authorities in order to deal with the large risk posed by this contaminated type of sediment.

An estimate from Swedish county boards shows that there are about 315 sites in Sweden where soil contaminated from paper and pulp industries is or may be present. Since these industrial processes are very water-consuming one could expect that there are recipients for wastewater adjacent to almost all of them, and likelihood for the presence of fiberbanks or fiber-rich sediments. The reported inventory method can be used for all types of fibrous sediments and can thus be applied to such deposition worldwide.

Characterization of anthropogenic magnetic signature in the Gier river sediments (France)

Mathilde Perrin; Jerome Bascou; Veronique Lavastre; Jean-Yves Cottin

Université de Lyon, Université Jean Monnet, FR

Introduction

Industries using high-temperature technological processes are known to be the cause of magnetic fractions associating Fe-bearing minerals with heavy metals (HM). It may then be interesting to consider magnetic techniques, which are faster and easy to use to assess HM pollution. To interpret magnetic maps in terms of anthropogenic pollution, it is important to identify the origin of magnetic minerals (natural vs anthropogenic) and to precisely define their relationships with HM particles. We present here the preliminary results of a magnetic study performed on sediments from the Gier river, one of the Rhone tributaries, where the activity of many steel industries from the late 19th century is located.

Sampling and analytical methods

Sampling was targeted on 23 sites located along the Gier river and its tributaries between Saint Chamond and Rives de Gier (about 16 km). These samples are located before and after the main industrial centres were still active. They consist of sand taken from the middle bed of the River. Afterwards, the sand was dried at 40°C and separated into two sub-samples consisting of a sand fraction lower than 2 mm and centimetric particles including rock fragments and anthropogenic scoriae. For magnetic measurements, the sand is put into cylindrical plastic vessels of 42 cm³ and then weighed. Bulk magnetic susceptibility (χ) was measured at room temperature and under a weak magnetic field (200 A/m) using the AGICO MFK1-FA Kappabridge at the University of Saint Etienne (France). In addition, in order to precisely define the magnetic mineralogy, thermomagnetic analyses (susceptibility vs temperature) were carried out between -192°C and 700°C.

Results

For each sampling site, values of χ for large particles are higher for industrial scoriae than for rock fragments. For example, we measured a typical χ value of 8.8×10^{-6} m³/Kg for anthropogenic scoriae and 1.3×10^{-7} m³/Kg for a piece of schist. The χ values measured on the sub-fraction of fine sand, and on the entire sampling, are of the same order but remain slightly weaker than the values measured on the scoriae. This observation shows the effect of mixing of anthropogenic and natural magnetic particles in the Gier sand. Mapping from χ value measurements in the sub-fraction of fine sand shows: - lowest values ($\chi < 1 \times 10^{-6}$ m³/Kg) for the most upstream site of the Gier, and for the non-industrial sites of the Gier tributaries, and - the highest values ($\chi > 5 \times 10^{-6}$ m³/Kg) for sites located after the industries, were still operating along the Gier river.

The study of magnetic mineralogy shows that magnetite is present only in sand with the highest χ values. The largest scoriae are characterized by the presence of magnetite ($T_c = 580^\circ\text{C}$) and/or maghemite ($T_c = 508^\circ\text{C}$) highlighting the weathering processes of the original magnetic minerals.

Conclusions

These first results clearly show the effect of particles coming from the heavy industries by the magnetic signature of the Gier river sediments. The spatial and structural relationships between the HM and magnetite in anthropogenic particles remain to be clarified.

Monitoring the hyporheic zone of small urban rivers with wooden sticks

Marie-Noelle PONS¹; Yuhai Zhang; Nouceiba Adouani¹; Pascal Breil²; Philippe Namour²

¹ CNRS-UL; ² Irstea, FR

River hyporheic zone is recognized as an important compartment of aquatic systems. Its study, especially in terms of vertical gradients, is not easy. The oxygen (or more generally redox) profile is a driver for chemical and biological processes taking place at different depths below the river bed. Redox is especially involved in nitrogen cycling (ammonification, nitrification, denitrification, etc.) and greenhouse gas emission (methane in anaerobic zones, nitrous oxide). In rivers impacted by urban and industrial discharges, these basic biochemical processes can be impeded by the presence of micropollutants (organic and/or inorganic) and by the clogging of interstitial spaces. Marmonier et al. (2004) proposed a skilled way to investigate the vertical oxygen gradient by inserting 30 cm long wooden sticks into the hyporheic zone of water streams accessible by foot. The sticks are collected after a few weeks and the color taken by the wood is related to the oxygen content: aerobic (yellow), anoxic/hypoxic (black) or anaerobic (grey). After recovery the sticks are scanned. This procedure allows to store the information into a database and facilitates the synchronic comparison between sites or, diachronic for a given site, according time. An image treatment algorithm has been developed to extract quantitative information on color, which can be interpreted according the redox gradient in the hyporheic zone.

Sticks have been deployed in rivers impacted by urban activities: a 500m-long reach of the Saint-Oger River (near Epinal, France) and a 250m-long reach of the Chaudanne River (Grézieu-la-Varenne, France). The sites receive untreated sewage and/or urban stormwater runoff. The results will be compared to the dissolved oxygen concentration, the redox potential and nitrogen species concentration of hyporheic water sampled close to the sticks.

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Comparison of tools and protocols for groundwater sampling

Fabrice Quiot¹; Nicolas Diard²; Mathieu Hubner³

¹ INERIS; ² ERG environnement; ³ EUROFINs, FR

Prevention or management of pollution of groundwater is based on sampling. Sampling leads to determine the water quality and in case of break down, to understand origin and evolution. Data must be reliable, the representativeness of a groundwater sample is essential. But obtain a sample which is "representative" of the water quality in the surrounding geological formation is partly related to the tools and protocols used. Remarkable progress has been done in site characterization, monitoring and field instrumentation over the past 25 years but some issues remain and profession lack of demonstration to clarify certain choices on tools and protocols best suited to the situation encountered and to the sampling purpose: use passive or active sampling technique? use multi-level sampling? loss of Volatile Organic Compounds? influence of vertical flows in wells? influence of purge? influence of filtration, decantation (site or laboratory)?... A comparison of existing technology, whether or not conventionally employed by operators, is currently underway by INERIS with academic and private partners - period 2014 to 2017.

This work aims to give illustrations, trends and recommendations on the influence of a change on concentrations results based on the data obtained on actual polluted sites and on an experimental tank (INERIS, Aix-en-Provence, Fr). This comparison process will lead to the acquisition of a large amount of data. Interpretation of the results will allow to answer some questions mentioned above. At this stage, for example, the acquired data concerning a surface sampling on three sites and tank show that for BTEX (benzene, toluene, ethylbenzene and xylenes), different sampling tools provide concentrations comparable considering analytical uncertainty (with Low-flow purging, packers coupling with bladder pump, bailer, discrete interval sampler...): the loss of volatile is small on different scale and concentration range, this trend indicate in this case (BTEX) a small influence of volatilisation in management of groundwater pollution

Work continues to assess reproducibility of these preliminary results. In some case trends are observed but not always, statistical methods will help us to complete interpretation.

Assessment of PFAS in Soil and Groundwater: Direct Comparison of New Analytical Technologies for Comprehensive Analysis of PFAS Including Precursors

Ian Ross¹; Allan Horneman¹; Jeff Burdick¹; Jake Hurst¹; Erika Houtz¹; Hans Slenders¹; Tessa Pancras¹; Thomas Held

¹ Arcadis, GB

Poly- and perfluoroalkyl substances (PFAS), including perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are commonly elevated in soil and groundwater associated with the use of fire fighting foams such as aqueous film-forming foams (AFFFs). Polyfluorinated compounds, in addition to many other perfluorinated compounds (collectively termed precursors), are biotransformed in the environment to form simpler perfluorinated carboxylates and sulphonates (such as PFOS and PFOA), which are persistent indefinitely in the environment as they are not susceptible to further biodegradation.

So in addition to PFOS and PFOA there are numerous other “precursor” compounds in firefighting foams which present an ongoing source of PFOS and PFOA and other perfluorinated sulphonates and carboxylates. PFAS contaminated source zones are often associated with large plumes as in some firefighting foam formulations the majority of PFAS are anionic and are not retarded significantly in aquifers, however in some foams cationic or zwitterionic precursors are at significant concentrations or dominate the formulations. These cationic / zwitterionic will bind to soils via ion exchange mechanisms, producing a lesser mobile source mass, which can evolve more mobile anionic perfluoroalkyl acids (PFAAs) as “dead end” daughter products via biotransformation reactions.

Precursors are not accounted for by US. EPA method 537 (LC-MS/MS) but have been identified as a source of PFAA's, so to characterize soil, sediment and waters impacted with PFAS it is important to also assess the precursor concentrations. This presentation will describe new analytical methods to quantify the total concentration of precursors and PFAA's in water and soil samples.

ARCADIS have implemented the use of multiple analytical methods to quantify the total mass of precursors and qualitatively assess the nature of individual precursors. The new methodologies employed include (1) the total oxidizable precursor (TOP) method (Houtz et al., 2013), (2) particle induced gamma emission (PIGE) spectroscopy and (3) adsorbed organic fluorine (AOF) using combustion ion chromatography, which are all appropriate for use at field sites. The conventional analytical methodology (US EPA method 537) was used for comparison. Data from recent publications describing the hidden mass of precursors (termed “dark matter”) in effluent from waste-water treatment systems (Dauchy et al., 201& Houtz et al., 2016) will be used to demonstrate the importance of assessing the total mass of PFAS to be protective of human health and the environment.

Soil and groundwater from PFAS contaminated sites as well as soil spiked with characterized AFFF were analyzed by conventional, and new and detailed analytical methods. Results demonstrate that PFOA and PFOS only account for only a small portion of the PFAS present in some impacted soil and groundwater.

This next generation of new PFAS analytical techniques will generate more comprehensive analytical data supporting more robust conceptual site models and improve understanding of PFAS fate and transport. Accounting for precursors will be key for successful design of remedial systems.

Calibration of the Polar Organic Chemical Integrative Samplers (POCIS) for Alkylphenols Monitoring in Produced Water: Effect of OASIS beads and Polyethersulfone Membranes.

Ludovica Silvani¹; Carmela Riccardi; Espen Eek; Marco Petrangeli Papini; Nicolas Morin; Gerard Cornelissen; Amy Oen; Sarah Hale

¹ NGI, NO

The produced water (PW) is one of the largest discharges from the oil and gas industry and includes both formation water and injected water. It contains several toxic compounds such as polycyclic aromatic hydrocarbons (PAHs), alkylphenols (APs), heavy metals, etc. PW is usually treated on the platform and then directly discharged into the sea. Despite the low content of toxic compounds that remain in PW after the treatment, the large volume of PW lead to high total amounts of toxic compounds discharged every year into the sea; an effective tool for monitoring the hydrophilic organic compounds (HpOCs) is therefore necessary.

Passive sampler devices (PSDs) are the most common tools for monitoring a wide range of organic contaminants in water. By this regard, several PSDs are used to monitor the hydrophobic organic compounds (HOCs) in the water, such as the semipermeable membrane devices (SPMDs). On the other hand SPMDs are not suitable for monitoring the HpOCs. It is therefore necessary to develop and standardize a passive sampler for HpOCs, such as APs.

Polar organic chemical integrative sampler (POCIS) is a PSD performed to detect a wide range of HpOCs. It allows to measure the time weighted average (TWA) concentration and thus assess fluctuation in discharge concentrations.

POCIS is composed by a solid sorbent, two polyethersulfone (PES) membranes and two stainless steel rings. POCIS is calibrated by evaluating the sampling rate (Rs), which correlates the contaminants concentration in the sampled media and in the sampler. Usually the contaminants concentration in the sampler is assessed by the extraction of the sorbent of the POCIS. In this study for the first time the Rs is evaluated by the extraction of both the sorbent and the PES membranes.

In the herein work a pharmaceutical-POCIS (OASIS HLB sorbent) was calibrated for a wide range of APs by extracting both OASIS beads and PES membrane. This study demonstrated that APs with $\log K_{ow} < 4$ were more effectively accumulated in the Oasis, while APs with $\log K_{ow} > 5$ were accumulated more efficiently in the PES membranes. We conclude that the extraction of both the PES membranes and the OASIS is needed when working with the POCIS in order to capture low contaminant concentrations and allow the detection of the less hydrophilic APs. This can be very useful in environmental applications because it may justify the use of only one passive sampler to monitor a wider range of contaminants.

1c. Molecular monitoring of microbial processes

Shining a light on anaerobic biodegradation of 1,2-Dichloroethane

Kristin McClellan; Daniela Papenbrock

Arcadis Germany GmbH, DE

The groundwater beneath a residential area in northern Germany was found to be contaminated with a mix of chlorinated ethenes and 1,2-dichloroethane. Found due to construction activities, the historical research and detailed site investigation produced no evidence of the original cause for contamination, yet two major source areas in the aquifer could be identified. The site presents challenging conditions with shallow groundwater, low permeability and low groundwater gradients in combination with residential housing over the plume, all of which greatly diminish options for active remediation.

Therefore, the extend of natural biological degradation under the existing anaerobic conditions was examined. Investigative methods included groundwater monitoring, direct push groundwater sampling, membrane-interphase probing as well as compound-specific isotope analysis (CSIA). Results from all investigative measures were combined in a hydrogeological and contaminant transport model of the site, which was used to simulate contaminant fate.

Multiple lines of evidence showed that active anaerobic biodegradation was responsible for decreasing concentrations of 1,2-dichloroethane. The degradation pathway was through productive dichloroelimination of 1,2-dichloroethane directly to ethene as the terminal product without the intermediary production of the more toxic vinyl chloride. The extend of chlorinated ethene dehalogenation was determined as well as degradation rates for all relevant processes. The contaminant transport modeling could show that active remediation is not necessary at this point, as natural anaerobic degradation is causing contaminant levels to decrease, and no sensitive receptors are being exposed at present.

Metabolic adaptation of an anammox consortium obtained from estuary sediments and its evaluation in the degradation of nitrogen pollutants

Arely Gomez Aquino¹; Ulises Duran Hinojosa²; Ana Elena Dorantes Acosta³; Sergio Martinez⁴

¹ Universidad Veracruzana; ² Universidad Nacional Autónoma De México; ³ Universidad Veracruzana; ⁴ Inbioteca, Universidad Veracruzana, MX

Anammox process is emerging as a promising biotechnology to improve NH_4^{4+} removal in a more sustainable fashion (Kartal et al., 2010). The process is mediated by anaerobic chemolithoautotrophic bacteria within the Planctomycete phylum, which catalyzes the oxidation of ammonium by nitrite to form dinitrogen gas (Jetten et al., 1999). Compared with conventional nitrogen removal processes, anammox offers significant advantages such as no demand for oxygen and organic carbon, low sludge production and reduced CO_2 or N_2O emissions (Kuenen, 2008). Despite this, the integration of anammox process into full-scale wastewater treatment system is still a challenge, due to its slow growth rate with doubling time typically 1-2 weeks (Van de Star et al. 2008). Therefore, several studies have been focused on evaluation of several factors, such as temperature, nitrogen compound concentration, inoculum source, etc (Xiong et al., 2013), in order to optimize its application. In this context, the objective of the present work was to evaluate the use of estuary sediments as inoculum source to cultivate and enrich anammox microorganisms by measuring the degradation of nitrogen compounds and monitoring the microbial populations. For this, estuary sediments from the "Ostion Lagoon", located close to the city of Coatzacoalcos, Veracruz México, were used as inoculum. Two sets of experiments were carried out. First, experiments were conducted in shaken bottles (1 L, filling cap with tree ports) containing 6 g VSS/L of inoculum and 800 ml of mineral medium (Martinez et al., 2013), supplemented with 1.32 mM NO_2^- and 1 mM NH_4^{4+} according to stoichiometric concentrations, which were periodically added as they were consumed. The bottles were hermetically sealed and purged (liquid and headspace) with He and CO_2 for 10 min each one and incubated at 150 rpm and 30°C. Two control assays (in duplicate) were also carried out, one without NO_2^- and the other one without NH_4^{4+} . Liquid and solid samples were taken for nitrogen compounds and molecular (DGGE) analysis, respectively. For the second set of experiments, assays were similar to described for the first set, except using serologic bottles (120 mL) supplied with 100 mL medium, containing 3 g VSS/L of sludge withdrawn from the shaken bottles (1L). The serum bottles were hermetically sealed with butyl rubber stoppers and aluminum caps. Each bottle was an independent experimental unit and was discarded after sampling. The NH_4^{4+} and NO_3^- were determined by selective ion electrodes, NO_2^- by spectrophotometry and N_2 by gas chromatography. For molecular analysis, DNA was extracted by a commercial kit, while for PCR specific primers for Planctomycetes (Pla 46F and pla1392R) and anammox microorganisms (GC-Amx368 and Amx820 R) were used. The amplicons obtained by PCR with clamp GC were separated by DGGE system (Muyzer et al., 1993). A denaturant gel gradient from 40% to 60% was used. The gel was dyed using SYBR Gold 1X (30 min) and visualized using a photodocumentator (Bio-RAD Laboratories). In results and discussions, in the first set of experiments, it was found that during the first 80 days of experimentation, in all assays (including controls) the consumption of ammonium and nitrite and the production of nitrate was irregular; however after that, the consumption of nitrogen substrates was simultaneous with a nitrate production close to stoichiometric values (only in bioassays). At these conditions, the degradation efficiencies were higher than 95% and the degradation rates significantly increased. For the second set of experiments, it was not observed a significant consumption of nitrogen substrates in the control assays, while in the others a simultaneous and total consumption was observed at the 10 days, with N_2 and nitrate production close to stoichiometry of anammox process. In the DGGE gel, more than 50 bands were detected, showing the structure of the microbial community at initial and final times of experimentation. Some differences in position, intensity, and number of bands by lane were noted. Currently, we are working on the obtaining of ecological indices and the reamplification and purification of bands for its sequencing. According to these results we can indicate that metabolic adaptation or enrichment of anammox microorganisms from estuary sediments was achieved, with the conversion of nitrogen pollutants to innocuous products.

Use of next generation sequencing to study the feasibility to apply monitored natural recovery in freshwater sediments affected by ancient human activity

Laura Madueño¹; Bibiana M Coppotelli¹; Viviana M. Starevich¹; Claudia Terada¹; Daniel O Nuccetelli²; Nuria C. Vidal³; María E Oneto³; María T Del Panno¹; Irma Susana Morelli⁴

¹ CINDEFI (UNLP-CONICET); ² YPF S.A.; ³ YPF-Tecnología S.A.; ⁴ CINDEFI (UNLP-CONICET), CIC-PBA, AR

The monitored natural recovery (MNR) is a remedial approach that relies on natural physical, chemical, and biological processes to reduce ecological and human health risks. MNR is a non-invasive technology which, carefully planned, allows remediation of sediment sites and can result in risk reduction in comparison with dredging and capping. The aim of this work was to evaluate the application of MNR from a freshwater course affected by human activity using sediments biological parameters and next generation sequencing methods (NGS) as potential indicators of biological processes.

The studied sediments come from a freshwater course with history of involvement by oil pollution, and whose recovery began projecting over 20 years ago. 30 sediments cores distributed in 5 transects along the water channel were extracted using a Hammer Piston tool. Physicochemical variables (humidity, pH, depth, total sulfide, total nitrogen and phosphate), enzymatic activity (dehydrogenase, lipase, protease, phosphatase, protease and aril-sulfatase) and Total Petroleum (TNRCC 1005), Aliphatic and Aromatic Hydrocarbons (TNRCC 1006) were determined at the different horizons found in each core. The hydrocarbons concentration was also determined in the water samples corresponding to the each core site. The bacterial and archaea diversity was determined by NGS (Illumina). Canonical correspondence analysis (CCA) between biodiversity and environmental variables were performed using the software Canoco version 4.5.

The water samples showed hydrocarbons concentration below de detection limit. In all studied cores could be differentiated a surface horizon, called H0, that showed the lowest or not detectable hydrocarbons concentrations and highest biodiversity index, dominated by Deltaproteobacteria, Actinobacteria, Anaerolinea and Methanobacteria classes. Hydrocarbons concentration increased and bacterial diversity decreased in deep horizons, characterized by a remarked dominance of Gammaproteobacteria and Bacilli classes.

CCA axes between bacterial community composition and physicochemical variables or enzymatic activities, explained respectively 42.6% and 46.3% of the total variance in community composition and 72.1% and 73.6% of the cumulative variance of the species–environment relationship. Spatial distribution of the communities correlated significantly ($P < 0.05$) with depth ($F = 8.10$), total phosphate ($F = 3.27$), protease ($F = 5.19$), and lipase activities ($F = 4.94$) but not for hydrocarbons concentration ($P > 0.05$, $F = 1.25$). The bacterial community of H0 showed a positive correlation with total nitrogen, humidity and lipase, protease, urease and alkaline phosphatase activities, suggesting that these horizons were characterized by their activity in recycling nutrients.

The great bacterial diversity and enzymatic activities detected in the H0 allow us to infer the presence of a natural “biofilter” able to process the organic matter, contributing to the pollutant degradation, confining it to the deepest horizons and preventing the hydrocarbons reentry to the watercourse; indicating that MNR would be a sustainable option for the recovery of this site.

Unveiling active microbial populations during in-situ bioaugmentation in two ETBE-polluted sites

Marc Viñas¹; Miriam Guivernau¹; Josep Ruiz¹; Isabel Mori²; Fernando García³; Patricia Piñuela³; Joaquim Vila⁴; Francesc X. Prenafeta-Boldú¹

¹ Institute of Agrifood Research and Technology (IRTA); ² Ibiotec Ambiental; ³ Compañía Logística de Hidrocarburos, CLH S.A.; ⁴ University of North Carolina at Chapel Hill, ES

Ethyl tert butyl ether (ETBE) is increasingly used as gasoline additive replacing lead-based compounds and for promoting the use of bioethanol. The high water solubility and low biodegradability of ETBE and its metabolite TBA (tert butyl alcohol) causes rapid and wide spreading plumes upon spilling and leakage events. During the in-situ bioaugmentation of polluted sites, the identification of active autochthonous/allochthonous microbial contributors to the ETBE/TBA turnover provides essential information in relation to the viability of long-term remediation actions. Most of ETBE-degrading bacteria belong to slow growing Actinobacteria, which usually are low in cell counts but relevant concerning the metabolic activity. Therefore, combined DNA/RNA-based tools emerge as a good alternative to monitor the actually active microbial key players during bioremediation studies.

The present study is aimed at gaining deeper insights into the identity of metabolically-active relevant bacteria during the in-situ aerobic bioaugmentation of two sites heavily polluted with ETBE/TBA (Site A: 5-16 mg ETBE · L⁻¹ and 5-8 mg TBA · L⁻¹; Site B: 137 mg ETBE · L⁻¹ and 37 mg TBA · L⁻¹). A novel DNA/RNA-based approach was applied to tracefunctional (RT-qPCR) and structural diversity (MiSeq) changes in microbial communities, along with the evolution of the ETBE, TBA and TPH concentration in groundwater during 196 days. Bioaugmentation was implemented upon amendments with oxygen releasing compounds (ORC) and nutrients (N, P). An ETBE/TBA-degrading microbial consortium was used as inoculum for bioaugmentation. This inoculum was composed by four pure strains (*Rhodoccus erythropolis*, *Gordonia* sp., *Hydrogenophaga pseudoflava* and *Sphingopyxis* sp.) previously isolated from an ETBE-polluted site, and were able to grow on ETBE aerobically without the transient accumulation of TBA.

The analysis of the active microbial populations (MiSeq RNA-based sequencing of 16S rRNA libraries) in the long term (196 days) in a bioaugmented well (I6-well, site A), revealed a high predominance of ribotypes identical to *Rhodoccus erythropolis* and *Gordonia* sp. (5.03% and 25.75% relative abundance, respectively) present in the exogenous inoculum. Surprisingly enough, these ribotypes were found in minor amounts in DNA ribotype libraries (<0.1%). This higher level of activity by inoculated bacteria was concomitant with a slight ETBE depletion and a significant enrichment of ETBE degrading microbial species throughout the treatment (as determined by qPCR ethB/16S rRNA gene ratios). These results demonstrate the viability of the consortium under the tested field conditions. The increased activity of a member of the genus *Hydrogenophaga*, a potential autochthonous TBA-degrader closely related to *H. pseudoflava* from the inoculum was also detected at site A. Hence, Site A encompasses favourable environmental conditions to maintain metabolically active ETBE/TBA degraders, either indigenous or exogenous. Conversely, none of the representatives from the inoculum displayed significant transcription activity in site B. Besides, no depletion of ETBE or TBA was observed in this site during in-situ bioremediation.

1d. Integrative methods, overall indicators

Salinity and modelling of the Annaba aquifer system, Northeastern Algeria

Habiba Majour¹; Azeddine Hani²; Larbi Djabri²

¹ Université Badji Mokhar Annaba; ² University Badji Mokhar Annaba, DZ

The potentiometer area in the Annaba basin, covering an area of 264 km², has declined considerably since 1995. The analysis of the chronological hydrographs (1991-2009) of the piezometric observations shows that this decline is related to about twenty years (20 years) drought that began in 1991. To synthesize hydrological data and study regional changes in aquifer interactions caused by changes in discharge, and determine the contamination of aquifers by salty intrusion in coastal areas, and making forecasts by the year 2023, a multi-layered transient model as well as a solute transport model have been developed. The groundwater flow was modeled using the finite difference method with a horizontal dimension of 500 x 500 m for the cells. The model consists of two layers, the first corresponding to the alluvial phreatic aquifer and the second to the deep confined aquifer, and is calibrated against the steady state groundwater heads recorded before 1996. Model verification was done by history matching over the period 1991-2009. Under steady-state conditions, the correspondence between simulated and observed water levels is generally good (average difference of 0.4 m). For the deep aquifer, the simulated time-series hydrographs closely match the recorded hydrographs for most of the observation wells. For the alluvial aquifer, the recorded hydrographs cover only a short time period, but they are reproduced. The model indicates that groundwater pumping induced a decrease in natural discharge, a downward leakage in most of the basin and a continual water-level decline. The model has also been applied to the analysis of recharge impact. Simulating the behaviour of the system over the period 1991-2009 without pumping indicated small changes in hydraulic head.

These results show that the groundwater reservoir has a low recharge, but excellent hydraulic properties; A solute-transport model was used to study aquifer contamination from salty intrusion in coastal sectors; it was extended to the year 2023 by simulating an optimistic hypothesis that maintains present pumping until 2023. The model indicates that the head decrease of the alluvial phreatic and deep confined aquifers will be 4 m and 5 m respectively. The solute concentration in the deep confined aquifer will increase from 1 g/l (prior 2009) to 5 g/l in 2023.

Keywords: salinity, contamination, Solute-transport model, Annaba, North-eastern Algeria.

Application of the ILTER decomposition protocol to brownfield soils

Marie-Noelle Pons¹; Florence Maunoury-Danger²; Michael Danger²

¹ CNRS-UL; ² LIEC-Université de Lorraine, FR

Litter decomposition represents one of the largest fluxes in the global terrestrial carbon cycle and already diverse large-scale decomposition experiments were focusing on this fundamental soil process. In the Tea bag method (Keuskamp et al., 2013) a simple, standardized, cheap and time-efficient-the litterbags are ready to use) method involving two types of tea has been proposed: Rooibos tea characterized by a slow decomposition rate and Green tea characterized by a faster decomposition rate. The ILTER TeaComposition initiative (<https://www.ilternet.edu/content/litter-decomposition>) aims to study the long-term litter decomposition and hence the long-term C dynamics (both the litter C-losses and C storage) and its key drivers.

In the course of this initiative, teabags of both types have been deployed in six brownfield soils (BS), contaminated by metals and PAHs, and retrieved after three months between June and October 2016. Their degradation is compared to teabags deployed in a reference soil (biological garden (BGS), temperate forest (TPS)). Furthermore, as the degradation is temperature dependent, short-term tests have been run in defined conditions in the lab at different temperatures in the same soils.

The results allow to estimate kinetic parameters defining the short-term and medium-term degradation of the litter and to compare the effects of the soil characteristics.

After three months all six BS as well as the TPS green tea bags were less decomposed (between 46% and 66% weight loss) than the BGS teabags (68% weight loss). The trend was inverse for the red tea bags except for one brown field soil, a former coking plant. This site had the lowest degradation rate with 46% for the green tea bags and 10% for the red tea bags.

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OAASIS™ : a decision support software as a service for childcare center projects

Benjamin Pauget; Cyrielle Chaize; Robert Carreras

TESORA, FR

Context

The french circular of 2007, February 8th states that sensitive establishments (such as schools, childcares...) must not be built on contaminated sites and especially not on former industrial sites. To this end, contracting owners must conduct (or have conducted) diagnostics by collecting the whole available information to highlight a potential contamination of the site. If a soil contamination is found and if another site cannot be identified due to urbanistic and/or social pressure, depollution of the site can be considered. It has to definitively prevent the young population from being exposed to soil pollution. The last decision is made by the administration who states if the project is to be done depending on what will be realised in order to protect sensitive populations.

A decision support software as a service : OAASIS™

To simplify the first step of the urbanism planning, the engineering firm specialized in polluted sites TESORA, (www.tesora.fr) has developped a decision support software as a service. OAASIS™ provides recommendations concerning the environmental studies to be realized to validate the building project.

Process

The whole information collected during the historic and documentary studies is encompassed in the software. By crossing all datas, OAASIS™ provides a decision according to the site pollution risk level (GO, Part-GO, No Part-GO, No GO). It also recommends the environmental analysis that have to be done (such as soil or soil's gaz analysis) and justifies the decision. A full report of the whole encompassed information can be consulted by the client.

Illustration

To illustrate the work of OAASIS™, a fictive work case has been created. On this site, the town hall wishes to build a two-storey childcare, with a playground containing earth areas for children to access.

The historic study has highlighten that the site is referenced in the BASIAS database for its former industrial activities (garage, coaling station, dyeing factory). Then an engraving firm bought the site and built a new place with cellars. The site is consequently referenced ICPE because of the use of abrasive stuff (1 bis).

This information is encompassed in the software and OAASIS™ provides both conclusion and recommendations for the town hall to follow.

Here, to validate the project, the contracting owner (the town hall) will have to check the absence of soil contamination by soil and air analysis.

Conclusion

The use of OAASIS™ has allowed to evidence the potential absence of soil quickly and reliably. It is important to note that the use of this software can not replace the skills of an expert who has to interpret the results and have a critical point of view about the recommendations. However, the use of a software based on requests instead of human analysis is reliable, reproducible and scalable according to the feedbacks, whoever the user is. It ensures the contracting owner the constancy of the results from one study to an other, regarding the administration.

1e. Groundwater-soil-sediment-surface water interaction and system dynamics

Methyl-mercury complexes: selection of the thermodynamic properties and application to the modelling of a column experiment

Philippe Blanc¹; André Burnol; Nicolas Marty; Jennifer Hellal; Valérie Guérin; Valérie Laperche

¹ BRGM, FR

The complexation with methyl groups produces the most toxic form of mercury, especially because of its capacity to bioconcentrate in living tissues. To understand and integrate methylation and demethylation processes is of utmost interest to provide geochemical models relevant for environmental assessment. In a first step, methylation is investigated at equilibrium, by selecting the thermodynamic properties of different complexes that form in the chemical system Hg-SO₃-S-Cl-C-H₂O. The selection includes temperature dependencies of the equilibrium constants when available. Adsorption and desorption reactions of both methylated and non methylated mercury onto mineral surfaces are also reviewed. Then the kinetic of methylation is assessed by comparing of a dedicated column experiment (Hellal et al., 2015) with the results provided by a geochemical model, including the testing of different methylation and demethylation kinetic rates laws. The column experiment corresponds to a simple media: silicic sand and iron hydroxides previously spiked with a mercury nitrate solution. The column is inoculated with a bacterial consortium and the inflowing solution is supplemented with magnesium sulphate and sodium lactate to enhance the growth and activity of sulphate-reducing bacteria (SRB). This simple design still allows implementing and testing the main mechanisms responsible directly or indirectly for the mercury speciation: bacterial growth, sulfate and iron reduction, sorption and precipitation/dissolution of Hg-bearing minerals.

The numerical modelling is realised by using the PhreeqC-2 code (Parkhurst and Appelo, 1999) and the Thermoddem database (Blanc et al., 2012). The conceptual model is based on a 1D-radial geometry. A tracer test is successfully simulated to verify the hydrodynamic set of parameters. The results are verified at the column breakthrough point and along the column, for the longest reaction time. The modelling of the methyl-mercury production with two different rate laws from the literature is bracketing the experimental results. Dissolved Hg, Fe and sulfate concentrations are also correctly reproduced. The sulfide concentration is under estimated by the model, probably because of a deviation of the redox equilibria from the equilibrium conditions. The internal evolution of the column is also correctly modeled, including the precipitation of mackinawite (FeS) and the evolution of dissolved Fe and sulfates. Eventually, the results underline the capacity of geochemical models to reproduce bacterial activity driven processes.

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Polar PAC (Polycyclic Aromatic Compound) mobilization and transfer in water in coal tar contaminated soils

*Marine Boulange*¹; *Catherine Lorgeoux*²; *Julien Michel*³; *Raymond Michels*⁴; *Pierre Faure*⁵

¹ LIEC - CNRS/Université de Lorraine; ² UMR 7359, CNRS/Université de Lorraine/CREGU; ³ INERIS; ⁴ Laboratoire GeoRessources; ⁵ Laboratoire Interdisciplinaire des Environnements Continentaux - LIEC, FR

Due to the coal transformation activities occurring between the 18th and 20th centuries, about 200 000 sites in Europe have been diagnosed nowadays as polluted by polycyclic aromatic hydrocarbons (PAHs). Because of their toxicity, mutagenic and carcinogenic properties, 16 PAHs, listed as priority pollutants by the US EPA, are regulated and measured for site diagnosis or monitoring during remediation treatment. However, associated to PAHs, polar PACs (O-PACs and N-PACs) occur and could induce a risk for water resources. O-PACs and N-PACs are present in the initial pollution (coal tars) as PAHs but can also be produced during remediation treatments or during natural attenuation processes. Moreover, recent studies revealed that O-PACs and N-PACs (i) are leached in higher proportion than PAHs and (ii) can be equally or more toxic than corresponding parent PAHs. All these reasons imply increasing of our knowledge on the mechanisms involved in polar PAC mobilization and transfer to water, especially by comparison to PAHs. In fine, should polar PACs be included in coal tar contaminated site diagnosis in order to improve risk evaluation?

In this project, the mobilization and transfer of polar PACs and PAHs were assessed via leaching experiments of aged contaminated soils from two former coking plants (Lorraine, France), which have undergone aging processes. A multi-scale approach was used: batch (50 g), laboratory column (2 kg) and pilot scale column (2 m³ lysimeter). In a first step, PAC mobilization was investigated at laboratory scale under various conditions of temperature, ionic strength, PAC availability and water flow rate. PAC transfer was also assessed in situ with a lysimeter column. Dissolved Organic Carbon (DOC) and dissolved PAC concentrations (including 16 PAHs, 11 O-PACs and 5 N-PACs) were measured.

Batch experiments, carried out on soils with a high available contamination, revealed that PAC (LMW PAH and polar PAC) mobilization was mainly controlled by dissolution processes according to the Raoult law. For aged soils (low pollutant availability), the mobilization of PACs was lower, especially for LMW-PAHs and polar PACs. In both case, HMW-PAHs were mainly released in association with colloids. The temperature increased the mobilization of all PACs while an increase in ionic strength caused a decrease in all PAC mobilization, with a lower impact on polar PACs compared to PAHs. Whatever the column scale (laboratory and field lysimeter), results tend to show a higher release of polar PACs. Polar PACs exhibited intermediate behavior between PAHs (hydrophobic compounds) and DOC. These first results showed that (i) the pollution availability is a fundamental parameter for PAC transfer, and (ii) that polar PACs seem to behave similarly to PAHs but with a higher mobilization and transfer rate. All these findings underline the need to include polar PACs in diagnosis and monitoring of potentially contaminated sites.

Oxygenated polycyclic aromatic compounds to discriminate the origin of suspended matter in the river of a past industrial valley

Laurence Mansuy-Huault¹; Catherine Lorgeoux; Valéry Collin; Fayez Abuhelou; Delphine Cattelain; Renaud Gley; Allan Bauer; Benoit Losson; Luc Manceau; Hussein Kanbar; Patrick Billard; Quentin Ravalet; Emmanuelle Montargès-Pelletier

¹ LIEC - CNRS/Université de Lorraine, FR

The Orne (northeastern France) is a small river (mean flow: 8 m³.s⁻¹) located in a watershed impacted by industrial activities (steelwork and coal use) that were stopped by the end of the 80's and were demolished by the end of the 90's. This past activities had left numerous wastelands in the valley, strongly contaminated by PAHs ($\Sigma 16\text{PAHs} \sim 1500$ mg/kg) and by oxygenated and nitrogen polycyclic aromatic compounds ($\Sigma 11\text{O-PACs} \sim 150$ mg/kg, $\Sigma 5\text{N-PACs} \sim 15$ mg/kg). In this context, we studied the impact of different hydrological events on water quality due to soil run-off and sediment remobilization. Two cores were collected in the riverbed upstream of small dams and allowed to evidence the presence of heavily contaminated strata between 8 and 60 cm with PAH concentrations ranging between 17 and 1600 mg/kg, O-PACs ~ 6 -360 mg/kg and N-PACs ~ 0 -30 mg/kg. Two other cores were collected on riverbanks showing sedimentological evidences of the alternation of flood events and emersion steps. 6 campaigns covering water flows from 0.5 to 60 m³.s⁻¹ were performed over two years and a half (2014-2016), at 4 different sites over a river section of thirty kilometers. Suspended particulate matter (SPM) was collected by continuous field centrifuge for particulate PAC measurements.

The surface sediments from the riverbanks showed rather low concentrations in $\Sigma\text{PAHs} \sim 1$ -7 mg/kg, $\Sigma\text{O-PACs} \sim 0.1$ -0.6 mg/kg and $\Sigma\text{N-PACs} \sim 0.1$ -0.9 mg/kg. Surface sediments (0-8cm) from cores collected in the riverbed were more contaminated with $\Sigma\text{PAHs} \sim 9$ -17 mg/kg, $\Sigma\text{O-PACs} \sim 1$ -25 mg/kg and $\Sigma\text{N-PACs} \sim 0.5$ mg/kg. PAH, O-PAC and N-PAC concentrations in SPM ranged respectively between 2.4-27 mg/kg with a median value at 4.6 mg/kg, 0.05-1.33 mg/kg with a median value at 0.31 mg/kg, 0.03-2.9 mg/kg with a median value at 0.2 mg/kg. SPM collected during low flow events (from 0.5 to 25 m³.s⁻¹) were enriched in high molecular weight PAHs and in O-PACs that accounted for 10 to 20% of the total PACs. Similar distributions were observed in the surface sediments from the riverbed particularly enriched in O-PACs. On the contrary, SPM collected during high flow events (flow rates > 50 m³.s⁻¹) were characterized by the predominance of low to medium molecular weight PAHs (2-4 rings), and by the lower abundance of O-PACs ($\sim 7\%$ of the total PACs). Such distributions were also observed in the strata of the riverbank cores identified as flood deposits and were also quite similar to the distribution observed in the contaminated soils bordering the river in this section. Thus, the depletion in O-PACs compared to PAHs revealed the contribution of run-off during flood events. New molecular ratios including O-PACs such as anthraquinone / (anthraquinone + anthracène) are then proposed as indicators of the origin of SPM in the river.

Turbidity data analysis to estimate soil and water losses in different soils managements

*Douglas Gomes Viana*¹; *Peiqi Peiqi Zhang*²; *Paulo Roberto da Rocha Junior*¹; *Raphael Bragança Alves Fernandes*³; *Rabin Bhattarai*⁴; *Prasanta Kumar Kalita*⁴

¹ Federal University of Espírito Santo; ² Zhejiang University; ³ Federal University of Viçosa; ⁴ University of Illinois at Urbana-Champaign, BR

Excess runoff and soil erosion from agricultural areas can lead to environment degradation, economic impact due to loss of productivity, and adverse impact on human health. Maintaining soil cover as in no-tillage systems, and contour practices can reduce soil and water losses. However, up and downhill cultivation along with removal of residue are still practiced in many countries. Field experiments are often conducted to evaluate the impact of management practices on soil and water losses, but procedures involved can be complex and expensive. The objective of this study was to evaluate the potential of water turbidity on runoff to estimate soil and water losses in different soil management systems. Field experiments were carried out between June-August 2015 at the South Farm Experimental Station of the University of Illinois at Urbana-Champaign, USA. Experimental area represented scenario of mountain agriculture, with plots of 2.44 x 10.62 m in size and 32% slope. Soil and water losses from three treatments (contour tillage, downhill tillage, and no-tillage) and a control (bare) plot were collected and measured after each rainfall event. Water samples were also analyzed to measure turbidity. It was observed that turbidity was correlated with rainfall amount ($r = 0.42^{**}$), but better correlations indexes were obtained with water ($r = 0.61^{**}$) and soil losses ($r = 0.67^{**}$). But the use of turbidity data to estimate soil ($R^2 = 0.46$, $Y = 0.0000004x^2 + 0.002x + 0.1258$) and water losses ($R^2 = 0.37$, $Y = -0.0000001x^2 + 0.0046x + 1.0563$) did not result in a satisfactory regression model. Although turbidity data is correlated with rainfall amount, their use to estimate soil and water losses does not result in a satisfactory prediction. Use of the turbidity may be considered to estimate soil and water losses if the measured data are not available.

Occurrence and fate of emerging pollutants in groundwater from a municipal landfill

*Cécile Le Guern*¹; *Béatrice Béchet*²; *Alexandra Lépinay*³; *Pierre CONIL*¹

¹ BRGM; ² IFSTTAR; ³ Université de Nantes, FR

The transfer to groundwater of emerging substances from a former landfill in urban areas has been studied as part of a research program dealing with the observation and the monitoring of the environment. Of the 261 substances sought (30 pharmaceutical molecules, 223 phytosanitary products and 8 other emerging substances), 11 pharmaceutical molecules in particular have been quantified in the leachates, 2 endocrine disruptors (bisphenol A and triclosan) and 10 phytosanitary substances. Most of these substances are found in groundwater immediately downstream of the site (including carbamazepine) at concentrations ranging between 0.1 µg/l and 10 µg/l. The number of detected substances appears much smaller a few hundred meters far from the landfill (bisphenol A and diclofenac in particular, with concentrations ranging from 0.1 to 1 µg/l and about 0.1 µg/l respectively). Natural attenuation occurs during transfer in the plume, as observed for PAHs or metals. The results show the interest of long-term hydrogeological and chemical monitoring. These are essential to the description of transfer processes of emerging substances.

Risk based quality criteria for re-use of soil and sediment in deep lakes

Johannes Lijzen¹; Charlotte Schmidt²; Jos P.M. Vink³; Rob N.J. Comans⁴; Tommy Bolleboom⁵; Leonard Osté³

¹ National Institute for Public Health and the Environment RIVM; ² Rijkswaterstaat; ³ Deltares; ⁴ Wageningen University; ⁵ Rijkswaterstaat, NL

In the Netherlands, soil and sediment is re-used in deep lakes to create more shallow surface water with other characteristics, e.g. higher biodiversity. Quality criteria for the re-use of soil and sediment were defined in the Soil Quality Decree in 2008.

Because of uncertainties and societal concerns that came up in 2010, a guidance was made to regulate the application of soil and sediment. The Ministry of Infrastructure and Environment launched a research program to reduce the uncertainties in environmental risks resulting from potential leaching of nutrients and metals. In 2015 the research led to a policy proposal on quality standards, which is currently being prepared for new standards on the re-use of soil and sediments in deep surface waters in the Decree on Environmental planning in 2019.

In the proposal, the quality of groundwater and surface water are considered the endpoints to be protected in order to meet the goals of the Water Framework Directive. Water type-specific goals for phosphate, metals and arsenic are related to local geochemistry, and hence bioavailability. Different standards for the bulk of the material and for the top layer of the new sediment are proposed.

The three-year research program yielded element-specific transfer functions to determine safe concentrations in soil and sediment to be applied under oxic and anoxic conditions. A dilute nitric acid method ("Aqua nitrosa"; recently standardized as ISO-17586:2016) that extracts the potentially available fraction is used in these relations, providing better predictions of dissolved (and hence bioavailable) concentrations than based on total soil content (Aqua regia). For organic compounds criteria were derived for all WFD relevant compounds.

This approach for assessing risks for large-scale soil and sediment applications will be implemented in the Decree on Environmental planning in 2019. A policy-working group is preparing a proposal in the beginning of 2017 that can replace generic quality criteria for soil and sediments for the reuse in deep lakes as stated in the current Soil Quality Decree. This proposal and the underlying principles will be presented, together with the expected policy planning.

The impact of anthropopression on surface and groundwater in the Babiogorski National Park (South Poland)

Małgorzata Malata¹; Adam Postawa; Grzegorz Malina; Jacek Motyka

¹ University of Science and Technology, PL

Physical-chemical properties of surface and ground waters depend on natural conditions that are modified under anthropopression. In mountain areas the anthropogenic impact on physical-chemical properties of water is mainly due to contaminated precipitation and mountain tourism, e.g. wastewater discharges from mountain shelters. It is manifested through increased concentrations of biogens, chlorides and sulphates. The area of Babia Gora, even though protected by law (the Babiogorski National Park, UNESCO biosphere reserve, Natura 2000), may be subject to strong current anthropopression caused by an intensive touristic traffic. Due to the recharge of groundwater from direct infiltration of precipitation and the conditions of groundwater circulation in this area both the shallow Quaternary and deeper Jurassic aquifers maybe at risk of being contaminated.

The goal of the research was to identify major sources of contaminants, and to determine the current level of anthropopression in the N-E part of the Babia Gora mountain range constituting the Babiogorski National Park (BNP). Water samples were taken in 4 sampling series in 2015-2016 from 8 main streams and 120 springs along one of the most popular mountain trails: from the Krowiarka to the PTTK Shelter of Markowe Szczawiny. Additionally.

The physical-chemical properties of the precipitation water were characterized by slightly acidic to neutral reaction (pH=3.8-7.7). The concentrations of biogens (in mg/L) were <0.001-24.1 (PO₄) and 4-60.8 (NO₃). The highest concentrations of metal ions (in µg/L) were measured for Ag (35.9) and Br (106.8). The pH and EC of spring waters varied from: 8 to 9.5 and 45 to 192 µS/cm, respectively. The concentrations of biogens (in mg/L) were of: 3.9-19.5 (SO₄), <0.001-1 (PO₄), 7.1-26.9 (NO₃) and 1-8.1 (Cl). The highest concentrations of metal ions (in µg/L) were observed for Al (1515) and Fe (1003). The pH of waters from streams was of 5.7-8.9 and EC varied from 56.1 to 270 µS/cm. The concentrations (in mg/L) of SO₄, PO₄, NO₃ and Cl were: <0.001-17.7, <0.001-0.3, 9.0-128.4 and 0.8-18.8, respectively. The highest concentrations of studied elements were of: 1180 (Al), 961 (Fe), 67.4 (Ag), 17.8 (As), 73.9 (Br), 285.8 (Cr), 25.8 (Sb), 240.8 (Se).

High concentrations of Al and Fe ions originate most probably from the natural geochemical processes and are affected by pH. The buffering of acid precipitation on aluminosilicates is a characteristic geochemical process that has an effect on the chemical composition of water in this area. However, high concentrations of As, Br, Cr, Se may be connected to past use of fertilizers and pesticides, which due to the runoff, subsurface flow and infiltration, could enter surface waters and soils. On the other hand, high concentrations of biogens and other elements are attributed directly to tourism.

Acknowledgement: The work was supported by AGH University project no. 11.11.140.797

Key words: the Babiogorski National Park, springs, streams, fertilizers, biogens, tourism

Groundwater flow and conservative transport model as a basis for an EOC behavior study in a surface mar (aquifer recharge) system

Lurdes Martinez-Landa; Cristina Valhondo, ES

Managed Aquifer Recharge (MAR) by means of basins is a powerful technology both for increasing groundwater availability and improving quality of water, because the aquifer acts as an additional treatment step. To properly understand the behavior of potential contaminants in the subsoil, a detailed characterization of the unsaturated zone and the aquifer is needed. Assessing the residence time distribution (RTD) of infiltrated water is of utmost importance for this purpose and requires a detailed hydrogeological characterization focusing on heterogeneity.

This work explains the characterization of a recharge pilot basin which diverts surface water from the Llobregat River, close to Barcelona and the Mediterranean coast. This site is on top of quaternary alluvial sediments forming stratified layers with different proportions of gravel, sands and clay, which controls the vertical movement of compounds through the vadose zone and the horizontal groundwater flow. As well as defining the geology, groundwater heads and flow directions during a 4 years period in order to take into account seasonal variations and typical interannual fluctuations, we conducted a conservative tracer test to evaluate the transport properties of the basin-aquifer system.

Flow and transport parameters were calibrated using a quasi-3D numerical model under two hypotheses, considering the aquifer as homogeneous or heterogeneous media. The latter provides better fits to measured concentrations at the 6 monitoring points, especially concerning the long tailings observed in breakthrough curves. This broad RTD is due to the complex geology of the sedimentary formation.

The approach described here has served to build up a reactive-transport model that makes insight into the behavior of EOCs present in recharge water through basins.

Can forest fires be a diffuse source of contaminants (PAHs) to the terrestrial system?

Isabel Campos; Nelson Abrantes; Bruna Oliveira; Carlos Vale; Jan Jacob Keizer; Cristina Micaelo; Patrícia Pereira, NL

Wildfire is a major disturbance of forests worldwide, posing an important threat to life, human goods and natural resources. Indeed, the environmental impacts of wildfires promote significant effects to the structure and functioning of the different ecosystem compartments. In particular, the effects of fire-induced release of contaminants such as polycyclic aromatic hydrocarbons (PAHs) are now believed to be of a specific ecological, biological and/or human significance, due to the compounds' high toxicity, persistence and tendency to bio-accumulate, but have been neglected till quite recently, including in Portugal. Hence, the present study aimed to clarify and evaluate the role of wildfires and time-since-fire in the production and mobilisation of PAHs. To this end, temporal trends and profiles of the fifteen priority PAHs (by USEPA) were assessed in samples of ash and (un-) burnt topsoil (0-2 cm depth) that were collected in eucalypt plantations immediately following a wildfire in north-central Portugal as well as 4 (after the first major post-fire rainfall events), 8 and 15 months later. The principal results obtained in this study were the following: (1) the levels of PAHs were higher in burnt soils than in unburnt soils (70%); (2) the levels of PAHs declined abruptly after the first rainfall event; (3) ashes were consistently enriched in PAHs relatively to the underlying topsoil; (4) the burnt soils and ashes were characterized by higher levels of light PAHs with three (phenanthrene and fluorene) to four rings (fluoranthene and pyrene). Moreover, the three rings showed a pronounced decreased over time-since-fire. Our results clearly suggest that PAHs produced by the forest fires seems to be adsorbed by soil and ash, being ash one of the main agent influencing the concentration of PAHs in the soil. Moreover, the decreased in PAHs levels over time, mainly due to the washout and/or leaching of the ashes, may indicate that PAHs can be transport downstream by soil/ash runoff. This study emphasized the role of wildfire in enhancing levels of PAHs in ashes and topsoil of forest plantations and their mobilisation during the first year after fire, and thus pointed towards recently burnt forest areas as a potential source of diffuse environmental contamination. It also point out the importance of further studies to assess the impact of PAHs in aquatic systems downstream to burnt areas.

Hydrocarbon cooling fluid leak delineation in soil and groundwater

Juliette Payet¹; *Vincent Besnier*; *Stéphane Poncet*

¹ Arcadis, FR

EDF is dismantling six French nuclear plants. In each case, a state-of-the-art site investigation is needed to define the subsoil quality in the area of dismantling. The areas to be investigated have been identified by EDF after preliminary assessments based on historical activities.

At the Chinon nuclear plant, one area contained three Thermip Aerial Storage Tanks (AST) and two fuel AST. Thermip was a specific oil used to cool the pre-stressed concrete of the A3 reactor chamber. This fluid is no longer used in nuclear plants. It is mainly made of naphthalene and methyl naphthalene. The area has been dismantled, and the tanks and part of the contaminated soil were removed. However, new soil, soil gas and groundwater investigations have been undertaken in this area to verify the subsoil quality. The methodology and findings of the investigations will be described in detail for this site, demonstrating how the contamination by different oil types was differentiated beneath a single site.

Total hydrocarbon and PAH (Polycyclic Aromatic Hydrocarbons) in soil and soil gas were found below and around the former tanks, which were subsequently investigated further to delineate the extent of this contamination. State-of-the-art geostatistical methods were used to map and visualize the plume in 3D, and to make a distinction between contamination related to fuel versus contamination related to the Thermip through use of contamination „markers“ in soil (naphthalene for Thermip impact and hydrocarbons sum less naphthalene for the fuel). This study also enabled estimation of the impacted soil volume, indicated by several compounds concentrations being greater than threshold values.

Groundwater quality was then investigated upgradient and downgradient of the soil impacted area to evaluate whether impacts had reached the groundwater. Thermip-related impacts were detected in groundwater but not fuel-related impacts. Light non-aqueous phase liquid (LNAPL) was observed just upgradient of the estimated soil source, with naphthalene and low fraction hydrocarbon concentrations measured downgradient of the soil source.

No significant TPH and naphthalene concentration were observed in the other investigated monitoring wells on site (50no.), helping to delineate the extent of the remediation treatment area and enable recommendations regarding remediation needs to be developed.

Degradation of the gas bubbles produced in the soil conditioned with a foaming agent and excavated by earth pressure balance TBM (EPB)

Moez Selmi¹; Mariem Kacem¹; Mehrez Jamei²; Philippe Dubujet¹

¹ Ecole Nationale d'Ingenieurs de saint Etienne; ² Ecole Nationale d'Ingénieur de Tunis, FR

Tunneling using the earth pressure balance machines method in clayey soils requires the addition of conditioning chemicals to reduce the torque moment of the machine and to guarantee a safe and economical excavation process. Injection of foams at the cutter head of the tunnel boring machine with subsequent remolding in the pressure chamber transforms the excavated material into a deformable soil paste with preferably low strength and adhesion. Several tons of sludge is produced by tunnel boring machines as a result of excavation processes: a scenario shows that 8 million cubic meters of flow are created as a result of the excavation of a tunnel 50 kilometers long and 100 m² of section. A possible use of this soil is limited by the consequences of his treatment.

In this work, we study foam's evolution in the soil through the study of the degradation of gas bubbles generated in the soil matrix. This study is carried out on sandy soil clay reconstituted from 60% sand and 40% of Kaolin. The soil is conditioned with a foaming agent CLB F5TM supplied by CONDAT. This surfactant generates liquid foam with gas bubbles ranging in size from a few microns to some millimeters. Three parameters allowing the quantity of the foam injected into the soil: foam injected ratio (FIR), Foam Expansion Ratio (FER) and surfactant dosage (Cf)

In a first part, we study the aging of the foam alone. Degradation of the foam is studied by following the phenomenon of drainage coalescence and ripening which occur over time. Foam degradation tests were performed in order to determine the half-life time of the foam and study their degradation in soil over time. These tests show that the surfactant is easily degradable without soil. The experimental tests show that our foam used has a half-life equal to 19 min.

Injected into the soil, the foam behaves differently. The phenomena of drainage, coalescence are observed but with a much lower velocity than the foam alone. Foam's gas bubbles are incorporated in the inter-granular porosity. The phenomenon of coalescence ripening and are followed by excessive water pressure in the soil. The degradation of the foam in the soil results in the degradation of the gas bubbles incorporated in the matrix thanks to the replication of the liquid films which surround them. Measurements tests of the percentage of gas bubbles in the soil over time were also carried on a soil treated with different FIR. Optical microscope tests were also carried out to describe the phenomena of foaming over time in the soil. Results show the degradation of gas bubbles in the soil matrix after 32 days.

Keywords: soil, gas bubbles, degradation, foam, tunneling.

Topic 2. Risk assessment

2a. Human health risks

Development of Risk Based Screening Levels (RBSLs) for soil and groundwater in the Niger Delta

George DeVaul¹; Matthijs Bonte¹; Kim Bye Bruun; Jonathon Smith

¹ Shell International Petroleum Co. Ltd, NL

Shell is working with the Nigerian National Oil Spill Detection and Response Agency (NOSDRA) and the Nigerian Department for Petroleum Resources (DPR) to develop Tier I Risk-Based Screening Levels (RBSLs) for soil and groundwater assessment in the Niger Delta. Tier I RBSLs are based on regional/local site conditions, and are used in place of “generic” criteria for initial risk assessment of soil and groundwater impacts.

RBSLs define contaminant levels above which additional assessment and/or remediation may be needed to ensure no unacceptable impact to human health and the environment. Nigerian soil and groundwater legislation allows for a risk-based approach, but actual implementation is still sporadic due to the lack of a consistent set of scientifically underpinned RBSLs. Currently, the default approach to determine the need for remedial action is by using the Dutch Intervention values, which lack any differentiation between different land use functions, and were developed for Dutch environmental, social and policy conditions. Development of locally applicable RBSLs, based on conceptual models of human exposure specific to the Delta, has also been recommended by the IUCN Niger Delta Panel and the UN Environment Program that reported on the state of Ogoni Land in 2011.

The Niger Delta RBSLs are developed using the ‘Risk Based Corrective Action’ (RBCA) framework developed by the American Society for Testing and Materials (ASTM). In order to make this model fit for purpose in Nigeria, an assessment was made on how people can be exposed to contamination and how this differs from exposure routes observed in other countries. This resulted in defining a number of Niger Delta specific exposure scenarios, including for example subsistence farming (where a land owner lives off his/her own land) and informal residential use (residents of dwellings directly exposed soil without constructed foundations and floors). Also, a number of model modifications were incorporated which make the RBCA approach better suited to assess risks to human health resulting from crude oil exposure instead of a single chemical release.

It is anticipated that the developed RBSLs will address the concerns raised by the IUCN Niger Delta Panel and UNEP team and will contribute to improved management of soil and groundwater risks in the Niger Delta.

Protocol for the selection of physico-chemical values for non-standardized contaminants for the establishment of soil limit values in Wallonia, Belgium.

Elodie Bouhoulle

Institut Scientifique de Service Public - ISSeP, BE

In Wallonia (Belgium), contaminated soils management is regulated by a decree (Soil Decree, MB 2009). It includes threshold concentrations values in soils for around 50 contaminants. Several guidelines have been established to accompany the decree and support experts in assessing soil contamination and human health risks, among others.

For contaminants for which no threshold concentrations in soils are included in the Soil Decree, a collaborative work between Walloon institutions and the regional authorities has been done to identify the most relevant physico-chemical and toxicological reference values to calculate "human safe" concentrations in soils using a risk assessment model.

This poster will present the resulting protocol for the selection of physico-chemical parameters values. On this basis, physico-chemical parameters values have been reviewed for around 200 non standardized contaminants. Limit values have then been calculated using those data and revised toxicological reference values.

Limit values and physico-chemical parameters values will be made available to Walloon soil experts in early 2017.

Risk Assessment performed by using multiple lines of evidence: a case study with soil gas and flux chamber measures

Francesco Ioppolo¹; Mara Bellavita¹; Simone Biemmi¹; Anne Delos²

¹ Arcadis Italia; ² ARCADIS ESG, IT

In the few last years, the collection and use of soil gas data and vapor flux measures from the ground using flux chambers are growing techniques in Italy. The aim of collecting such data is to better understand whether there is an actual human health risk generated by the volatilization pathway, for contaminants in soil, groundwater and non-aqueous phase liquids, in the indoor and outdoor environment. These approaches are validated by specific regulation and technical guidelines (note Prot. 0029706/TRI of 11.18.14 of the Italian Ministry for the Environment, and the Decree of the Ministry of Environment No. 31/2015 of 02.12.15).

In cases where indoor/outdoor inhalation exposure pathways have been identified as a concern, from the examination of experience gained both at the national and international level, it has emerged that the standard human health risk assessment procedure used in Italy often provides conservative outputs, especially regarding indoor air exposure. This is particularly the case for petroleum hydrocarbons, where the actual concentrations of these contaminants in air (at the point of exposure) have been found to be much lower (even several orders of magnitude) than those predicted by the simulation model first developed by Johnson and Ettinger.

A field case study to assess the success of a simulation model in predicting the contribution of contaminated vapors originating from soil and groundwater contamination versus other sources of contaminants in air, for a petrol station, will be described. The applied method combines multiple lines of evidence. At this petrol station, petroleum hydrocarbon contamination had been found in groundwater and near-surface and deeper soil. First, the conceptual model of the site was defined. Second, forward risks and threshold target remediation limits ("CSR") were calculated in a "classical" way – relying on a simulation model to predict the migration of contaminants from solid/liquid matrix to the gas matrix—which indicated unacceptable risks may be present in comparison to legally-defined limits. Thirdly, a more detailed investigation was undertaken to measure the actual transfer of the contamination from the solid/liquid matrix to the gas matrix and to estimate the degree of biodegradation of the contamination from ground/groundwater to the measurement/exposure point above the ground. Two sampling campaigns of soil gas in nested probes were completed, alongside one campaign sampling for vapor emission using a dynamic flux chamber. Finally, the predicted concentrations in indoor and outdoor air were calculated using an integrated approach (combining the empirical data with modelling) and through use of attenuation coefficients. The results of this study will be described, demonstrating that the collection of targeted empirical data allowed a more refined understanding of the actual risks to human health and development of site specific CSR; the case study is considered to illustrate how assessment of the phenomenon of vapor intrusion can be made more site specific, sustainable, and realistic through the collection of data which reduces uncertainty in the modelling process.

Laboratory tests to assess trace element mobility at various physico-chemical conditions: tools for soil remediation options, and GW risk assesement

Valérie Guérin¹; Philippe Bataillard; Dominique Breeze; Elicia Verardo

¹ BRGM, FR

Understanding of chemical phenomena in the unsaturated zone (ZNS) is of great interest to more accurately assess the risk in the long term for groundwater. In this study (Caphéine project, funded by Ademe), we wanted to go further: i) than standard leaching tests (XP CEN ISO / TS 21268-2) that are commonly used; ii) the common approach which consider that all leachable elements reach the groundwater, while ignoring the potential protection provided by the vadose zone.

In order to do so, we applied two tests i) to evaluate the future mobility of trace elements (TE), ii) to guarantee the stability of the material:

The first one is the acid and base neutralization capacity test (ABNC; XP CEN / TS 15364, September 2006) dedicated to waste characterization in soil. The aim was not only to obtain data to predict material behaviour under specified conditions (here, the pH), but also to associate TE release as a function of pH as an indication of the stability of the studied soil (natural soil or treated soil).

The second one, "redox test", is not subject to a standard. This method proposes to change redox condition in a soil by adding organic matter (lactate solution 10mM, easily degraded) in a closed environment. This will cause oxygen consumption in the reactor by bacterial respiration and gradually allow the expression of anaerobic microbial communities. This procedure is considered to be more realistic than tests involving chemical reductants to evaluate effects of changes in redox conditions (capping, OM content...).

We have applied those tests to a former manufacturing plant of mineral fertilizers polluted by residues of pyrite roasting, rich in trace elements (arsenopyrite (arsenic, As), sphalerite (zinc, Zn), chalcopyrite (copper, Cu), galena (lead, Pb), ... etc..). The possible management options are: capping, on site landfilling, use as raw materials, all options that request an assessment of the potential release of materials according to the environmental conditions that will prevail in the future.

Laboratory tests were carried out on two soils (S & T) according to the proposed scenarios. In parallel, standard soil leaching tests are carried out for comparison (with same S/L ratio=1/10).

The ABNC test showed that soil "S" may be sensitive to environment acidification. Thus, it might be necessary to lime it if it were retained or used as a building material (road under-laying for example) to limit the mobility of TE.

For soil "T", the "redox" test showed an increase in arsenic and lead mobility while promoting zinc and cadmium fixation. For the soil "S", anoxic conditions increased TE mobility for all studied elements (zinc, arsenic, lead and cadmium).

The implementation of these experiments is to be considered when studying the behaviour of TE in soils:

- To help choose remediation options, by focusing specifically on actions that could eliminate/control TE transfer,
- To evaluate the mobility of TE in soils in foreseeable environmental conditions which may be induced by human activity or climate change.

Integrated approach for the development of tier iii human health risk assessment

Francesca Motta; Fabio Canova; Daniela Reale; Elena Leale

AECOM, IT

This work presents the results of a Tier III human health risk assessment that was developed combining classical groundwater characterization techniques, with Membrane Interface Hydraulic Profiling Tool (MIHPT), characterization of bacterial potential and activity by Quantitative-Polymerase Chain Reaction (qPCR), fate and transport (F&T) numerical model, and Johnson and Ettinger Model to assess risk posed by groundwater contaminated by Trichloroethylene (TCE) to off-site residents through indoor inhalation of vapour.

A 3d numerical model was built using the finite elements code FEFLOW. The model domain (16 km²) was defined adopting physical (real) boundary conditions, while top and bottom of the alluvial phreatic aquifer were derived by open source data, based on thousands of boreholes. 16 layers were implemented, deriving hydraulic parameters both from literature and from hydraulic testing at the Site, to calibrate the model reproducing July 2016 Site groundwater elevation data. The TCE source geometry and initial concentrations were defined based on the MIHPT investigations results. Site-specific transport parameters (i.e. Koc, Foc) were also implemented, based on results obtained from soil samples results. Biodegradation processes were not considered in the model, as site specific results obtained with qPCR analyses identified the presence of dehalococoides (genus responsible for performing reductive dehalogenation to ethene) in DNA but not in RNA. The model was then used to run predictive simulations showing the TCE plume extent downgradient the Site, until a good fit of the July 2016 TCE concentrations was reached. The results of the F&T model showed that the TCE plume could reach a maximum distance of 500 m downgradient the Site.

The range of concentrations of TCE underneath a building located off-site were estimated by the fate and transport model. With that concentration input, the Johnson and Ettinger model was then applied to assess risk posed by TCE to off-site residents through indoor and outdoor vapour inhalation. The results of the study showed that risk was within acceptable target levels set by Italian Regulation.

The application of detail characterization techniques applied to define the source geometry and biodegradation setting of groundwater, combined with numerical modelling, allowed to supersede the default conservative approach and analytical modelling of Tier II risk assessment, with robust site-specific data that lead to defining a more representative risk value to off-site residents.

Modelling of source to building exclusion distances at petroleum contaminated sites

Iason Verginelli; Renato Baciocchi

University of Rome Tor Vergata, IT

The role of biodegradation in attenuating petroleum hydrocarbon vapours migrating into indoor environments has been the subject of several papers in the last decade. Despite this, due to the too conservative character of the screening models generally used in the risk analysis framework, vapour intrusion still results a critical pathway in several petroleum-contaminated sites. To overcome this limitation, in the last decades more detailed models accounting for biodegradation were developed. More recently, a big effort was also made to identify source to building separation screening distances, beyond which the potential for vapour intrusion can be considered negligible. This was mainly made by carrying out statistical analysis of large soil vapour datasets collected from the field. However, these empirical screening distances are associated to a certain probability percentage (e.g. 95% of cases) that for a given type and source concentration (e.g. dissolved-phase or LNAPL source) the contaminant of concern will be attenuated below a target soil-gas screening level. To support and further justify these empirical analyses, mathematical modelling can be certainly of help. In this work, we present two simple analytical models that allow to directly estimate, on a site-specific basis, the risk-based screening distance for petroleum hydrocarbons. The proposed solutions rely on a 1-D vapour intrusion model that incorporates a steady-state subsurface vapour source, diffusion-dominated vapour transport in a homogeneous soil, aerobic biodegradation limited by oxygen availability, diffusive and convective mass transfer across the building foundation and mixing within the indoor environment. In addition, the models account for the transport of oxygen due to diffusion and its consumption to sustain the aerobic reaction. In nearly all simulated conditions, source to building vertical separation distances greater than 2 m or 5 m were found to be sufficient to attenuate to acceptable risk-based levels petroleum hydrocarbon vapours from dissolved-phase or LNAPL sources, respectively. These results are consistent with the empirical screening criteria of 1.8 m (6 feet) for dissolved contamination and 4.6 m (15 feet) for LNAPL sources suggested by U.S.EPA (2015). On the other hand, it was found that the lateral exclusion distance for petroleum vapour intrusion can be set equal to 6 m for groundwater sources and to 9 m for soil sources, regardless of the source concentration and depth. These exclusion criteria can be significantly reduced for low to moderate source concentration. For instance, from low to moderate source concentrations (e.g. for benzene concentrations lower than 5 mg/L in groundwater and 0.1 mg/kg in soils) and deep sources (e.g. deeper than 5 m) the simulations carried out suggested that the lateral screening distances in principle may be set equal to zero. Indeed, for such scenarios a source to building vertical separation of few meters is already enough to attenuate petroleum vapours below acceptable levels.

2b. Environmental risks, including bio-availability

Ecological risk assessment for a contaminated sediment site

Elisa Bizzotto; Sara Ceccon; Fabio Colombo, IT

The presentation reports the experience gained from an Italian case study, an historical DDT and Hg industrial contamination in a river-lake system. The lake and the river were extensively studied in collaboration with public agencies and research institutes. Investigation design and data interpretation were based on a tiered approach, verifying at each step if further investigations were necessary to evaluate potential effects for the aquatic ecosystems. The design took into account also the current European legislative framework for the protection of surface waterbodies. Ecological Risk Assessment (ERA) was the decision-making tool proposed to support environmental management. Since in Italy there is not a specific guidance for ERA of freshwaters contaminated sites, a Technical Board was established with the participation of several experts from academia, public environmental agencies, research institutes and industry, with the final aim of developing a shared approach. Risks to invertebrates were evaluated considering: (1) comparison of site-specific sediment data to benchmarks derived from literature research to assess cause-effect relationships; (2) comparison of invertebrate tissue concentrations to effects thresholds; (3) community structure assessment; and (4) sediment bioassays. Risks to fishes were evaluated considering: (1) comparison of fish tissue concentrations to effects thresholds; and (2) comparison of water concentrations to benchmarks. Finally, risks to wildlife (mammals and piscivorous birds) were evaluated considering (1) comparison of dietary exposure to effects thresholds; and (2) evaluation of site-specific data. Moreover, a Human Health Risk Assessment was undertaken considering exposure from fish tissue concentrations. A participatory approach involving environmental and health authorities, public and private research institutes and industrial managers was applied in the decision process; this approach was fundamental for the overall process, since it has facilitated scientific discussion, communication and decision-making process bridging the gap between stakeholders. The participatory experiences gained in this case-study could represent an example also for other Italian contaminated sites.

Multi surface modeling of trace metals behavior in treated dredged sediment: experimental study and modeling of metals retention on artificial assemblage of natural sorbent phases.

Louise Chenoy; Guy De Weireld; Anne-Lise Hantson

University of Mons, BE

In Walloon Region dredged sediments are classified as waste materials and must eventually (depending on their pollutant content and release) be treated before valorization or disposal. During several years 6 million of m³ of sediments have been accumulated in waterways, whose about 65% are polluted by heavy metals or organic compounds.

Over the past few years SOLINDUS and VALSOLINDUS projects aimed to assess the feasibility of sediments treatment and reuse. Considering that contaminants are generally concentrated in fine fractions, the treatment developed consists in a mineralurgic process to separate unpolluted coarse fractions (> 63 µm) from polluted fine fractions (silt fraction 15-63 µm and fine fraction <15µm). An additional flotation step is then applied to the silt fraction to attempt to further purify it.

In a previous work, three samples of sediment silt fraction were characterized and leaching behavior of trace metals (Zn, Cd, Pb, Cu, Ni) was studied. A multi surface model was constructed with PHREEQC v.3.0. in order to improve the comprehension of metals retention phenomena. This comprehension is of importance to improve the treatment and evaluate environmental risks linked to further sediment reuse.

The geochemical model combines thermodynamic models for inorganic speciation and dissolution/precipitation of mineral phases with ion binding models to account for metals retention on the phases constituting the sediments. The generalized 2-layer model (GTLM) of Dzombak and Morel is used to model binding to iron and aluminum oxides, the Windermere Humic Aqueous Model (WHAM) VI for binding to organic matter and an ion exchange model for binding to clays. This modeling approach supposes additivity of sorption on the different phases. At this time, results of modeling represents pretty well the general behavior of trace metals in function of pH. However, the model could be improved.

Indeed, real samples of sediments are complex mixtures and their accurate characterization in order to use ion-binding models is difficult. This study aims to test the modeling approach against experimental data of metals sorption to artificial assemblages of well characterized phases. The first studied system will be constituted of synthetic amorphous iron oxide which is according to the model results the preponderant sorbent phase in the sediments studied. Batch sorption experiments will be conducted firstly with Zn and Pb (alone and in mixture) as they are the most problematic trace metals in the sediment samples. The influence of quartz and calcite will be also assessed like these phases are present in large quantities in sediments. Pure clays or organic matter (purified humic or fulvic acids) could also be studied separately and further included in the artificial assemblage.

Springtails: The canaries for soil pollution

Marlea Wagelmans; Dick Roelofs; Maurice Henssen¹

¹ Bioclear, NL

The Dutch government has determined a list with sites that potentially have ecological risks due to severe soil pollution. These risks have been determined by means of a (deliberately) conservative computer model. However, it is important to determine the actual ecological risks at a given site. Traditionally, ecological risks are determined by means of the Triad approach, a combination of chemical analyses, bioassays and ecological field observations. Although this approach gives insight in the actual ecological risks at a site, it does not explain the cause of the effects. Therefore VU Amsterdam has developed a test together with Bioclear, within the programm BE-Basic, that is able to assess not only the actual ecological risks at a location but also the cause of the risk: the invertebrate Soil Quality (iSQ) test with springtails.

Springtails are sensitive to various types of soil pollution. The presence of pollution in soil leads to a stress response in organisms due to detoxification. Different compounds cause different stress responses. This stress response is measured with molecular analyses (RNA) on specific proteins that code for specific enzymes. This enables us to distinguish effects caused by for instance metals from effects caused by PAH even when organisms are simultaneously exposed to both. The amount of proteins that is produced also gives an indication of effects on reproduction which enables us to link specific exposure to effects on reproduction.

In this presentation we will explain the mechanism of the test and we will give three examples of sites where this test was used to make a decision based on actual ecological risks. The first site is located in the dunes (client: ODWH). The site has been elevated and leveled out with domestic waste. This has caused a severe soil pollution with heavy metals. At this site a so called 'social consideration' was performed in which, based on all kinds of facts about the site, ecological risks were not expected. The second site is a former flow field from textile industry (client: Province Noord Brabant). This has caused a severe pollution with mainly chromium. At this site a Triad approach has been performed. In this approach, negative effects were found but these could not be linked to the pollution present. The last example is a former landfill at which a Triad approach has been performed (client: Province Zuid Holland). High concentrations of both metals and PAH were present. Risks to soil organisms could only be linked to PAH exposure.

By means of our examples we will show that with the iSQ test ecological risks as well as the cause of risks can be determined fast and accurate. The test is applicable for screening of risks, as part of the Triad approach, for objectifying the (Dutch) 'Social consideration' for ecological risks, as additional support for (previously determined) values for remediation and prioritizing remediation of sites based on ecological risks. Remediation of sites can thus be limited to those sites where ecological risks actually are present.

Geospatial distribution of trace element availability

Juan Pedro Martín Sanz¹; Juan Pedro Martín Sanz¹; Ana De Santiago Martín²; José Ramón Quintana Nieto¹; Cristina Vaquero Perea¹; Antonio Vázquez de la Cueva³; Concepción González Huecas¹; Antonio López Lafuente¹; María Inmaculada Valverde Asenjo¹

¹ Universidad Complutense de Madrid; ² Laval University; ³ Centro de Investigación Forestal-INIA, ES

Large industrial areas, communication networks, secondary urban centers and farms are concentrated in the peri-urban areas of large cities, increasing trace elements (TE) in the soil, including Cd, Cu, Pb and Zn. In order to study the environmental risk involved in this increase, the total TE content is not a good indicator, so it is necessary to determine its availability in the soil. The objective of this work was to study the geospatial distribution of the total content and availability of Cd, Cu, Pb, and Zn using EDTA and CaCl₂. For then, 125 points were sampled in an area of 1050 km² in the SE of the metropolitan zone of Madrid with two overlapping meshes (one regular every 5 km and another random 1x1 km) presenting varied lithology (gypsum, limestone, gravel and sand, urban debris, conglomerate) and land uses (industrial, agricultural, forest, residential). The study of geospatial distributions was performed using geostatistical techniques, with variogram modeling and kriging of data. Results showed that the geospatial patterns of the total and available TE contents did not correspond, which emphasize the need of assessing the pollutant availability in order to establish their environmental risk. The geospatial pattern CaCl₂-extracted Pb and Zn concentration was randomized. In general, TE concentrations (both total content and availability) were higher near to Madrid City and to industrial areas, with a hot spot in all cases in the area surrounding a landfill with a waste incineration system. Spatial distribution of TE availability indexes did not match with the distribution of total TE. In the case of Cd, there were maximums in the gypsum zone and in the confluence of the two main rivers in the zone of study, whose main use is the crop in irrigation. In contrast, EDTA-Cu concentrations were the highest in the calcareous zone, consistent with the presence of a cement factory and some mining exploitations. This EDTA-Cu maximum was spatially correlated to total Zn. The highest total and EDTA of Pb and Zn concentrations appeared in the vicinity of Madrid, near the landfill as well as to the road network. The use of geostatistical methods for mapping the TE distribution allowed observing the different patterns of total and available TE concentrations. Interestingly, two zones presenting greater environmental risk were differentiated in the case of TE availability, being different from that of the TE total content. The areas with the greatest risk of TE contamination, total and available, depended on the lithology, land use and presence of contaminant sources (proximity to city, surrounding industrial areas or road network). Other potential sources (such as landfill with waste incineration, mining areas or cement factory) would require a more comprehensive study. This work was supported by the Madrid Autonomous Region through the CARESOIL Programme (Ref.P2013/MAE2739).

Using bioindicators to set up the management plan: a case study on a former mining site

Benjamin Pauget¹; Annette de Vaufleury²

¹ TESORA; ² University of Bourgogne Franche-Comté, FR

Past industrial activities have contaminated the environment with trace metals (TMs) and we have now to evaluate and to limit the impact of this pollution. Biological methods using bioindicators of accumulation to assess in situ the fate of TM are scarce. On the former mine of Saint Laurent le Minier (30, France) soils are highly contaminated by arsenic, cadmium, lead and zinc (mainly). To evaluate current exposure of soil organisms to metal pollution, two biological indices have been developed based on the determination of the Sum of the Excess of Transfer of metals to the plants (Phytomet) and (SET indice) to the common land snail *Cantareus aspersus* (<https://ecobiosoil.univ-rennes1.fr/ADEME-Bioindicateur/english/worksheet.php>). The aim was to rank the management priorities of the 8 plots of the site based no longer on the total TMs concentrations in soil but on the metal bioavailability (i.e. on the excess of transfer) of 14 TM to plants and to land snails caged for 28 days on site. Results showed abnormal transfer on all plots except on the control one. For plants, an excess of Pb and Cd transfer were evidenced on all plots. For snails, the highest transfers were found for Cd, Pb, Tl and Zn. For the first time, extremely high internal concentrations of thallium were evidenced (up to 2639 mg.kg⁻¹, 3595 higher than the TI-CIRef value) in the snail viscera. SETplots were from 57 to 3876 and the SETsite was 924 based on the analysis of 14 TMs. Previous studies using the SET indice only reached SETsite of 7.7, showing the very high bioavailability of TM on the studied site. The use of these indices allows ranking the plots according to the biological assessment of bioavailability of TMs; the biological ranking does not match with the chemical ranking based on total concentration of TM in soils. For example, the soil of one of the most contaminated plot presents a transfer close to the transfer determined on the less contaminated plots due to a reduce bioavailability. Present results show how bioindicators of accumulation (plants and snails), that integrate in situ the influence of various environmental parameters (soil characteristics, season, plant contamination), can contribute to the assessment of fate of pollutants in the field and also to the development of a management plan adapted to the context of the polluted site.

Microbial respiration of added ^{13}C -labelled sugar in the field – A step towards a non-invasive assessment of ecological functions of polluted sites of high ecological value

Ingrid Rijk¹; Alf Ekblad²

¹ Örebro University / Structor Miljöteknik AB; ² Örebro University, SE

Ecological risk assessment of polluted areas is slowly shifting from a chemical-value based approach to a more holistic view on the performance of critical soil functions and ecosystem services.

Microorganisms have an essential role in soil nutrient cycles, and may be studied to identify whether critical soil functions (e.g. carbon and nitrogen cycles) are impaired. Although most methods to study microbial functioning are laboratory based, field methods are preferred because digging, storage and sieving of soils alters both the mobility of pollutants and soil biology.

To assess whether the microbial activity was disturbed in a Pb-polluted NATURA2000 area, an exploratory field experiment was carried out using a non-invasive technique to study soil microbial C-mineralization in situ. We measured soil respiration rates and isotopic signatures of respired CO_2 one hour and two days after inducing polluted (mean=2300 mg Pb/kg soil) and non-polluted (<50 mg Pb/kg soil) plots with cane sugar (naturally ^{13}C -labelled) and water (control). In this way we could distinguish between respiration of soil endogenous C (root and microbial) and of the added C (microbial). Preliminary results show that total respiration rates are similar in both unpolluted and polluted soils. However, respiration of only the added C (microbial) was significantly impaired by 45% ($p=0,03$) in the polluted plots after one hour, but not after two days. The results suggest that the Pb pollution was affecting the microbial activity (one hour measurement) but not the growth of the microorganisms (two days). Combined with a significant higher C content of the Pb polluted samples ($p=0,002$) it is indicated C mineralization is disturbed leading to accumulation of organic matter.

This approach is a first a step to a more functional ecological risk assessment directly in the field. This method could be especially beneficial to polluted areas with a well-developed ecosystem and a high ecological value (e.g. NATURA2000), where the ecological status of the site is crucial to determine whether remedial actions are needed to be taken.

Heavy metal pollution, fractionation, and potential ecological risks in sediments from Lake Chaohu (Eastern China) and surrounding rivers

Lei Zhang

Nanjing Institute of Geography & Limnology, Chinese Academy of Sciences, CN

Heavy metal (Cr, Ni, Cu, Zn, Cd, and Pb) pollution, fractionations, and ecological risks were studied in the sediments of Lake Chaohu (Eastern China), its eleven inflowing rivers and its only outflowing river. An improved BCR sequential extraction procedure was applied to fractionate heavy metals within sediments, a geoaccumulation index was used to assess the extent of heavy metal pollution, and a risk assessment code was applied to evaluate potential ecological risks. Heavy metals in the Shuangqiao and Nanfei Rivers were generally higher than at the other studied sites. Of the three Lake Chaohu sites, the highest concentrations were identified in western Chaohu. Heavy metal pollution and ecological risks in the lake's only outflowing river were similar to those in the eastern region of the lake, to which the river is connected. Heavy metal concentrations occurred in the following order: Cd > Zn > Cu > Pb ≈ Ni ≈ Cr. Cr, Ni, and Cu made up the largest proportion of the residual fraction, while Cd was the most prominent metal in the exchangeable and carbonate-included fraction. Cd posed the greatest potential ecological risk; the heavy metals generally posed risks in the following order: Cd > Zn > Cu > Ni > Pb > Cr.

Comparative Metagenomic Analysis of Local Metabolic Pathways Hints at Past Natural Attenuation in Groundwater from an Old Gasworks Site

*R. Costeira*²⁻¹, *R. Doherty*³⁻¹, *C. Allen*²⁻¹, *M. Larkin*²⁻¹, *L. Kulakov*²⁻¹

¹Questor Centre ²School of Biological Sciences ³School of Natural and Built Environment, The Queen's University of Belfast, United Kingdom

Physical and chemical environmental clean-up of contamination is expensive, energy-consuming and not always friendly to nature. Self-sustainable and eco-friendly remediation approaches are sought after by the scientific community and bioremediation has proven to be a prime candidate. Bioremediation approaches are based on the use of microbes, particularly bacteria, to clean-up events of contamination. Natural attenuation, the progressive removal of contamination by local microbes, is least invasive and most cost-effective form of bioremediation. To implement efficient and successful bioremediation strategies it is important to thoroughly investigate the local microbial communities at a site, their genomes and the metabolic pathways they encode.

In this study, we analyzed microbial communities present in contaminated (C1) and non-contaminated (NC1) groundwater from an old gasworks site in Northern Ireland. This site has suffered from organic contamination in the past. To conduct the analysis, total microbial DNA was purified and shotgun-sequenced using Illumina HiSeq 4000 Technology. Sequencing of 16S rRNA amplicons was performed using Illumina MiSeq Technology.

Assembly of C1 and NC1 contigs was performed with metaSPAdes yielding 248,567 and 224,811 contigs with a maximum size of 190,287 and 210,857 bp for respective samples. Annotation of features was performed with Prokka, finding 194,459 CDS for C1 and 211,145 CDS for NC1. Using DIAMOND, 44% and 48% protein BLAST hits were found for C1 and NC1 in the RefSeq database. Using MEGAN, we found that a lot of protein BLAST hits for C1 matched with Bacteroidales (20%) while for NC1 the majority matched with Proteobacteria (40%). This differential abundance is supported by 16S rRNA amplicon sequencing data, analyzed with QIIME. GhostKOALA was used for protein annotation against a KEGG GENES database and KEGG Mapper was used to visualizing the metabolic pathways of the samples. We found that the NC1 microbial community has a more diverse metabolic capacity than C1, with 3.2x more the number of enzymes responsible for degrading aromatics, including enzymes that degrade benzene, ethylbenzene, toluene, and methyl-substituted aromatic compounds. This evidence allows us to hypothesize that past clean-up of NC1 groundwater could have been partially due to natural attenuation by local microbial communities.

Ongoing work follows the evolution of the microbial communities at the site over time and we aim to assess the functional relevance of our findings by metatranscriptomic analysis. Furthermore, we will evaluate the relations between bacterial and viral communities at the site. In particular, we are interested in investigating the impact of phages on bioremediation and the usefulness of them as biomarkers.

2c. Risk assessment of emerging pollutants and multi-compounds

Pollutant fluxes in small catchments: Impact of urbanization, flow dynamics, and pollutant degradation

Gaëlle Guillet¹; Marc Schwientek¹; Bertram Kuch²; Hermann Rügner¹; Peter Grathwohl¹

¹ University of Tübingen; ² University of Stuttgart, DE

Emerging pollutants as pharmaceuticals, personal care products, urban pesticides, and other wastewater-related compounds are constantly introduced into aquatic systems by wastewater treatment plants (WWTPs). Hydrophobic and thus mainly particle-related chemicals such as PAHs or PCBs are typically released more episodically during intense precipitation events and the resulting combined sewer overflows. In this study emerging and particle related pollutant fluxes are assessed for the Steinlach and Ammer rivers as well as for the Goldersbach river (a nature reserve), all three being tributaries of the River Neckar in SW-Germany. For emerging pollutants (e.g. carbamazepine, HHCB-Lactone) which are mostly transported as dissolved species annual loads have been estimated based on various sampling campaigns including monthly and high-resolution sampling during base flow and flood conditions. By use of Lagrangian type sampling along river segments, also the degradability of these pollutants could be assessed. For persistent hydrophobic pollutants (PAHs) water samples were collected during flood events and concentrations on suspended solids were calculated based on a correlation of total concentrations of pollutants versus turbidity and/or total suspended solids. Such correlation coupled with continuous monitoring of discharge and turbidity enabled the calculation of particle-bound pollutant loads. Generally, annual loads are related with the number of inhabitants in the catchment. In the Ammer and Steinlach catchments (each having approx. 50.000 inhabitants) fluxes for PAHs, carbamazepine and HHCB-Lactone sum up to several kg per year. Accordingly, pollutant fluxes in the uninhabited Goldersbach catchment are negligible. The results also show that particle-bound pollutant fluxes are positively correlated with particle flux and thus require a detailed monitoring or assessment of sediment transport. Concentrations of wastewater-associated pollutants are typically diluted during flood events, indicating a source limitation. As a practical consequence, annual loads of compounds such as carbamazepine may be estimated based on only few samples during base-flow conditions. The estimation of loads is complicated for degradable chemicals as shown for HHCB-lactone where fluxes are dependent on the WWTP performance – which may be variable over time – and the distance from the WWTP outfall. Thus an assessment of persistence and conditions which govern degradability might be required. However, it may be argued that in particular the group of persistent compounds is of environmental concern.

Fate and Transport Modelling of PFOS in a Fractured Chalk Aquifer Towards a Large Scale Drinking Water Abstraction

Erika Houtz; Ian Ross; Jake Hurst; Jonathan Miles; Jeff Burdick

Arcadis, GB

In December 2005 the largest explosion in Western Europe since World War Two occurred at the Buncefield Oil Storage Terminal in the UK. In controlling the resulting fires approximately 250,000 litres of firefighting foam containing PFOS were deployed, a proportion of which directly impacted the underlying chalk Principal Aquifer which lies within a protected drinking water abstraction zone. Investigations identified PFOS to be present in groundwater beneath the site resting at approximately 35m below ground level, source concentrations of PFOS ranged from between 20 to 50µg/l well above the 0.3 µg/l guidance values in the UK.

Many questions remain regarding the fate, transport, attenuation, and remediation of PFOS, which is classed as a persistent organic pollutant (POP). Recent advancements in the science of environmental toxicology of PFAS have drawn attention to these chemicals and the need for a better understanding of their behaviour in the environment.

We evaluated the transport of PFOS in fractured bedrock groundwater towards the drinking water abstraction. In this case, PFOS was discharged concurrently with the fuels and provided an opportunity to characterize the transport of both PFOS and hydrocarbons including benzene, toluene, ethylbenzene, xylenes (collectively, BTEX), and the fuel oxygenate methyl tertiary butyl ether (MTBE). The transport properties of BTEX and MTBE are well known. Therefore, comparing the transport of these hydrocarbons with transport of PFOS at this well-characterized site after a known discharge event has afforded a unique opportunity to gain insight into the transport of PFOS in the environment.

Site investigation activities included the completion of soil boring and bedrock boreholes, downhole geophysical investigations and the installation and sampling of groundwater monitoring wells for concentrations of PFOS, BTEX, and MTBE. Routine sampling of monitoring wells has ensued on a near-monthly basis for a period of up to five to seven years, thereby providing a detailed record of environmental monitoring. Contaminant modelling has also been undertaken during the quantitative risk assessment process along with remediation activities including groundwater pumping and capping of 12,000m³ of shallow soils impacted with PFOS both designed to remedy the potential impacts of the original incident.

The project has resulted in significant insights being gained regarding transport of PFOS in fractured rock at the site, including characterization of background PFOS concentrations and attenuation mechanisms such as retardation and dual-porosity mass transfer characteristics. Giving the significant increase in recognition of the number of potential PFAS source zones globally and the significant number of drinking water supplies at risk these insights will be of interest to a wide audience.

„Dealing with the End of Armageddon“: ammunition burning-grounds of the interwar-period as a source of soil contamination

Daniel Hube

BRGM, FR

The damage caused by warfare on physical landscape is one anthropogenic impact upon the environment. Very few research has been done how the use and destroying of explosives and chemical warfare agents have modified the properties of the soils of the World War 1 frontline in Belgium and France. One century ago, by the time of siege war (1915-1917), explosives ammunition were being deployed at an unprecedented scale following the mandate which stated that "Artillery conquers, Infantry occupies". The former frontline, is among the most heavily shelled area in the world. Over 1 thousand million projectiles have been fired on the western front, and 25% of them didn't experienced detonation. Researchs conducted by BRGM prove that at the Armistice, more than 1 100 000 tons of ammunition left as surpluses or been salvaged on the former battlefields had for the first time in Human History be massively and quickly destroyed, first by the armies then by private compagnies. They operated using innovative methods to avoid accidents and to optimize the efficiency of the recovery of the valuable material forming the projectiles. Ammunition of the participating armies have been destroyed by open-detonation (OD) or open-burning (OB) causing locally zoogeomorphic disturbance upon the landscape and severe contaminations of the top soils by metals and metalloids, high explosives (HE), chemical warfare agents, transformation and pyrolysis by-products. 5 ammunition burning-grounds (ABG), discovered through historical researchs, following those of T bausinger (2007, 2008), have been studying during 2014 – 2016, with soil, crop sampling, detailed and specific analysis, local LIDAR overflying, deep soil assessment. Photos from private archives have been collected too, providing an overview how OB had been operated there. The results show local severe contamination with chemical fingerprints in relation to the specialization of the ABGs. High grades of Zn (> 100 g/kg), Cd, Hg are measured where fuzes had been burned. Inorganic As over 10 g/Kg occured where emetic arsenicals agents had been burned, associated with high grades of PCDD & PCDF (> 10 µg/kg), other pyrolysis by-products (As-PACs), and traces of high explosives. Lead, leachable bromid, Br-aromatic compounds fingerprint the destruction of lachrymatory agents. Moreover, there is some evidence that yperit („mustard gas“) shells had been broken-down too, regarding typical ammunition parts discovered and the occurrence of chlorobenzene (solvent) and thiane compounds in soils (impurities giving the typical smell of garlic of this agent). 90 years after, contaminations remain, hindering in many places the growth of crops and vegetables. Near Verdun, in 2015, cereal crops, milk and meat have been destroyed, to prevent exposure of population due to potential bioconcentration of arsenicals present in soils and the uncertainties concerning their toxicology. Many OB sites do exist but weren't studied yet, what raised the question of risk for groundwater, human health and the environment.

Comparison of column and batch tests for assessing leachability of PFC from soils

Ute Kalbe¹; C. Piechotta²; R. Rothe²

¹ Bundesanstalt für Materialforschung und -prüfung (BAM); ² BAM Federal Institute for Materials Research and Testing, DE

Leaching tests are fundamental tools for the assessment of groundwater impact by contaminated soils concerning the soil-groundwater pathway. Such procedures are supposed to serve as the basis for a reliable leachate prognosis. They can be applied to determine the short and long term leaching behaviour as well as the source term of contaminated soils. For this purpose two types of leaching procedures have been validated in Germany for the examination of the leaching behaviour of frequently occurring organic substances (DIN 19528 - column test and DIN 19529 - batch test). A liquid-to-solid ratio (L/S) of 2 L/kg and 10 L/kg is the basis for the risk assessment which is implemented in different German regulations. The equivalence of test results for both tests for the same material under investigation has been investigated for a variety of pollutants in order to assess their reliability in compliance testing. However, for emerging pollutants there is hardly data available on this issue.

Leaching tests on soils contaminated with emerging pollutants such as PFC (Perfluorinated Surfactants) are currently coming more into consideration due to the increasing detection of contaminated sites.

Therefore, two soils were investigated in this study from different contamination source (paper sludge containing compost and fire distinguishing foam) using both leaching tests and both liquid-to-solid ratios. The leachability of the various perfluorinated compounds in relation to their content in solid matter was considered. Furthermore the eluate pre-treatment prior analysis (in particular liquid/solid separation step needed for batch tests) has been taken into account.

The comparability of the results from batch and column is dependent on the solubility of the various compounds, on the L/S and on the turbidity in the eluates.

Understanding Fate and Transport of PFAS to Develop Effective Conceptual Site Models

Jonathan Miles¹; Ian Ross¹; Erika Houtz²; Jeff Burdick²; Jeff McDonough²; Jake Hurst¹

¹ Arcadis UK; ² Arcadis US, GB

Poly- and Perfluoroalkyl substances (PFAS) are used in a wide range of industrial applications and commercial products due to their properties. PFAS are also major components of firefighting foams such as Aqueous Film Forming Foam (AFFF). The PFAS group of compounds consists of both perfluorinated compounds or perfluoroalkyl acids (PFAAs), where all carbons are saturated with F atoms, and polyfluorinated compounds, where both fluorine saturated carbons and carbons with hydrogen bonds are present. Polyfluorinated "precursor" compounds biotransform to produce PFAAs as dead end extremely persistent daughter products. The understanding of the fate and transport of these compounds in the environment is complex and challenging and will be discussed. The concepts of in situ generation of PFAAs via precursor biotransformation will be used to explain how significant PFAS mass remains hidden in source areas.

PFAA precursors are so named because they transform slowly over time through abiotic and biological processes to the PFAAs. There is a natural "biological funneling" in which a whole host of PFAA precursor compounds containing a range of perfluorinated alkyl chain lengths and functional groups, aerobically biotransform to persistent PFAA products.

Fire-fighting foam formulations and many fluorochemicals used across multiple industries are composed of many PFAS that are PFAA precursors. Unlike the PFAAs, these species are not strictly anionic, as some contain multiple charges (zwitterionic) or are positively charged (cationic). Zwitterionic and cationic PFAA precursors are currently undetected by conventional analytical tools and are thus termed "Dark Matter". A significant mass of PFAA precursors in addition to the PFAAs have been detected in both fire-fighting foam-impacted soil and groundwater. A conceptual site model describing PFAS fate and transport at a firefighter training area is hypothesized and will be presented, as described below.

Cationic and zwitterionic precursors will be retained in the soils at the source zone via strongly binding ion exchange processes. The source zones will be anaerobic as a result of the presence of residual hydrocarbons used in firefighter training, so these strongly sorbing cationic precursors will biotransform very slowly to simpler, anionic PFAA precursors and PFAAs under these redox conditions. Anionic PFAAs and PFAA precursors will migrate away from the source as they enter the redox recharge zone where conditions become increasingly aerobic thus promoting in situ generation of detectable PFAAs from the hidden anionic PFAA precursors. PFAAs will not break down further, and will continue to migrate as a plume with shorter chain PFAAs generally migrating further.

The concepts of "biological funneling" and "dark matter" show that PFAS behave significantly differently to other contaminants and existing conceptual site models (CSM) need to be adapted to adequately understand the fate and transport of these contaminants. Examples of CSMs from AFFF impacted sites will be presented. The common breakdown products from PFAS in other sources, such as landfills and waste water treatment plants will be described.

New Concawe/ NICOLE technical report on the environmental fate and effects of PFAS, remedial options and legislative developments

Tessa Pancras¹; Hans Slenders¹; Birgitta Beuthe²; Jonathon Smith²; Mike Spence²; Tomás Albergaria³

¹ Arcadis Netherlands; ² Concawe; ³ NICOLE, NL

A recent report commissioned by the European Petroleum Refiners research division (Concawe) and the Network for Industrially Contaminated Land in Europe (NICOLE) brings together published data on the environmental fate and effects of poly- and perfluoroalkyl substances (PFAS), of which perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are the most well-known.

The unique surface tension lowering properties of PFAS have led to their use in a wide range of domestic and commercial products including high-performance class B fire-fighting foams, which are used to prevent and contain flammable liquid fires at industrial sites and airports. Emissions of PFASs may therefore arise from landfills, urban wastewater treatment facilities and fire-fighting facilities at airports, military bases and large industrial facilities.

PFOS and PFOA have been identified as PBT (persistent, bio-accumulative and toxic) for humans and wildlife, which has led to low regulatory limits for these compounds. Moreover, as knowledge of the class of PFAS substances increases, restrictions are being extended to other PFAS compounds that have the potential to degrade to form PFOS, PFOA or other long-chain PFAS. Current remedial options for PFAS in soil and groundwater, including excavation and treatment with activated carbon, are resource intensive and so research is needed to develop more cost-effective, sustainable, solutions.

In addition to PFAS environmental fate and effects, the report provides a concise overview of global regulatory controls, chemical analysis methods and remedial techniques to support effective, risk-based, decision-making. While the report has been produced to support the work of Concawe and NICOLE members, it is anticipated that the document will be a useful source of information to others working in this area.

1,4-dioxane and 1,3-dioxolane: presence and mobility of contaminants of emerging concern on 1,1,1-trichloroethane polluted sites in Flanders

Roeland Van Muylder¹; Martijn van Houten²; Samuel Van Herreweghe³; Griet Van Gestel⁴; Nele Bal⁴

¹ Witteveen+Bos Belgium NV; ² Witteveen+Bos; ³ EnISSA; ⁴ OVAM - Public Waste Agency of Flanders, BE

Chlorinated solvents have played an important role in the degreasing process of manufactured metal products. To improve the stability of these solvents, stabilizers were added to prevent corrosion on metal surfaces. 1,4-dioxane and 1,3-dioxolane have been widely used as stabilizers of 1,1,1-trichloroethane (methyl chloroform) in quantities up to 6%. For that reason, 1,4-dioxane and 1,3-dioxolane are expected co-pollutants at 1,1,1-TCA contaminated sites.

The physical and chemical properties and behaviour of 1,4-dioxane in the environment create challenges for its characterization and treatment. 1,4-dioxane is highly mobile and has not been shown to readily biodegrade in the environment. 1,4-dioxane is also toxic to humans.

Since soil and groundwater investigation in Flanders has focused on the key pollutants such as petroleum hydrocarbons and chlorinated solvents, little is known about the presence and potential risk of additives to groundwater systems. Therefore, OVAM, the Public Waste Agency of Flanders, commissioned a study on solvent stabilizers to Witteveen+Bos Belgium to gain a better understanding on these co-contaminants in Flanders.

In this study 16 1,1,1-TCA polluted sites were selected throughout Flanders based on criteria such as degree of 1,1,1-TCA groundwater contamination, industrial activity, stage of remedial actions, presence of groundwater wells. On each monitoring site a number of 4 to 5 groundwater wells in the source and plume zone of the 1,1,1-TCA contamination were randomly sampled for laboratory investigation on chlorinated solvents, 1,4-dioxane and 1,3-dioxolane. A total of 72 samples and laboratory results were collected with HS GC-MS and EPA method 522 for 1,4-dioxane determination.

The results showed that at 13 monitoring sites the groundwater concentration of 1,4-dioxane was exceeding the guideline value of 50 µg/l with a maximum concentration of 26.000 µg/l in the source zone. At 6 sites 1,3-dioxolane has been detected above the detection limit of 10 µg/l. Also 1,1-dichloroethylene and monochloroethane were measured in significant concentrations exceeding the guideline values.

The ratio's of 1,4-dioxane to chlorinated ethanes observed in the groundwater were significantly higher than the ratio's in the stabilized solvent. This can be explained by differences in solubility, sorption and biodegradability of stabilizers and chlorinated solvents in the groundwater system. It is also very likely that 1,4-dioxane forms larger contamination plumes compared to chlorinated solvents. Furthermore, the plume of 1,4-dioxane was detected in the shallow groundwater while chlorinated solvents have the properties to form DNAPL's. Further investigation will be done in this study to get a better understanding of the general conceptual model of plume behaviour of the solvent stabilizers in relation to its mother solvent.

Based on these results, we can estimate that approximately 200 1,1,1-TCA sites in Flanders are potentially contaminated with 1,4-dioxane. In addition, the specific plume behaviour and properties of the solvent stabilizers are imperative when assessing potential risks and designing remedial actions.

Topic 3. Advances in remediation technologies

3a. Bioremediation

Experimental investigation of temperature effect on poly-hydroxybutyrate (PHB) fermentation rate to control electron donor production over time and enhance biological reductive dechlorination of chlorinated aliphatic compounds

Firoozeh Arjmand¹; Martina Buglioni; Lucia Pierro; Bruna Matturro²; Simona Rossetti²; Marco Petrangeli Papini³

¹ Sapienza University of Rome; ² IRSA-CNR; ³ University of Rome "La Sapienza", IT

Highly chlorinated hydrocarbons such as PCE and TCE can be anaerobically transformed to less chlorinated or non-chlorinated compounds through a process known as reductive dichlorination (RD). RD involves the sequential replacement of chlorine with hydrogen and in the case of PCE, transformation occurs via TCE, cis-dichloroethene (cDCE), vinyl chloride (VC) until ethene (ETH). Each dechlorination step requires two electrons, so an electron donor must be provided to sustain this metabolism. Usually, the lack of a suitable electron donor is the limiting factor in the natural attenuation processes and injection of different substrates (source of electron donors) is required in order to enhance the RD. By this regards several commercial products are available in the market, from molasses to easily biodegradable organic substrates, with different release kinetic characteristics.

Often, the major drawback in the use of these products is the need for their delivery in the groundwater in different campaigns for a lengthy period. Long periods are usually required to achieve the remediation goals using this approach. In some situations, discrete injection of electron donors could be advantageously substituted by different approach such as up gradient permeable "active" barrier filled with solid slow releasing electron donor source or continuous production and delivery of electron donors via combination with groundwater Circulation Wells. Previous studies of our research group (Aulenta et al., 2008; Baric et al., 2012 & 2014; Petrangeli papini et al., 2016) have shown that PHB (poly-hydroxybutyrate) could be an effective source of carbon and electron donor by its fermentation products (i.e. acetate and H₂) to enhance the biological reductive dichlorination in both lab and field scale.

The aim of this study was to investigate some of the parameters (for i.e. temperature and flow rate) affecting the fermentation rate of PHB. Experiments were carried out in two identical columns filled with same amount of PHB and sand, and fed by tap water for 6 months. Columns were kept in the same controlled temperature (27°C) during a first phase whereas in the second phase the temperature of one of the two columns was increased to 35 °C. Influent and effluent samples (from IN and OUT valves) were collected on a daily base and several column profiles have been acquired for each column. Microbiological characterization performed at the end of the experimental investigation allow to characterize the quality and quantity of microorganism population in the two different columns. The experimental results have clearly shown the possibility to use the temperature as an operating parameter to easily control the fermentation rate and consequently the production rate of electron donors.

Biotreatment for in-situ dredging of sediments from the Golfe Juan marina: results of microcosms experiments

Fabienne Battaglia-Brunet¹; Catherine Joulian¹; Jean Philippe Dos Santos²; Nicolas Marmier³

¹ BRGM; ² HTS BIO; ³ Université de Nice Sophia Antipolis, FR

Inoculation of selected bacterial strains in aquatic sediment in order to decrease their volume and organic matter content has been proposed as an alternative to classical dredging. Whereas increasingly applied, this type of in-situ biotreatment was not entirely studied in terms of environmental impacts, such as influence on biodiversity and possible mobilization of pollutants from the solids to the water phase. In parallel to an experimental in-situ operation for the treatment of sediments from the Golfe Juan marina, microcosm experiments were performed at laboratory scale in order to monitor the evolution of bacterial biodiversity in the sediment and pollutants concentration in the water phase after addition of a commercial inoculum to the sediment. Experiments in flasks showed that the rate of mineralization of the organic carbon, initially present in the sediment, increases with the quantity of added inoculum, and that the effect of added bacteria on the CO₂ production is still significant after 80 days for the highest inoculum dose. The inoculum seemed to stimulate metabolisms involving both oxygen and ferric iron as electron acceptors. Column experiments showed a limited increase (maximum 20%) of As, Cu and Zn concentrations in the water column after the addition of inoculum. The concentrations decreased down to the initial value 60 days after inoculation. The structure of the sediment bacterial community showed only slight changes, suggesting that the inoculated bacteria did not become major microbial components of the sediment microflora.

This study was supported by the Alpes-Maritimes Department, the CCI Nice Côte d'Azur, and the technical support of the French government services.

Engineered Retardation Factor Manipulation using PlumeStop® Liquid Activated Carbon for Passive Management of Plume Dynamics

Jeremy Birnstingl¹; Kristen Thoreson²; Craig Sandifur²

¹ REGENESIS Remediation Solutions, Europe; ² REGENESIS, USA, IE

Monitored Natural Attenuation (MNA) represents a valuable tool in the remediation toolkit, but it takes time. Whereas this may be no more than an inconvenience on some sites it may prove a critical issue on other sites. Examples would be where short advection distances and/or rapid groundwater flow result in insufficient time for plumes to attenuate to acceptable levels before a boundary, receptor or other compliance point is reached.

Such cases preclude MNA, requiring some form of active intervention instead. This may be through increasing the biological attenuation rate using Enhanced Natural Attenuation (ENA), reducing the source and / or plume concentrations using physical treatment or in situ chemical oxidation (ISCO), actively managing the advection through groundwater pumping, or any combination of these or other approaches. Each approach typically presents increased costs and/or disturbance over MNA.

A hitherto unexplored alternative that may be used alone or integrated with the above approaches is to 'splice in' additional attenuation time into shorter distances by engineering the retardation factor of the matrix. This slows the contaminant advection relative to the groundwater velocity. In so doing, this increases the residence time available for (principally biological) attenuation within a given compartment, enabling natural attenuation to proceed to target over a far shorter advection distance. In this manner, attenuating plumes may be kept within site boundaries, prevented from reaching receptors or simply prevented from expanding while natural attenuation proceeds.

The use of PlumeStop® Liquid Activated Carbon® represents a new means of securing this end. The technology provides a flow-emplacable means of coating the subsurface flux channels with micron-scale activated carbon. 'Dialing-in' the required retardation factor may consequently be achieved through a one-time, injectable intervention – essentially engineering the 'effective foc' of targeted flow-channels. Principles of use of the approach together with corroborating placement and performance validation methodologies are presented in this talk, supported by data from lab and field.

Retardation factor increases ranging from several hundred percent to multiple orders of magnitude may be readily secured using the approach. The extent of this increase is determined by the interplay of contaminant concentration relative to carbon emplacement, the nature of the contaminants themselves, and the specific / dynamic mix of contaminants and / or competing sorbate species as degradation proceeds.

The predictive integration of the approach into a wide range of contaminant fate and transport models to aid in concept evaluation, performance-prediction and engineering design is discussed.

Effect of Pyoverdine-producing bacteria on lead speciation in non-point source contaminated soils

*Dorine Bouquet*¹; *Alexandra Lépinay*²; *Pierre Gaudin*³; *Cécile Le Guern*⁴; *Liliane Jean-Soro*⁵; *Thierry Lebeau*²

¹ LPG-Nantes; ² Université de Nantes; ³ Université de Nantes; ⁴ BRGM Nantes; ⁵ IFSTTAR, FR

Phytoextraction has been studied for decades, and up to now has not been applied widely because of the extended period of time required for soil cleaning-up. To improve its efficiency, phytoextraction could be associated with soil bioaugmentation, in particular with siderophores producing bacteria (SPB). Siderophores are iron complexing agents able to complex others metals including lead (Pb). This study aims at evaluating the potential effect of pyoverdine (Pvd), a siderophore produced by *Pseudomonas fluorescens*, on Pb mobility and on phytoextraction efficiency in the example of a non-point source contaminated soils (geogenic vs. anthropic Pb).

Brassica juncea is cultivated on three different soils: the first one contains geogenic Pb (soil E) and the two other soils were contaminated by anthropic activities (soils O and M). Soils E and O – same loamy-sandy texture and same total Pb concentration – were sampled from urban allotment gardens in Nantes (France). The soil M is a sandy-clay agricultural soil closed to Metaleurop, a former smelter located near Lille (France).

Purified Pvd or bioaugmentation-assisted *B. juncea* were tested. Pvd-producing bacteria were previously selected based on biochemical tests. The content of Pb in shoots and roots of *B. juncea* is measured as well as the Pb speciation in soil by using chemical and physical methods: selective extractions with CaCl_2 and DTPA, sequential extractions, XRD analysis on the most concentrated fractions, Raman analysis, etc.

Work is in progress. Expected results are clay weathering and an impact of Pvd on others Pb bearing phases, as already shown by Hazotte et al. (2016) and the increase of phytoavailable Pb and eventually higher phytoextraction rate.

Optimization of phenol extraction from Olive Mill Wastewater (OMW) and their utilization in microalgae cultivation

Fabrizio Di Caprio¹; Paolina Scarponi¹; Pietro Altimari¹; Gaetano Iaquaniello²; Luigi Toro¹; Francesca Pagnanelli¹

¹ Sapienza University of Rome; ² Biop, IT

Olive mill wastewater (OMW) is the main waste produced in industrial plants of olive oil production. Annual worldwide production is estimated between 7 and 30 million m³, localized mainly in the Mediterranean basin. Due to its high content of COD, phenols, phosphorous, nitrogen and other compounds, its management still represents a serious environmental issue. Phenols, in particular, have antimicrobial and phytotoxic effects which also limit their treatment in conventional biological processes. Microalgae have proven to be able to degrade phenols and to grow in presence of them in OMW. This work is part of a larger project in which the aim is the optimization of a process for microalgae cultivation with wastewaters. In this project phenols from OMW are used to limit selectively contamination of bacteria and fungi in reactor used for heterotrophic or mixotrophic cultivation of microalgae. A strain of *Scenedesmus* sp. was tested. Here results for phenols and phosphates extraction from OMW are reported. Different precipitation methods and absorption with resin have been tested. Extracted phenols have been used to optimize microalgae cultivation in order to improve OMW utilization. By alkaline precipitation phosphates and phenols were removed from OMW until to 55 % and 50 % respectively. However this method was not efficient for phenol reutilization, indicating degradation phenomena. On the contrary phosphates were recovered with 75 % of yield. By resin treatment 60 % of the phenols were recovered from OMW, also in repeated cycles. For microalgae cultivation the best results have been obtained by using phenols from resin. Instead direct utilization of OMW led to increase the contamination by other microorganisms, like fungi and bacteria, with reduced microalgal growth. Different physiological states of the inoculum were tested indicating that an inoculum in exponential state of growth is required for *Scenedesmus* sp. to grow in presence of phenols with a reduced contamination. In the tested conditions of cultivation phenol concentration has been reduced during growth until to 60 %.

Exploiting wood rotting fungi as tools to enhance the bioremediation of an artificially polycyclic aromatic hydrocarbons polluted soil.

Natalia Di Clemente¹; Maria T Del Panno¹; Mario Saparrat²

¹ CINDEFI (CONICET - UNLP); ² INFIVE (CONICET - UNLP), AR

Two main groups of fungi belonging to phylum Basidiomycota that attack wood may be distinguished as white (WRF) or brown (BRF) ones. WRF thanks to their extracellular, oxidative enzymes, have ability to degrade lignin as well as cellulose and hemicellulose. BRF degrade cellulose and hemicellulose present in wood after only a partial modification of lignin by a nonenzymatic Fenton-type catalytic system. However, all these wood rotting fungi have several mechanisms to transform and detoxify environmental chemicals. Although they are potential agents in bioremediation strategies for contaminated soils, up to now most of the data available are from axenic cultures, so further work is required to study their capacities in nonsterile soil and taking into account the natural variables and their practice applicability in systems at large-scale or at field.

Initially we analysed the ability of the WRF *Coriolopsis rigida* LPSC 232, *Peniophora albobadia* LPSC 285, *Gelatoporia subvermispora* FBCC 313 and *Grammothele subargentea* LPSC 436 as well as the BRF *Gloeophyllum sepiarium* LPSC 735 to degrade and tolerate phenanthrene (Phe, 30 mg %) when supplemented to agar (0.8 %) basal medium or one supplemented with carboxymethyl-cellulose (CMC) at 1 %. The isolates LPSC 436 and LPSC 735, which tolerated Phe in a 70 % and 50 % respectively compared to control cultures, showed Phe-degrading capacity. However, the isolate LPSC 735 was the one with higher cellulolytic ability, being unaffected by the presence of Phe. In addition, the coinoculation of the fungi LPSC 436 and LPSC 735 showed a synergistic effect on the degradation of PAHs in agar plate.

Then, on a microcosm system containing an artificially contaminated soil with 2500 ppm of Phe and using wheat straw as a fungal carrier and as nutrient sources, the degradative ability of both fungi was analysed, either individually (axenic) and through their coinoculation. An abiotic control was done in parallel using non-inoculated sterile wheat straw.

Also the effect of the autochthonous soil microbial community was evaluated through similar microcosms but using either sterilised or non-sterilised soil.

After 90 days, a significant removal of Phe was detected in sterile soil microcosms inoculated with LPSC 735. The coinoculated soil showed a delay in the degradation activity, becoming effective after 120 days.

Since both fungi were able to decrease Phe levels even in unsterile soil microcosms after 30 days, a synergistic interaction between inoculated fungi and the autochthonous microbiota might be implicated. Although Phe elimination was also delay when the fungi were coinoculated, which was detected after 90 days, the soil microbial community was unable to counter the competition between the inoculated fungi.

Based on these preliminary results and applying the same study system, we are now evaluating the total hydrocarbon content and phytotoxicity of an artificially contaminated soil with a petrochemical sludge (100 ppm PAH) at 5 and 10 % (w/w) after 30, 60 and 90 days of the fungal inoculation as well as different enzymatic activities relation to degradative processes.

It works! Enhanced Reductive Dechlorination on two different geological settings in Denmark

Anne Gammeltoft Hindrichsen; John Ulrik Bastrup

Geo, DK

Geo has performed remediation of contamination with chlorinated solvents on substations in Denmark. The program is funded by DONG Energy and performed by Geo. On two substations Geo has performed enhanced reductive dechlorination (ERD) with organic molasses as donor and bacterial culture (KB1®). The presentation will focus on the full-scale remediation set-up and the results of the following monitoring results. The degradation of the chlorinated solvents will be discussed in relation to redox conditions, bacteria concentration and the availability of NVOC. We will show that it is possible to perform ERD and achieve full degradation of chlorinated solvents and metabolites (including vinyl chloride (VC)) to below the stop criteria, both in sand magazine and in low permeable settings with small sand lenses.

The source areas were in both cases removed by excavation before the groundwater remediation. Pilot tests were conducted before full scale implementations. On the first location, the remediation was carried out in low permeable till and in small sand lenses in the till. The remediation were conducted as passive remediation with direct injections. No recirculation was carried out, due to low permeable conditions. On the second location, the remediation was carried out in a sandy aquifer with recirculation of groundwater. The injections were conducted in injection wells.

Two rounds of injection of substrate has been conducted followed by 6-7 monitoring rounds with 20-25 water samples per. event. The water samples were analyzed for chlorinated solvents, ethylene and ethane, and selected samples were analyzed for bacteria, NVOC and redox parameters.

The results for the low-permeable site showed immediately decrease in the mother compound TCE to below the stop criteria from ~300 µg/l to below 22 µg/l, simultaneously a very steep increase was observed in the concentration of degradation products. As an example, the concentration of sum of DCE increased from about 60 µg/l to 5.000 µg/l. 6 months later the concentration had decreased to 40 µg/l, and at the 2 last monitoring rounds the concentrations of metabolites (DCE and VC) was below the stop criteria on respectively 22 µg/l and 4,4 µg/l.

At the site where ERD was conducted in the sandy aquifer, there was observed an increase in the DCE concentrations, and the concentrations of VC were constant. The analysis of the NVOC content in the ground water showed lack of donor. An additional injection of molasses was done to boost the degradation. After the second injection a decrease in the concentrations of VC was observed, and the concentrations decreased to below the stop criteria.

On both locations investigations for back diffusion has been performed and shows that back diffusion is not occurring. The conclusion is that it is possible to degrade chlorinated solvents and degradation products fully to ethylene and ethane through ERD with molasses, both in sandy sediments, with recirculation of groundwater and in low permeable deposits. The time horizon for the remediations were in both cases 3-4 years from first injection to site closure, which is very satisfactory for a non aggressive in situ remediation.

Removal of Residual TPH from Weathered Clay Soil During Composting in Bioreactor with the Use of Solid Digestate

Anna Gielnik¹; Yoan Pechaud; David Huguenot; Giovanni Esposito; Gilles Guibaud; Eric D. van Hullebusch

¹ Université Paris-Est-Communauté, FR

Background/Objectives.

Detoxification of TPH contaminated sites is especially challenging if the pollutant remained in soil for a long period of time and if the soil is characterised by high amount of fine particles, e.g. clays and/or soil organic matter which are responsible for strong sorption phenomena. Addition of mature organic matter to soil is a sustainable and economical bioremediation strategy. Organic matter provides nutrients to soil microorganisms and improves soil quality. Organic matter is also a resource saving alternative to chemical fertilizers. Reasonable practice of waste management encourages soil application of organic waste and thus reduction of the amount of wastes deposited on landfills and facilitation of carbon cycle. Digestate is a by-product of biogas production which constitutes valuable organic amendment rich in nutrients and characterized by elevated biological stability. However, digestate may contain pathogens, thus a post-treatment is recommended before its land application. In the present study, composting of digestate mixed with TPH contaminated soil and bulking agent has been proposed as an innovative and promising double-benefit technology: a way to increase digestate quality and a soil remediation strategy. The main objective of this study was to develop an appropriate strategy for field scale bioremediation of TPH contaminated soil during composting in biopiles with digestate.

Approach/Activities.

The experiments were performed in specially designed glass bioreactors with active controlled aeration, gas analysing system and temperature monitoring probes. Analysis includes integrated study of TPH and some of its metabolites in soil, leached water and gas phase. An extended ecotoxicological study was performed during the composting process to assess the changes in soil toxicity. Toxicity analysis included molecular markers like soil dehydrogenase activity and bioassays employing organisms from three different trophic levels – bacteria, plants and invertebrates.

Results/Lessons Learned.

Soil respiration provides valuable information about the activity of microorganisms, which are driving force of bioremediation process. In performed experiments, addition of solid digestate to a TPH contaminated soil resulted in moderately enhanced oxygen consumption. It may be caused by additional carbon supply and maintenance of soil conditions (pH, moisture content). Interestingly, combination of digestate with bulking agent had immediately accelerated respiration process which may be caused by the different carbon source present in bulking agent as well by improved soil aeration which facilitates the access to the oxygen by microorganisms. Further results will indicate if the enhanced microbial activity was correlated with TPH depletion and overall decrease of soil toxicity.

Stable Isotope Analysis: A tool to assess contaminant remediation

Sara Herrero-Martín¹; Albert Soler i Gil²; Neus Otero²; Mònica Rosell²; Cristina Domenech²; Manuela Barbieri²

¹ Universidad de Barcelona; ² Universitat de Barcelona, ES

Stable isotope analysis is a useful tool to identify contaminant sources, to assess and quantify their natural degradation processes, and to monitor the success of remediation strategies at contaminated sites. Stable isotope composition of contaminants provides unique information that cannot be given by concentration data alone, which is often insufficient to prove degradation. This is due to the fact that non-destructive abiotic natural processes such as dispersion, sorption or volatilization produce a decrease in concentration, but generally do not cause significant isotope fractionation. In contrast, biotransformations and chemical reactions involve the formation or cleavage of chemical bonds, leading normally to enrichment of heavy isotopes in the remaining substrate because light isotopomers (e.g., ¹²C, ¹H, ³⁵Cl, ¹⁴N, ¹⁶O) typically react faster than heavy isotopomers (e.g., ¹³C, ²H, ³⁷Cl, ¹⁵N, ¹⁸O). Significant changes in isotope ratios over time and space can be used to assess and quantify natural and induced attenuation processes.

Here we present diverse studies (at laboratory and field scales) in which we have applied stable isotope methods for the identification of contaminant sources, and for the assessment and quantification of natural attenuation, induced natural attenuation treatments (in situ biostimulation), and abiotic remediation strategies (such as permeable reactive barriers (PRB) or in situ chemical oxidation (ISCO)).

The contaminants of focus are among the most common contaminants found in groundwater: (i) Nitrate, is mainly linked to the intensive use of synthetic and organic fertilizers as well as to wastewater discharges. (ii) Chlorinated volatile organic compounds, including carbon tetrachloride (CT), chloroform (CF), tetrachloroethylene (PCE), trichloroethylene (TCE), cis-1,2-dichloroethene (c-DCE), have been widely utilized for many years as solvents, cleaners, dry-cleaning and degreasing agents. Environmental pollution caused by these compounds usually results from their industrial manufacturing and use, commonly by their inappropriate handling and storage. (iii) Petroleum hydrocarbons, such as BTEX (benzene, toluene, ethylbenzene and xylenes) and methyl tert-butyl ether (MTBE), usually discharged into the environment by leakages from underground storage tanks or accidental spills.

We use state of the art methods for compound specific isotope analysis (CSIA) of different elements (C, N, Cl, H and O), depending on the target compound. The results of the different studies presented here, provide a robust demonstration of the power of stable isotope analysis as a tool to assess contaminant remediation.

Groundwater Circulation Well (IEG-GCW®): Distribution of Organic Reagent, Analysis of Biostimulation Processes and Innovative PACE3D Modelling

Marina Badia-Fabregat¹; Irene Jubany¹; Francesc Travesa²; Eduard Alesi³; Melanie Esslinger³; Marcel Alesi³; Gert Rehner³; Christoph Gielisch⁴; Aron Kneer⁴; Britta Nestler⁴

¹ Fundacio CTM Centre Tecnologic ES; ² Hidronit Medioambiente, ES; ³ IEG Technologie GmbH; ⁴ Karlsruher Institut für Technologie (KIT), DE

Soil and groundwater pollution by chlorinated aliphatic hydrocarbons (CAHs) is a widespread problem in industrialized areas. The chlorinated compounds perchloroethylene (PCE), trichloroethylene (TCE) and their metabolites cis-1,2-dichloroethylene (cis-DCE), trans-1,2-dichloroethylene (trans-DCE), 1,1-dichloroethylene (1,1-DCE) and vinyl chloride (VC) have been detected at an industrial site near Barcelona (Catalonia, Spain) at concentrations up to 170 mg L⁻¹ (TCE). In the last years, bioremediation of CAHs has gained attention both in research and full-scale remediation. Biodegradation of PCE and TCE usually occurs through the reductive dehalogenation pathways especially performed by bacteria from the genera Dehalococcoides and Dehalogenimonas. In Catalonia, only a low percentage of full-scale bioremediation systems are implemented. Due to site specific conditions more lab scale research and pilot tests at real contaminated sites are needed in order to gain specific knowledge.

The present work is a project called MICROBIOME with the participation of IEG Technologie GmbH, IMP (Germany), Hidronit and CTM (Catalonia) and co-founded by EU FEDER programme. In this project, a novel technology combining biostimulation of indigenous microorganisms with in situ groundwater circulation is being evaluated.

Preliminary microcosm experiments were performed to determine the bioremediation capacity of the soil and to evaluate the most suitable organic amendment for the biostimulation of microorganisms. In particular, different compositions of organic amendment were tested. Results showed that microorganisms at the site are able to degrade PCE, TCE, cis-DCE and 1,1-DCE. Next generation sequencing (NGS) of bacterial 16S rDNA of the original groundwater at the end of the microcosmos experiments will allow a better adjustment of the operational parameters in the pilot plant. Additional isotope analysis and qPCR analysis on bactraps will also be performed.

Virtual models of the different soil cores were generated. With numerical simulations the flow resistance of the anisotropic porous structures will be resolved and extracted. The combined groundwater and forced convection flow is being calculated via numerical simulations methods (PACE3D phasefield approach).

IEG-GCW® is an innovative system that allows a better spreading of the organic amendments for a faster bioremediation in the radius of influence (ROI). GCW technology increase the bioavailability of the pollutants even in soils containing low permeable layers. The pilot plant of the project consists of a GCW, a metering system for organic carbon solution, two Multilevel Sampling Wells (MLSW) and four additional Multilevel-Injection Wells (MIW) for spreading the inoculated groundwater to peripheral areas. Results of the first 6 months of operation of the pilot plant will be presented in the conference.

Fungal stimulation biopiles for remediation of soils contaminated with recalcitrant hydrocarbons

María Cecilia Medaura¹; Germán A. André¹; Evangelina Balada²; María Ruth Clausen³; María Esther Barbeito⁴

¹ Movilidad Sustentable S.A.; ² YPF S.A., CILC, Brandsen s/n; ³ Universidad Nacional de Cuyo; ⁴ 4. Laboratorio de Análisis Químicos e Instrumentales, Facultad de Ingeniería, Universidad Nacional de Cuyo, AR

Under the premise of taking a sustainable decision to remedy a liability of a petroleum refinery of the West-Center of Argentina consisting of 4000 m³ of contaminated soil, in the year 2015 fungal stimulation biopiles was chosen as the treatment technology. Soil pollutants in oil refineries consist of a complex mixture of high molecular weight hydrocarbons, including polycyclic aromatic compounds (HAPs). These compounds are resistant to biodegradation and highly dangerous due to their toxicity, genotoxicity and carcinogenicity. Therefore, restoring and maintaining the life of such impacted sites implies a challenge.

Fungal stimulation biopiles are based on the composting principles with a design and calculation of nutrients oriented to the optimization of the development of fungi populations, organisms that by co-metabolism cleave the complex hydrocarbon molecules facilitating their subsequent degradation by bacterial inhabitants. This technology proved to be efficient in the degradation of heavy hydrocarbons in previous scaling studies under complex and extreme environments. Soils treated under this technology exhibit a change in their structure and in their physical, chemical and microbiological characteristics, which make them suitable for re-use.

Excavations were made at sites determined in previous studies to extract the contaminated soil and 20 treatment units of approximately 200m³ of soil were assembled. Total petroleum hydrocarbons content (TPH) of the soil was between 19,000-81,000 mgTPH· Kg⁻¹, while that of benzoanthracene 20-30 mg BAA· kg⁻¹ and benzopyrene 25-32 mg BAP· kg⁻¹. Each of the biopiles conformed after the addition of the conditioners were daily controlled temperature, humidity and pH and monthly hydrocarbons and their fractions content. The process was developed during the fall and winter.

The biological activity was notoriously intense and uniform in all biopiles, which was evidenced by a remarkable rise in temperature up to 45 ° C and the visual manifestation of different sequences of fungal populations during the first 90 days of the process.

At an average time of 140 days for all biopiles, HTP were intensively removed at levels below 10,000 mgTPH· Kg⁻¹ and aliphatic hydrocarbon fractions showed a slight shift toward those with higher molecular weight. PAHs were degraded almost entirely, while benzoanthracene and benzopyrene declined to undetectable values. All hydrocarbons reached levels well below those required by local regulations for a soil of industrial use.

The improvement of soil quality and the recovery of its fertility achieved with the treatment was evidenced by the natural revegetation of the biopiles with autochthonous vegetal species, which in a period of four months covered most of the surface and persisted in time.

Fungal stimulation biopiles proved to be an efficient and low-cost technology for field-scale remediation treatment of soils contaminated with recalcitrant hydrocarbon fractions

Application of Biostimulation and Bioaugmentation to Promote In Situ Biodegradation of Chlorinated Ethenes in Complex Hydrogeology

Mark Mejac; Laurie LaPat-Polasko; Carol Aziz

Ramboll Environ, US

Introduction: The purpose of the in situ bioremediation system was to promote biodegradation of chlorinated ethenes in groundwater via biostimulation in combination with bioaugmentation. The groundwater contains elevated concentrations of the following chlorinated volatile organic compounds (cVOCs): tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), and 1,1-dichloroethene. Elevated levels of 1,4-dioxane have also been observed in some areas of the site. A preliminary natural attenuation evaluation indicated that reductive dechlorination was occurring in several of the on-site monitoring wells. An in situ microcosm evaluation using Bio-Traps demonstrated that the combination of biostimulation and bioaugmentation showed the highest level of conversion of chlorinated ethenes to the final end product, ethene. The site is located in a groundwater discharge zone where groundwater moves not only laterally along fractures and bedding planes but also upward from depth.

Approach: A pair of recirculation wells was installed to inject the carbon sources and microbial consortium into the groundwater. The injection program was conducted in two steps: 1. biostimulation with EOS QR, a quick release carbon substrate to promote rapid microbial growth and an emulsified oil substrate (EOS 100) to sustain the microbial population for several years and support reductive dechlorination, and 2. Bioaugmentation with Dehalococcoides microbial consortium (BAC-9) to promote complete reductive dechlorination of the chlorinated ethenes. Once the oxidation reduction potential (ORP) was maintained at less than -150 millivolts (mV), 20 liters of the Dehalococcoides consortium (BAC-9) was injected into the groundwater and recirculated using the paired wells. The groundwater was monitored over time for various parameters to evaluate the effectiveness of the amendments.

Results: Within a few weeks after injecting the carbon substrates, there was an increase in conductivity in downgradient wells. The carbon substrate impacted wells further downgradient than was anticipated based on current knowledge of the hydrogeologic conditions. Within two months after the EOS QR and EOS 100 injection, there was a significant decline in the DO levels to less than 0.5 mg/L and likewise, there was a corresponding decrease in the ORP levels to less than -150 mV. The Dehalococcoides population and corresponding key enzymes (e.g. tceA reductase, vcrA reductase) markedly increased in downgradient wells after the bioaugmentation event. The geochemistry indicated that competing electron acceptors, oxygen, nitrate and iron were considerably reduced in the groundwater and conditions were appropriate for reductive dechlorination, which was demonstrated by the major decreases in PCE, TCE and cis-1,2-DCE concentrations in downgradient wells. Likewise, ethene levels are increasing in downgradient wells. This presentation will discuss how the injection approach impacted distribution of the various amendments in the complex hydrogeology and impacted biodegradation of cVOCs.

Biological remediation of PCE in clay at a former dry cleaning site in Värnamo, Sweden

Helena Nord

RGS 90, SE

A former dry cleaning site in Värnamo, Sweden is contaminated with chlorinated solvents (PCE). The source area comprises approx. 1200 m² and up to 100 000 µg/l of PCE in groundwater and 2 000 mg/kg PCE in soil has been found on the site. The groundwater plume has spread down to 40 mbgl and over 400 meters to the municipality drinking water facility. The site presents many challenges as it is located above a loop in the river Lagan, and the source zone is situated right next to a steep instable slope separating the former dry cleaner site and the Lagan river. The geology consists of sand and silt 0-8 mbgl, clay 8-12 mbgl and graven 12-35 mbgl with groundwater approximately on 9 mbgl. Target levels for groundwater are: PCE 80 µg/l, TCE 80 µg/l, DCE 800 µg/l and VC 8 µg/l.

As a first step of the remediation, installation of a MPE (multi phase extraction) system was carried out 0-8 mbgl. A total of 25 MPE wells were installed across the source zone area. Additionally, 15 air intake wells were installed to allow air to pass through the soil as the vacuum is applied to MPE wells. Five control stations were also installed. After 32 months of MPE, 860 kg of PCE had been removed.

For the treatment of the saturated zone in the clay, 8-12 mbgl, enhanced reductive dechlorination was performed using direct push injections of HRC from Regensis, a safe-to-use product specifically designed for this form of treatment. Upon contact with groundwater, the poly-lactate ester material of HRC becomes hydrated and subject to microbial breakdown releasing hydrogen for periods of up to 18-24 months on a single application. This hydrogen release lowers the redox and enables the indigenous microorganisms to perform the natural occurring process of enhanced reductive dechlorination.

The treatment was tailored for this site in three different areas with different doses. Furthermore, the very steep and geotechnical unstable slope towards the river Lagan made it impossible to inject with a conventional drilling rig in parts of the treatment area. The injection works went as planned and the requisite doses of substrate were placed in the designated locations. As for injection time and volumes, the directional drill offered a very effective alternative to vertical direct push injection. Injections were carried out "top down", and to prevent the creation of contaminant migration paths, bentonite was injected on the way up.

Since the after the injections of HRC, the means levels of PCE has risen from app 10,000 µg/l to 12,000 µg/l due to the release of soil-bound PCE. Thereafter, the PCE content has declined and 22 months after injections, the levels were app 2,000 µg/l. The biological degradation has shown a significant increase in all daughter products, as well as ethane and ethane. The levels of TCE have also declined and the levels of DCE are expecting to decline in the next measurements.

To further display the status of the remediation the degree of dechlorination is a measure of to what degree/percentage the PCE concentrations have been fully degraded to the harmless substance ethene. Calculations show that the dechlorination now has risen from 2 % before treatment to 48%.

Application of chemostat systems for adaptation of microbial communities to emerging pollutants

Baptiste. A.J Poursat¹; Martin Braster²; Rick Helmus¹; Rob J.M Van Spanning²; W. Pim de Voogt¹; Wilfred F.M. Röling²; John. R Parsons¹

¹ University of Amsterdam; ² VU University Amsterdam, NL

Persistency of organic pollutant in aquatic and soil ecosystems is strongly connected to the biodegradation capacity of native microbial community. Microbial degradation is one of the major processes that affect chemical persistency. However, not all microbial communities have the capacity to efficiently degrade emerging chemicals. Several investigations have shown the adaptation capacity of microbial communities to new chemical. In their natural environment microorganisms tend to adapt to pollutants upon long term exposure, allowing for the development of efficient and fast degradation over time. This adaptation capacity of microorganism could be used to develop adapted inoculum in an objective of bioremediation in order to degrade emerging pollutants that were initially persistent.

The aim of our project is to study microbial adaptation to persistent chemicals using long term exposure in various culturing systems. This in turn might lead to a faster rate of degradation of chemicals that were initially persistent. Our approach is to expose microbial communities from activated sludge, growing in chemostat and batch culturing systems, to different chemicals for a long term and under defined conditions. Three molecules are used in this project; 4-chloroaniline, N-Methylpiperazine and Metformin. These products are considered as emerging pollutants and are environmental persistent according to the ready biodegradation testing. The biodegradation capacity of pre-exposed inoculum is assessed in biodegradation testing and changes in community structure are followed by Illumina amplicon sequencing in time. Removal of tested chemicals and their transformation products are determined by LC MS/MS. Results of this experiment are expected to show biodegradation capacity enhancement of the inoculum after pre-exposure. They will result in a better understanding of the relationship between microbial adaptation and biodegradation performance. Ultimately they will also allowed a better prediction of the biodegradation outcome and the design of adapted inoculum with enhance degradation capacity for specific molecules.

Remediation of Free-Product 1,1,1 TCA and PCE in Low Buffering Capacity Sands

Miet Van Den Eeckhaut; Karen Van Geert; Wouter Gevaerts

Arcadis Belgium, BE

Background/Objectives. On a former telecommunication site two source zones with 1,1,1-trichloroethane (TCA) and tetrachloroethylene (PCE) groundwater contamination were encountered, with concentrations up to 200,000 and 100,000 µg/l respectively. Due to a high vertical gradient groundwater is contaminated between 3 and 21 m-bgl. The local lithological constitution, i.e. glauconitic (iron) fine sands with low buffering capacity, hardly influences the choice of the remediation strategy.

Approach/Activities. In order to select the most efficient remediation strategy, a multiple step pilot test on enhanced reductive dechlorination (ERD) is currently carried out in the source zone with the highest concentrations. The set up of the test is incorporated in a decision tree. The test foresees at most 3 injection rounds, each lasting about one week. After each test a set of relevant questions (e.g. successful distribution of C-source (Na-lactate) and NaOH, increase in pH, optimization of redox parameters, presence of Dhc and Dhb bacteria, degradation of ethenes and ethanes,...) have to be answered. The answers allow to evaluate whether it is worthwhile to proceed with the test or to stop and conclude that reductive biological degradation is not BATNEEC for the site.

Consequently with the field test, in order to test the possibility of TCA removal using hydrolysis, a laboratory test is carried out in which TCA concentrations from a groundwater sample collected in the source zone are measured after heating at 4, 25, 35 and 45°C and after 1, 24, 48, 120 and 144 hrs.

Results/Lessons learned. After one injection round in the field it is clear that the high vertical gradient largely influences the distribution of the C-source and NaOH, and that upon arrival of the NaOH the pH almost immediately decreases to its original value (< 5). Low pH values hamper the survival possibility of the injected Dhc and Dhb bacteria and thus the biological degradation. Therefore recirculation of C-source and NaOH was tested the second injection round. It proved successfully as arrival time and injection volumes were reduced, the latter by 60%. During the pumping we succeeded in keeping pH constant at about 5.3. The results show that recirculation is the way to go, but further optimization of the pH of the injected C-solution is required.

The results of the laboratory test on hydrolysis somewhat deviate from previous study as initially, after 24 and 48 hrs, TCA increases with time: The increase is highest for the lowest heating temperature.

3b. Chemical remediation

Oxidation of PAHS and their by-products (polar PACS) in the saturated zone of DNAPL-contaminated sub-soils after pumping

*Clotilde Johansson*¹; *Philippe Bataillard*²; *Coralie Biache*³; *Stéfan Colombano*²; *Alain Dumestre*¹; *Jérôme Frayret*⁴; *Antoine Joubert*¹; *Catherine Lorgeoux*⁵; *Thierry Pigot*⁴; *Pierre Faure*³; *Patrick Charbonnier*⁶

¹ SERPOL; ² BRGM; ³ CNRS, Université de Lorraine, UMR7360 - LIEC; ⁴ Université de Pau et des Pays de l'Adour, UMR5254 – IPREM; ⁵ CNRS, Université de Lorraine, CREGU, UMR7359 - GeoRessources; ⁶ ArcelorMittal Real Estate, FR

The remediation of former industrial sites is, for many reasons (health and environmental risks, land use...), of great concern. Soils encountered at former steelwork sites, including coking plants, exhibit multiple chemical contents, and are often impacted by PAHs inherited from coal tar storage and dissemination.

The present work specifically focuses on improving the effectiveness of in situ chemical oxidation (ISCO) to reduce DNAPL (Dense Non-Aqueous Phase Liquids) remaining after pumping in the saturated zone of impacted sub-soils. The study is part of the BIOXYVAL project, which brings together many representative actors (private companies, academic laboratories...), dedicated to the remediation of contaminated sites by coordinating various innovative processing techniques on the former industrial site "M", an impacted area of a former coking plant in the north east of France.

The purpose of this work is to better understand the oxidation of PAHs including the formation/elimination of selected by-products, especially polar Polycyclic Aromatic Compounds (PACs, including oxygen/nitrogen/sulfur-containing PACs) which have greater mobility in groundwater compared to PAHs and can be more toxic. Additional efforts (pretreatments, additives...) required for complete PAC oxidation or for achieving harmless level of contamination, will also be studied.

The efficiency of five different chemical oxidation processes is compared first through some batch experiments. Sodium permanganate, Fenton-like (pH 4-5), persulfate and heat-activated persulfate are used as referents. Their efficiency is compared to an innovative and very powerful oxidant made of potassium ferrate (FeVI), whose reaction products, consisting of iron hydroxides (iron III) are expected to be less harmful to the environment. First tests are performed on a reference matrix (Fontainebleau sand) with DNAPL concentration extracted on site, at what is expected to be on-site residual concentration after pumping. Selected oxidants are applied at different concentrations, and the sand-DNAPL mixtures are sampled after two reaction times. PAHs and polar-PACs are quantified by GC-MS after freeze-drying and solvent-extraction of the samples. The same tests are then carried out on site scale contaminated sub-soil. These preliminary experiments allow us to select the most efficient oxidants to apply in laboratory column tests and, finally, on the field.

Perspectives of clay-salt slimes use for rehabilitation of agricultural soils, contaminated with ^{137}Cs

Leanid Maskalchuk

International Sakharov Environmental University BSU, BY

The problem of rehabilitation of agricultural soils of Belarus, Russia and Ukraine, radioactively contaminated in the result of the Chernobyl NPP accident, is known to be extremely important nowadays. According to a big practical experience on minimization of Chernobyl NPP radiation accident consequences, mainly clay minerals with 2:1 layer structure (montmorillonite, vermiculite, illite and others), potassium fertilizers (for ^{137}Cs) and carbonates (for ^{90}Sr) are considered as the most effective sorbents to prevent radionuclides migration from soils to plants. In this case radionuclide sorbents should have the following properties: affinity to the soil, high dispersion and large active sorption surface, high selectivity and immobilizing ability towards ^{137}Cs and ^{90}Sr .

One of the perspective solutions of the radioactively contaminated soils rehabilitation problem is using of natural raw materials (sapropel) and chemical industry waste (clay-salt slimes) as radionuclides sorbents. Clay-salt slimes (CSS) are the large-tonnage waste products resulting from the sylvinitic ore recycling at JSC "Belaruskali" and represent a suspension of clay particles in a saturated salt solution. On the date 01.01.2016 the total amount of CSS accumulated in the special slime storages of JSC "Belaruskali" was more than 110.5 million tons.

The results of the preliminary studies of the physicochemical properties and characteristics of CSS indicate that CSS are clay minerals. The solid phase of CSS in finely dispersed fraction: particles with size less than 20 μm form 70 wt% of the phase, specific surface area – 40-45 m^2/g . CSS main components are calcite, dolomite, montmorillonite, illite and quartz. The distinctive feature of CSS is the constancy of morphological features in the entire sample, and it is a determining factor ensuring a high sorption degree towards radionuclides, especially radiocaesium.

The CSS fixing ability towards ^{137}Cs from multicomponent solutions is about 75-84 wt% of its initial content. The Radiocaesium Interception Potential (RIP(K)) determined by the J. Wauters method is 6631 ± 216 mmol/kg . The immobilization of ^{137}Cs in the CSS samples occurs mainly in the spontaneous illite interlayer boundary areas collapse and in result of the ^{137}Cs ions diffusion deep into its crystal lattice. Since the main sorption-active minerals relative to ^{137}Cs in the CSS are illite and montmorillonite, using of simple CSS enrichment techniques can increase the content of these minerals by 3.5 times. In this case RIP(K) can be about 22000 mmol/kg .

Results of field experiments showed that insertion of the CSS-based sorbents into contaminated with ^{137}Cs sandy and sandy loam soddy-podzolic soils (RIP(K) is 100 ± 10 and 400 ± 35 mmol/kg) in dose of 1 wt% allows to decrease migration of ^{137}Cs from soil to wheat grain by the 8 and 3 times respectively.

Therefore, we can conclude that the results obtained indicate the perspective of the CSS-based sorbents application for rehabilitation of sandy and soddy-podzolic soils of Belarus contaminated with ^{137}Cs .

Evaluation of field test of a novel high-pressure ozone injection method for remediation of chlorinated solvent source zones in fractured limestone.

Hasse Milter¹; Jane Piper²; Henrik Aktor³; Lone T. Karlby⁴; Reza Gooya⁵; Jens Mortensen¹; Chapman Roos⁶

¹ Region Zealand; ² Piper Environmental Group; ³ Aktor Innovation; ⁴ HOFOR; ⁵ University of Copenhagen; ⁶ Geosyntec, DK

Background/Objectives. Deep lying source zones (i.e., more than 40 meters below ground surface (m bgs)) in fractured limestone are often remediated by pump & treat (P&T) methods. Given the long, high operating cost of implementing P&T remedies in fractured bedrock, alternative methods are needed. The longevity of these source zones is driven by the effects of the long back diffusion time from the bedrock matrix into the fracture water, the quasi-static water in the fractures and the uneven distribution and sizing of the fractures in the matrix. As an alternative to P&T the objective was to use high-pressure in situ chemical oxidation (ISCO) with ozone with injection pressure up to 7 bar, only limited by the lack of backpressure. The test was performed at a shallow fractured limestone site at the Oelsemagle. The site was contaminated with low levels of tetrachloroethylene (PCE) (i.e., 100 to 4500 µg/L), after the main spill has been excavated, and the depth to contamination was approximately 5 - 9 m bgs. The field test was performed before entering a full scale field test with source lying more than 70 m bgs.

Method. The injection consisted of ten injection wells where both a combination of air and ozone was injected as well as water extracted from downgradient. The gas mixture was delivered to the subsurface through a 15-cm long stainless steel diffuser installed in the bottom of a 5-cm stainless steel well screen in ten wells, spaced by 10 meters. A total of 980 kg O₃ and 24500 kg O₂ were injected over a period of 9 months. Monitoring were carried out in the injection field as well as in the source near plume.

Injection pressure was monitored online and automated pressure compensation allowed consistent injection flow rates for individual wells despite varying back-pressures. Injection operated with a preprogrammed sequence, creating an oxidizing front, flowing with the natural gradient in the fractures. Intensive monitoring of the water chemistry was carried out in the time under and after the injection to be able to determine the progress in the remediation as well as the release of Ni, As as well as other metals. Furthermore, cores were drilled out of the limestone at the test site as well as the planned full scale site, before injection for characterization and reactive transport modelling at micro-scale to determine the radius of influence of ozone for degrading PCE in the matrix.

Conclusions. Testing at the shallow site consistently showed degradation of the PCE in the source area as well as in the plume. Desorption of contaminants was expected and showed as rising levels of PCE in the early stages of the injection. Continuous monitoring shows continuous decrease of primary contaminants in the source area as well as falling levels in the source-near plume. Release of high levels of Ni and lower levels of As were seen during the test, which highlighted the need for ongoing risk assessment before, and during injection. The test also clarifies that the risk assessment carried out before the injection has to involve a cost benefit analyses including the unintended side effects seen in context of the source remediation.

Groundwater remediation with ozone in limestone reservoirs; a reactive transport modelling study

Reza Gooya¹; Lone T. Karlby²; Dirk Münter¹; Henning Osholm Sørensen¹; Hasse Milter³; Susan L. S. Stipp¹

¹ University of Copenhagen; ² HOFOR; ³ Region Zealand, DK

Fast characterization of rock microstructure has huge potential for the water industries. We combined X-ray tomography experiments with reactive transport modeling to delineate the radius of influence for groundwater remediation with ozone, that was injected into a fractured rock contaminated with tetrachloroethylene (PCE), trichloroethylene (TCE) and cis-dichloroethylene (cis-DCE). Injection of oxidising compounds, such as ozone and chlorine, normally ends up decontaminating the high permeable fractures while the matrix remains contaminated. The purpose of this work was to estimate the decontamination time for PCE, TCE and cis-DCE using ozone in a fractured limestone, at the pore scale, where the pore structure was extracted from X-ray tomography data of real samples.

This work was performed using both experimental and numerical methods. X-ray tomography experiments were performed on a sample of limestone from the contaminated site. We extracted 3D images of material with 1 μm resolution. Then reactive transport models, using a code that we developed, combined transport and reaction at the pore scale were used to simulate transport of the ozone inside the fractures and the matrix while ozone was degrading the PCE, TCE and cis-DCE.

With the combined method, using X-ray tomography imaging and reactive transport modeling, decontamination times for all contaminants were estimated in a limestone with both fracture and matrix porosity (dual-porous medium). Results showed that higher pressure gradient in the domain causes larger difference between ozone transport in the fracture and the matrix, i.e. there is greater delay between ozone transport in the fracture and the matrix. Degradation of cis-DCE is the fastest (50 seconds), then TCE (100 seconds) and finally PCE (>160 seconds), using 190 Pa pressure gradient over a 2D domain with 400*800 μm dimensions.

We concluded that this method provides several parameters that are important for decontaminating aquifers in a cheap and fast way. In this case study, we concluded from ozone transport in a dual-porous medium, that the pressure gradient plays an important role in the difference between ozone migration in the fracture and in the matrix. It was also seen that diffusion increases the area of coverage by contaminants significantly in all directions (also downstream), which increases risk of contaminating a larger area.

Alkaline hydrometallurgical approach for steel slag management

Fernando Pereira¹; Olivier Faure; Véronique Lavastre; Didier Graillot; Jean-Michel Herri; Jean-Yves Cottin

¹ Mines Saint-Etienne, FR

Steel slags are artificial mineral matrices produced by the steel and iron industry. While they are considered as industrial waste, these slag heaps represent an important potential economic resource. The importance of hydrometallurgy in production and recycling of strategic metals cannot be stressed enough. Nevertheless, their use is increasingly under economic pressure since 2014. Clearly, improving or even optimizing these processes is required. In addition, although steel slags are classified as non-hazardous thermal waste, it is well known that most metals they contain are quite toxic to living organisms and pose serious environmental issues. Thus, reusing steel slags appears the option of choice to ensure their sustainable management.

At present, a number of technical options are available for contaminated mineral matrices (such as slags) treatment. Presently, the metals, oxides and hydroxides recovery from slags has been and still is the subject of numerous studies. The techniques implemented generally use hydrometallurgy and involve mechanical, magnetic, chemical and/or physicochemical separation processes in various combinations. The solutions reported in the literature for the dissolution of the metallic parts are, moreover, generally exclusively acid. Incorporated into mineral matrices and sometimes committed in the form of ferrites type, strategic metal-based (Cr, Mo, ...) non-ferrous oxides have rarely been the subject of specific treatments. When keeping the mineral matrix intact is desired for its subsequent valorization, processing technologies with acid leaching agents are inapplicable and to be avoided. The alkaline earth metals rich composition of steel slags are attractive materials for potential users. When acid leaching, the release of lime presents a major inconvenience. Hence, this causes an overconsumption of reagents and an excess of salt production.

The EAF-S ("Electric Arc Furnace slags from Stainless steel production") considered in this study results from the mechanical treatment of part of Dorian's (Loire department) heap. The current mechanical process, developed by Harsco Minerals France, recovers 99,7 % of the EAF-S metals. However, it doesn't allow the metal oxides extraction limiting thus the metals compounds exploitation in terms of reuse. The innovation was implementing selective unitary operations set on the chemical nature of (EAF-S) non-ferrous metals. The scientific approach consisted in adapting the alkaline middle (use of soda ash as leaching agent) of selective lixiviation and the separation methods in order to optimize the strategic metals extraction rates while choosing conditions and environments that do not present side effects and allow a minimization of the environmental impacts. Soda ash's weak corrosion power and selectivity showed many benefits. Iron and calcium, present in (EAF-S), were poorly leached at the end of alkaline treatment (mineral matrix preservation). Moreover, adding lime in a soda ash solution precipitated the silicates and carbonates thus returned the leaching solution to its initial state. The poster will propose to give a brief report on the principal results obtained.

Chemical and ¹⁴C Carbon radioactive waste management for orphan polluted site remediation

Stéphane Poncet; Marine Dumoussset; Raphaël Zanetta

ARCADIS France, FR

Among its missions, ANDRA (French National Agency for radioactive waste) has a public service mission in terms of i) collection of waste of the "small-scale nuclear activities" producers or owners (including the so-called "household" radioactive waste, ie waste owned by private individuals) and ii) clean-up and rehabilitation of orphan polluted sites.

ANDRA is in charge of the abandoned laboratory Isotopchim in Ganagobie (France) which used to synthesize radiological marked molecule, essentially 14 Carbon. The final aim is to remediate and demolish this contaminated building.

After several remediations, radiological and chemical radioactive products are still staying in the laboratory.

For the majority, these products are chemically unknown and need to be characterized or pre-treated before being able to be accepted by a nuclear treatment site.

Arcadis is recognized for its skills to manage chemical and radioactive products without solution for treatment in the nuclear industry.

ANDRA has instructed Arcadis to :

- Define the specification for the transportation of 1650 solids conditioning in small packaging ;
- Package these 1650 solid products in order to transport them to a CEA site ;
- Put together 450 liquid products (representing 2000 liters) in order to be acceptable by ANDRA.

For this mission, Arcadis organized a team composed by an expert in mixed contaminated products, an expert in chemical waste especially unknown chemical waste, an expert in radiological measure.

These operations need to be working on-site. Operators are trained and authorized to work on radiation and chemical conditions. Because of the 14 Carbon contaminated air, operators work with individual air conditioning protections.

To define the specification for transportation, Arcadis sorted out the different solid products with simple on-site analyses sufficient to classify them in chemical transportation families according to the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR). One part of products needs both radioactive and chemical waste ADR transportation conditions and the other part, only needs chemical waste ADR transportation conditions. These packaging and transportation conditions, after being validated by CEA and ANDRA, has been validated by ASN (French Nuclear Safety Authority). We operate the mission of packaging these products.

To put together the liquids within ANDRA formulations, we have studied the risks associated to chemical and radioactive context. We have designed reactors to mix singly 3 different categories of liquids according with ANDRA specifications (aqueous, oily, solvent), allowing to control the chemical risk of reaction. We have defined chemical and radioactive gas air monitoring, the reactors monitoring, the radioactive and chemical parameters controlled before and during the mixing in order to assure the final result. After reaction, we have managed the separation of different physical phases. We have packaged 9 types of products we characterized in an external laboratory in order to check their compatibility with ANDRA specifications.

Numerical modeling of an in-situ immobilization of arsenic in the subsurface using ferrous chloride

Micha Roemer¹; Timo Krüger²; Ilka Wallis³; Hartmut Holländer¹

¹ University of Manitoba; ² Ingenieurgesellschaft Heidt + Peters mbH; ³ Flinders University, CA

At a military site in Northern Germany, the aquifer is contaminated through the infiltration of high quantities of arsenic (As) from chemical warfare agents (CWA) and their degradation products. As concentration up to 9 mg/L was found and defined as mainly organically bound (~90%) and occurred in the form of phenylized As compounds (Krüger et al. 2008). In regards to the high degree of contamination and the existing threat to surrounding groundwater pumping wells, a pilot plant and well doublet was installed parallel to the groundwater flow direction and downstream from one of the hot spots for an in-situ immobilization of the remaining arsenic. An upfront laboratory test concluded that bivalent ferrous chloride (FeCl₂) would be best suited for the immobilization of As (Krüger et al. 2008). The field study spanned almost two years, and a total of 2.3 kg of As was immobilized through the pilot plant. The initial arsenic concentration in the vicinity of the pilot plant was reduced from 1.65 mg/L to less than 0.3 mg/L (Krüger et al. 2014). The recorded data showed remaining inorganic As concentrations of <1% and organically bound As concentrations of <18%. The objective of the present study was to design a numerical flow and reactive transport model for the conducted arsenic immobilization field experiment at the military site in Northern Germany, which provides a quantitative framework to evaluate the arsenic fate in the aquifer system.

In order to adequately simulate the arsenic fate in the aquifer system over the two-year remediation period, the two model components, groundwater flow, and solute transport had to be coupled with a geochemical reaction model. Three As species, As³⁺, As⁵⁺, and org-As were included into the reactive transport model. The groundwater flow model included constant head boundaries, well boundaries and a recharge boundary. The injection of the FeCl₂ was implemented by means of constant concentration boundaries assigned to the filter screens. A tracer test was conducted prior to the initial start-up of the pilot plant using dissolved oxygen. The tracer was injected into one of the pilot plants' bivalent wells and measured downstream with a multi-parameter probe. The measured breakthrough curves were used to calibrate the controlling solute transport parameters, porosity, and dispersivity. A reliable match between observation and simulation was found for a porosity of 0.2 and dispersivity of 0.005 m with R² > 0.92. The simulated arsenic concentrations were calibrated on the observed values from the two-year pilot study to determine the species corresponding equilibrium constant for the adsorption of the arsenic on precipitated iron hydroxide compounds (Fe(OH)₃). The model results showed a higher immobilisation rate at the downstream located well after the 2nd year immobilisation period. This was due to the Fe-enriched plume, which moved in the groundwater flow direction. The completed geochemical model is transferable to similar case studies that involve arsenic contamination and is tested recently to provide an estimation of the remediation potential at a Canadian case.

Using Potassium Persulfate as an Extended Release Oxidant for Sediments, Low Permeable Soils and as a Permeable Reactive Barrier

Brant Smith

PeroxyChem, AT

Background: In situ chemical oxidation (ISCO) technologies are among the most common remedial methods used to treat a wide assortment of environmental contaminants of concern. Each ISCO technology has unique characteristics that are utilized by design engineers and implementers to select the optimal technology to be applied at each site. One of the most prevalent ISCO technologies is activated potassium persulfate, which is based upon a highly soluble environmental grade sodium persulfate. This high solubility has enabled the injection of a significant amount of oxidant in reasonable injection volumes.

Potassium persulfate is another commercially available persulfate that, once activated, releases the persulfate anion that can be activated to form various oxidative and reductive radicals. Potassium persulfate has two critical characteristics different than sodium persulfate: i) the theoretical solubility is over an order of magnitude lower than sodium persulfate, and ii) the use of potassium salt could be beneficial at sites that have regulatory guidance on sodium (Na) concentrations in groundwater.

Objectives: This study was intended to evaluate and compare the performance of activated potassium persulfate, and the potential advantageous use of its unique characteristics in several different site conditions, including i) as an ISCO permeable reactive barrier (PRB), ii) for treatment of sediments, iii) emplaced near lower permeable materials to persist as contaminants back diffuse, as iv) polishing step after sodium persulfate applications at sites with low remedial goals, and v) in locations with regulatory limits on sodium.

Activities: Tests were conducted in a series of batch and column studies. Batch tests included comparing solubility under different conditions, evaluating characteristics of several activation methods, and measuring residual sodium content. Column studies were conducted evaluating the treatment efficacy of common aqueous phase contaminants, such as 1,4-dioxane, MTBE, and potential longevity under different treatment conditions.

Summary: The data show that persulfate derived from potassium persulfate is capable of treating multiple contaminants of concern, and that potassium persulfate exhibits different key characteristics that can be used by design engineers and implementers for a variety of site specific applications. The lower solubility of potassium persulfate would allow it to be mixed with soils and sediments. If dosed above its theoretical solubility limit, potassium persulfate will persist for an extended period of time, allowing for the possible treatment over a period of months to years.

Chemical Destruction of Persistent Organic Pollutants Using Sorption-Active Reactive Composite Materials

Sarah Sühnholz, Katrin Mackenzie, Anett Georgi and Frank-Dieter Kopinke

Helmholtz Centre for Environmental Research UFZ, DE

The regeneration of adsorbents by in situ chemical degradation of the adsorbed pollutants is one of the future drivers for material design in the field of water treatment. This applies in particular to special adsorbents for micropollutants in wastewater treatment approaches which cannot be frequently replaced as well for in-situ sorption-active reagents used for groundwater treatment. With Carbo-Iron® the UFZ presented such a sorption-active colloidal composite material for groundwater treatment (Mackenzie, 2012, 2016). It focuses on a new remediation strategy – the in situ generation of a permeable sorption-reaction barrier in contaminated aquifers. Permeable reactive zones for the remediation of groundwater are generated by particle injection and targeted placement. Carbo-Iron has proved suitable for not only plume cut-off but also source attack, due to its ability to interact with organic phases. As an improved alternative to conventional nanoiron materials, the combination of activated carbon and embedded zero-valent iron structures has proved suitable for an efficient treatment of common water pollutants such as chloroethenes. Carbo-Iron now is in its commercialization phase and is mainly being applied for this purpose. Trap-Ox Fe zeolites are a second type of sorption-active reactive particles for in-situ groundwater treatment building permeable reaction zones (Gilles et al. 2016). Here, the Fe-zeolite is sorbent and ISCO-like oxidation catalyst together generating OH-radicals in the near vicinity of the sorbed pollutants.

Both materials not only provide the reaction function but, due to the sorption-active carriers also offer the function of collecting the hydrophobic pollutants. This principle can be the key for many future treatment options, especially when facing extremely low pollutant concentrations. The potential for the combination of sorptive enrichment of low-concentrated water pollutants with their destruction in the sorbed state may reach far beyond the typical target contaminants for which the materials have so far been used. Further investigations were conducted in order to evaluate the principal application areas and to make amendments to the composite in order to achieve specific properties for efficient reduction of other persistent organic pollutants.

The presentation will focus on the lessons learnt while using such a reactive and sorption-active material. Design tips, approaches and possibilities for property adjustment will be given.

Acknowledgements: This work was supported partly by funding from the European Union within the NanoRem project.

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Reductive degradation of organochlorine pesticides by biochar-supported nano zero-valent iron materials

Jinzhong Wan¹; Qun Li; Shengtian Zhang; Tao Long

¹ Nanjing Institute of Environmental Science, Ministry of Environmental Protection of China, CN

Site contamination with organochlorine pesticides (OCPs) has been a severe soil environmental problem in China. Biochar-supported zero valent iron (BC/ZVI) composites, which combines the highly reductive reactivity of nano-scaled zero valent iron and the adsorptive capacity as well as soil improvement property of biochar, are expected to be a new environment functional material and play an important role in the remediation of OCPs-contaminated soils. In the present study three kinds of biochars were prepared from peanut shell, rice straw and corn straw, respectively, and the corresponding biochar-supported nano zero-valent iron (BC/nZVI) composite materials were synthesized. The composite particles were characterized by BET, SEM, XRD to study their physicochemical and structure properties. The reductive degradation performance of the BC/nZVI materials were then tested by a typical OCP— γ -BHC in aqueous solution. The results showed that the peanut shell, rice straw and corn straw under the preparation conditions of 300 °C had higher yields and better adsorption effect. The BC/nZVI particles had spherical structure and their specific surface areas were folds of nZVI. In aqueous phase experiments, the removing effect of BC/nZVI was better than that adding biochar or nZVI alone. Among three kinds of biochars, the peanut shell based BC/nZVI material exhibited the highest adsorption rate of 87.53% for γ -BHC, and the degradation rate was 82.33% at the time of 6 h

3c. Physical techniques, including thermal techniques

Designed hydrocyclone for contaminated soil particles separation

YiKuo Chang¹; Yi-Liang Shu; Cheng-Di Dong; Chiu-Wen Chen; Chia-Ying Li

¹ Central Taiwan University of Science and Technology, TW

In this work, hydrocyclone separation for heavy metal contaminated soils are studied. The contaminated farmland soils are collected from central Taiwan. The basic characteristics such as pH value, heavy metal content and toxic characteristic leaching procedure (TCLP) are conducted to examine the properties of the contaminated farmland soils. In addition, the separation processes, hydrocyclone treatment, is designed to separate coarse and fine-grained particles by high settling velocity of particles. Ideally, hydrocyclone separator could be applied to reduce contaminated soil volume and concentrated the pollutants into fine particles as overflow stream during hydrocyclone operation. The coarse particle possess less contaminant, it might be help to achieve the reduction in volume of contaminated farmland soils. Furthermore, the FLUENT flow simulations are help to calculate the cut-off size and fractional efficiencies in hydrocyclone separators. The demonstration of liquid-solid flow and the simulation results are feedback to the hydrocyclone operating parameters.

Overview of the current injection technologies for in-situ remediation with focus on experiences from a new emplacement technology

Uwe Dannwolf¹; Gordon Bures¹; Michael Mueller²

¹ RiskCom GmbH; ² PeroxyChem Environmental Solutions, DE

The injection of remediation reagents into groundwater impacts continues to receive growing acceptance by stakeholders involved with contaminated site remediation. This paper presents an overview of currently available in-situ injection techniques, their characteristics, including advantages and disadvantages associated with each. Experience has shown that getting sufficient amounts of remediation reagent into contact with contaminant treatment zones for a sufficient amount of time is key to a successful remediation project. A drawback of almost all currently available injection technologies is dependency on subsurface permeability, which limits accessibility to low permeability hotspots. Proof of established contact for conventional injection techniques can only be derived indirectly. Direct proof through surface geophysical measurements, such as tilt meters, is only available for injection by hydraulic stimulation.

The “i-SAV[®] in-situ Efficiency Programme” is an innovative field engineering technique. It targets specific contaminant zones and facilitates the hydraulic emplacement of treatment amendments at problem sites with limited access, or where low permeability subsurface conditions are encountered. The i-SAV[®] process allows injection of slurries containing highly concentrated remediation reagents (up to 80% solids) into the contaminated zones during drilling. The reagents can be formulated to establish a treatment train, for example by producing an oxidation then reduction sequence, and stabilising steps designed to ensure project success.

i-SAV[®] hydraulic emplacement works on the principle of the earth’s “at rest” pressure coefficient, and is independent of permeability. i-SAV[®] was especially developed for overcoming the limitations of in-situ remediation in low permeability soils including bedrock, and can be deployed in both the unsaturated and saturated zones, as well as in permeable strata.

Examples will be given for a successful project where Potassium-Permanganate has been emplaced in a double-porosity sandstone by conventional techniques (Germany), and up to two projects will be presented where the i-SAV[®] Injection technique has been used to emplace reagents into a sandstone formation (Germany), and dense clay formations (Italy, Canada).

The Canadian example depicts TPH and BTEX contamination in tight clays, successfully remediated in soil and groundwater within 15 months by:

1. establishing a permeable network of sands through an injection with i-SAV[®];
2. flooding the sands with biologically degradable tensides;
3. repeated injection of activated persulphates.

An i-SAV[®] pilot test was conducted in a sandstone with BTEX and chlorinated hydrocarbon contamination (Germany). The goal was to demonstrate proof of concept. 1.3 tons of activated potassium persulphate were injected as a 10% suspension at three injection boreholes within three days.

Another i-SAV[®] project shows the distribution of persulphates within tight clays at active service stations in Italy. On-line tiltmeter monitoring was employed to live monitor the emplacement. The typical radii of influence were around 5-6 m from each Geoprobe injection borehole.

Thermal treatment dimensioning regarding to energetical cost and contaminant behavior according to temperature

Maxime Emery¹; Christophe Chene

¹ SOLEO SERVICES, FR

In many cases, thermal treatment is considered as a heavy treatment so as to remediate a contaminated site quickly. However, treatment by thermal desorption shows high treatment's efficiency on volatile compounds despite a high treatment cost, high setup cost and expensive effluent treatment process. So as to optimize heating time (and thus energetical consumption) it is important to define precisely the temperature to reach in soils according to contaminant behavior.

Work has been done to build a simulation model of contaminant distribution between adsorbed phase, dissolved in aqueous phase and gas pure phase, depending on temperature.

This tool allows, depending on the way of proposed treatment (Soil Vapor Extraction, or MultiPhase Extraction), to find flows of contaminant that will be collected and thus to scale the treatment in a suitable way. The parameters considered are among other things, the nature and quantity of contaminants, the soil organic matter content and the amount of subsurface water.

In addition, in the case of treatment of pure phases, temperature elevation induced changes viscosity of the contaminants, and thus its behavior in the ground (permeability's modifications).

Once evaluated the behavior of the pollutant in soil under temperature's effect, the behavior of the ground under the effect of the thermal energy input is modeled to precisely evaluate the heating means to implement.

Thermal energy's consumption is first evaluated by a global approach. The global amount of energy to introduce in soils is evaluated regarding to the average temperature to reach, the time dedicated and the estimated losses of energy that can come from the groundwater or surface in the open air. So as to proceed, depending on the temperature to reach (higher or lower than 100 ° C), is addressed by successive steps:

- Energy to heat a mass of soil, water and pollutant up to 100 ° C;
- Energy to evaporate the water mass temperature present;
- Energy to raise a mass of dry soil from 100 ° C until the target treatment temperature.

Treatment of saturated soils, complexify the dimensioning by introducing into the volume to heat a flow of water to heat and evaporate that is necessary to quantify.

Then, a precise digital modeling by finite element is computed, to allocate the heating elements in the ground subsurface regarding to geology encountered and soil thermal parameters. A geometric model is built, meshed, and submitted to the hypothesis (heating flow, flow of energy dissipation,...).

Finally, a security approach is lead to estimate the heat effects on the environment:

- Potential soil dilatations and effects on the constructions;
- Potential concrete dilatations and effects on the constructions;
- Underground network issue;

A precise technical answer is then applied so as to offer a perfectly dimensioned and secure thermal treatment.

Multiphase flow modelling of the pumping of a DNAPL: case study of hexachlorobutadiene in a shallow alluvial aquifer

*Quentin Giraud*¹; *Benoît Paris*¹; *Julio Gonçalves*²; *Antoine Joubert*³; *Stéfan Colombano*⁴; *David Cazaux*⁵

¹ INTERA; ² CEREGE; ³ SERPOL; ⁴ BRGM; ⁵ INOVYN, FR

In France, volatile organo-chlorinated compounds (VOC) are responsible of about 15% of contamination of soils and groundwater. In this context, the SILPHES project combines innovative characterisation tools and emerging remediation technologies applied on VOC-contaminated groundwater.

For this project, four square impermeable concrete compartments of 9.5 m long and 10 m deep were dug at the location of a free-phase source zone of VOC, mainly composed by hexachlorobutadiene (HCBD). The aquifer is made of superficial alluvial materials, from fine sand to gravel, reversely graded.

A numerical modelling was elaborated, with the three-dimensional and multiphase flow simulator TMVOC, to model, at the field scale, the VOC pumping, in one of the compartments.

Interpolation of geological layers was done with LeapFrog, from drilling survey data. Chemical data of 8 VOC was computed to fit TMVOC parametric requirements. Soil and hydrogeological parameters were obtained either from literature or experiments (i.e. water/VOC retention curves). Numerical model grid consisted of 10 layers for a total of 5060 3-D grid blocks, modelling the interior volume of one concrete compartments, the concrete walls and an exterior band of 0.5 m where boundary conditions apply.

Numerical modelling results show an excellent match between simulated and field data of VOC and water pumped masses and a very good match between simulated and field data of the water/DNAPL interface elevation during pumping.

Partitioning tracer tests will be conducted in the compartments to assess the efficiency of the pumping scenario and evaluate the volume of residual VOC.

This study is, at the best of the knowledge of the authors, the first multiphase flow modelling of a VOC source composed mainly by HCBD, a chemical which has a poor occurrence data in the environmental literature. It offers a new perspective in remediation, by using multiphase flow numerical tools to predict immiscible pollutants behaviour in groundwater, in natural or forced flow.

STARx for the Treatment of Contaminated Soils and Liquid Organic Wastes – From Prototype to Full Scale Application

Grant Scholes¹; Gavin Grant; David Major; Cody Murray

¹ Savron, CA

STARx for the Treatment of Contaminated Soils and Liquid Organic Wastes – From Prototype to Full Scale Application

Grant Scholes (gscholes@savronsolutions.com), Gavin P. Grant (ggrant@savronsolutions.com), David Major (dmajor@savronsolutions.com), Cody Murray (cmurray@savronsolutions.com),

STARx systems use smoldering combustion for the treatment of contaminated soils and liquid organic wastes. The process is self-sustaining following a short duration, low energy input 'ignition event'. The energy released from the reacting contaminants is used to pre-heat and initiate combustion of contaminants in the adjacent area. A combustion front will continue to propagate through the contaminated media, provided that a sufficient flux of air is supplied. This presentation describes the modes of application for STARx, a rigorous testing program to develop the STARx soil piles, and presents a case study of a full scale field application of STARx for hydrocarbon-impacted sludge materials at an oil and gas facility in South East Asia.

STARx can be used for the treatment of excavated contaminated soils and organic wastes such as lagoon sludges and waste oils when the waste material is mixed with a porous media to establish the conditions required for smoldering combustion. The process can be carried out in large-scale reactors or in simple engineered soil pile systems depending on the needs of the application. Reactors suit low volume (i.e., inventory control) applications where facility footprint is limited, while soil pile systems are designed for high volume STARx applications. A modular engineered base system was developed to enable the application of STARx via soil piles. These bases, called Hottpads, are a low profile trafficable surface containing the heat and air distribution for ignition and propagation of the smoldering reaction. The Hottpads can be networked together to meet the throughput requirements of the given project.

The case study presents a Hottpad STARx application to treat hydrocarbon impacted sludge at an active oil and gas facility in South East Asia. The system, consisting of a network of 6 Hottpads, was designed to treat approximately 3500 m³ of sludge material. Operation of the full scale STARx system demonstrated effective and efficient scale up of the technology and rapid sludge destruction. The results of system operation will be presented.

Thermal remediation of bedrock on development site in Stockholm

Jesper Holm¹; Göran Nilsson²; Niklas Törneman³; Janna Svensson³; Matilda Johansson³

¹ Krüger A/S; ² KUAB; ³ Sweco, DK

The area of interest is located on Kvarnholmen, a peninsula located near the center of Stockholm. The area is under upcoming urban development. In part of the development area storage of chlorinated solvents for industrial use has previously taken place in above ground silos. Despite no historical record of spills, investigations in the area have shown the presence of PCE and degradation products in top soils and in the underlying bedrock formation. Investigations were carried out by Sweco.

Therefore, remediation of the site has been initiated by the developer KUAB. Contaminated top soils have been excavated. Remediation of the contamination in the bed rock remains. This will be obtained through thermal remediation.

The aim of the planned remediation is to remove contamination in the bedrock down to a level where it will not pose a threat to the indoor climate of the proposed housing in the area.

To our knowledge, this project will be the first project to undertake thermal remediation in crystalline bedrock in Europe. The site installation is currently close to being finished. Operation on the site will start after new year 2017 with a planned active remediation period ending in may 2017.

The presentation will show remediation design, experiences from installation and results from operation.

The Remediation of an Acid Tar Lagoon in Mons, Belgium

Adrien Kahn; Cédric Oger; Catherine Van Wouwe; Pietro Perseo

SUEZ REMEDIATION, BE

1. INTRODUCTION

Acid tar is a hazardous waste generated by refining processes, namely refining of benzole, refining of used oils or refining of petroleum by addition of sulphuric acid. Historically, acid tars were frequently dumped on land causing contamination of land, surface water and groundwater.

2. THE ACID TAR LAGOON IN MONS

In 1884, a coking plant and a facility for the recovery of coke residue were in operation on site. In the late 1920s, the activities expanded with a benzole refining and a tar distillation plant. In 1985 all the facilities were decommissioned. During this period, the residual tars from the benzole refining and wastes from other activities were dumped on land and covered with soil.

The acid tar present on site arises from the refining of benzole by addition of sulphuric acid, resulting in tar with a very low pH and containing a high concentration of sulphur and VOCs, in particular benzene and toluene. The tars are severely acidic and contain a high sulphur content. Locally pH values below 1 are encountered. The sulphur content of the acid tar reaches 7%. Emissions of VOCs, hydrogen sulphide and sulphur dioxide originate from the acid tar, especially when the waste is handled

3. THE SITE REMEDIATION WORKS

The remediation plan defined by the client SPAQUE consists mainly of:

- Removal of the pollution source or the acid tar until reaching the soil layer
- Neutralization of the acid tar on-site before transport to approved waste treatment facilities
- Emission management, control and mitigation
- Backfilling using clean soils

Prior to commencement of the works, SUEZ performed a detailed study of the acid tar lagoon. The study consisted of

- Mapping of the contaminated area
- Laboratory tests to determine the most suitable neutralization additive and the required quantity to achieve the required pH
- Air quality measurements during trial pit excavations

The acid tar is neutralized on-site before being transported to approved waste treatment facilities for further treatment to approved waste treatment facilities. The choice of treatment depends on calorific value, sulphur content, concentrations in mercury, arsenic and benzene. The treatment techniques used are:

- Co-incineration in cement kilns
- Incineration with energy recovery
- Thermal treatment by pyrolysis
- Thermal desorption

Ambient air quality monitoring is performed during the remediation works and includes near-source and perimeter monitoring stations measuring TVOC, benzene, toluene, SO₂, H₂S and PM₁₀.

Various measures are taken to mitigate emissions, such as:

- Reducing the size of the in-situ neutralization or excavation area
- Covering of the acid tar with compost or foam
- Use of a water spraying system with odour control agent to reduce odour nuisances
- Use of an air ventilation system to blow air away from the receptor
- Stop remediation when the wind is unfavourable

For health and safety concerns, the hazardous properties of the acid tar require the use of chemical and acid resistant gloves, boots, overalls and respiratory protection for all personnel working or entering the area. The respiratory protection is a self-contained breathing apparatus with an independent air supply.

Surfactant Foam Technology For Soil Remediation: Effect of Soil Characteristics and Heterogeneity on Foam Propagation.

Julien Maire¹; Emmanuelle Brunol¹; Iheb Bouzid¹; Nicolas Fatin-Rouge¹; Quentin Giraud²; Benoît Paris²

¹ Université de Bourgogne Franche-Comté; ² INTERA, FR

Background: Surfactant foam technology is a new disruptive tool for soil remediation. Technological locks for field applicability were recently released. Since, the efficiency of surfactant foam technology was proven at lab and field scale for various remediation strategies: Pure phase recovery, remediation reagents delivery, permeability reduction. While it is known that formation and propagation of foam in soil strongly depends on soil characteristics and heterogeneity, those works were always conducted on a limited set of soils because of the work required. So far, theoretical and systematic knowledge about soil characteristics and heterogeneity effect on foam behavior is not available. It would be beneficial to extrapolate remediation results obtained on one type of soil to other soils, with heterogeneity. Moreover, it would define limits of this technology and will encourage the development of adapted injection strategies for soils where initial strategy wouldn't work as is.

Approach: A systematic study was conducted at lab scale. First, foam propagation was studied in 1-D cell filled with soil with different characteristics. Twenty different soils from fine sand to gravel were studied. Each one was characterized for: Granulometric descriptors, soil grains morphology (Sphericity, roundness, roughness), permeability, composition (carbonates, organic matter, mineralogy), surface wettability and surfactant adsorption on soil. Finally foam propagation was statistically analyzed to find the effect of each soil characteristic onto it. Different modes of foam injection were experimented. The work was completed with experiment in 2D cells in that were filled with patterns of soils with different properties to assess the propagation of foam in heterogeneous soils. This work focused on permeability and wettability heterogeneity that are common on contaminated sites. Numerical modeling tool was realized by adapting TMVOC software to allow for predictive foam behavior in soil.

Results: Results of 1-D experiments show that some soils characteristics have significant effect on foam propagation, while other might not be relevant. It will be discussed. The propagation behavior of foam in heterogeneous soils and its implication for soil remediation will also be discussed. Finally, numerical modeling results will be presented.

Surfactant Foam Technology For Enhanced Hydrogen Delivery In Contaminated Groundwater

Julien Maire¹; Emmanuelle Brunol¹; Nicolas Fatin-Rouge¹; Antoine Joubert²; Alain Dumestre²; Stéfan Colombano³; Hossein Davarzani³; Christophe Avril⁴; Benoit Delobelle⁴; Cédric Marion⁵; David Cazaux⁵

¹ Université de Bourgogne Franche-Comté; ² SERPOL; ³ BRGM; ⁴ Mahytec; ⁵ INOVYN, FR

Background: To enhance the reductive dehalogenation of chlorinated organic compounds (COCs) in contaminated aquifers, H₂ gas is commonly delivered into groundwater. Several commercial solutions are available to deliver this poorly soluble gas: -In situ production of H₂ by fermentation of organic amendment in soil. Passive and simple but it is a slow process. - Emitters based on diffusion of H₂ through a membrane. High density of emitters are required to increase exchange surface. -Direct gas injection (sparging). Inefficient since the H₂ gas bubbles quickly migrate upward, out of the contaminated zone. Here, we have investigated a disruptive solution to improve H₂ delivery in the saturated zone by immobilizing it as a foam. Since foams behaves as a high viscosity fluid in soil, the sequestered amounts and the persistence of H₂ in the saturated zone are increased. Within the SILPHES project (French acronym for Innovative Solutions for the Remediation of Aquifers Contaminated with COCs) that involves academic and industrial partners, foams have been assessed for the delivery of H₂ in a plume downstream of a historical contamination by a COCs DNAPL located at the bottom of a sandy aquifer (K~10-4 m.s-1), 8-12 m below ground surface. H₂ delivery should be targeted to the deepest meter of soil as a priority since it is responsible for the contamination of upper layers by back diffusion.

Approach: Foams have been assessed to maximize H₂ injection and dissolution in the targeted zone. Evaluation took place at lab- and field-scale. Optimal injection parameters (well geometry, surfactant formulation, foam type...) were first assessed in 2D-cell containing inert glass beads bed with permeability identical to the one of the study site. H₂ sequestration, lateral propagation, foam lifetime and dissolution were monitored (ORP, [H₂]). Modeling of H₂ delivery as a foam and dissolution was modeled. Foam propagation was modeled using generalized Darcy's law, Van Genuchten's and Mualem's models. Dissolution of H₂ was modeled by considering diffusion and advection. This model will allow for predictive estimation of foam propagation and gas dissolution at larger scale. At field scale, H₂ foam was formed around an injection well 12 m bgs. Five monitoring wells were placed up- and down- stream to monitor [electron acceptors], [contaminants] and general water parameters. H₂ was supplied by tailor-made metal-hydrides storage cylinders designed for long autonomy, underground storage and ability to passively output high pressure and flow in field conditions. Delivery by lactic acid fermentation and diffusion-based emitters were assessed on field for comparison.

Results: Foams allow better gas lateral propagation; sequestered amount of H₂ is several times higher than sparging and no alteration of dissolution kinetics was observed. This results in quick and targeted H₂ delivery in the contaminated stratum. However, lab experiments show that injection parameters and surfactant formulation should be carefully tuned for process success. This technology could reduce operational costs and wells density.

Biochar for the remediation of atrazine from soil and groundwater - effects of ash content and pH on atrazine degradation and transport

Oliver McMillan

University Of Cambridge, GB

Biochar is the solid product of the pyrolysis process, and has gained increasing attention in recent years for its potential application in remediating contaminated soil and groundwater. Biochar results in a number of environmental benefits, including increased plant growth, increased soil water holding capacity, increased soil pH and the sorption of heavy metal and organic contaminants. Atrazine is a tri-azine herbicide commonly used to control weeds on corn, sugarcane and other crops and is a common groundwater contaminant with potentially harmful effects on aquatic life and human health. In this study, the sorption and degradation of atrazine in the presence of eight biochars was investigated. The biochars investigated were produced from rice husk, soft wood, miscanthus straw or rape seed, each at either 550°C or 700°C, and have ash contents ranging from approximately 1% to 48%. Sorption capacity was positively correlated with ash content, although the ashes themselves had a much lower sorption capacity than any of the biochars investigated. It is hypothesised that at high pH values the ash can catalyse the hydrolysis of atrazine, resulting in increased apparent sorption, while at low pH values hydrogen bonding to the char component of biochar will dominate the removal of atrazine. These results suggest that biochar for managing atrazine in the environment should be carefully designed so that immobilisation or degradation can be achieved as desired.

Thermal Remediation Sustainability: How Does Modelling Help?

Joanne Pennell¹; James Baldock; Jay Dablow

¹ ERM, GB

Thermal models were constructed for two sites impacted by Light Non-Aqueous Phase Liquid (LNAPL), where remediation was to be implemented within relatively high permeability sand and gravel deposits using steam enhanced recovery. Planned depth of treatment at a site in the UK was relatively shallow (4m below ground level (bgl)) and at the other site, in the US, contamination was deeper at circa 60m bgl. The objective of the modelling at both sites was to evaluate heating methodology and associated heat energy consumption, predict heating duration and determine the optimum well spacing and recovery mechanism to achieve the Target Treatment Temperature (TTT) in the most energy efficient manner. Each thermal model was developed using PC based PetraSim™ software.

Two different methods of heating were assessed at the UK site. Initially, the application of combined steam injection and In-Situ Thermal Desorption (ISTD) was modelled, assuming a TTT of 150°C, which could not be reached using steam alone, to enable contaminant recovery via volatilization: 36 ISTD locations at a 6m spacing were used to simulate 113kg/hr of heat input per well to the vadose zone, together with 6 steam injection wells at a spacing of 16m and flow rate of 40kg/hr of steam per well to heat the saturated zone simultaneously. However, subsequently obtained bench test data suggested the LNAPL could be mobilized, rather than volatilised, and recovered at temperatures of between 70 and 90°C; a range that steam in isolation could achieve and was therefore modelled using 19 injection wells (4m ROI) at a flow rate of 79kg/hr/well (1,500kg/hr total).

At the US Site, two scenarios were modelled to evaluate total steam injection rates of 2,050 and 5,000kg/hr total flow, with a corresponding well spacing of 10m (50 wells) and 14m (41 wells), respectively. This was undertaken to estimate the timeframe needed to achieve the TTT of 70°C, to enable LNAPL mobilisation.

At the UK site, the combined ISTD/steam injection scenario showed that the TTT would be achieved after 3 months, using a predicted energy consumption of 9,434,920kg. However the use of steam in isolation predicted a much lower steam consumption of 3,285,000kg to achieve a reduced TTT within the same time frame, representing a 65% energy saving. This highlights the benefits of the bench test data to confirm the lower TTT, enabling a change to a lower carbon footprint heating methodology.

At the US Site, the TTT was predicted to be reached within a time period of 5 or 19 weeks, depending on well spacing and steam flow rates. The longer time period reflects lower steam injection rates and greater spacing of the injection wells, with an associated steam consumption of 6,543,600kg; however when steam flow rates were doubled and well spacing increased, steam consumption decreased to 4,200,000kg, a reduction of 35% energy reduction and significant time savings.

Both projects illustrate the energy, cost and time savings that can be made via the modelling process to optimize the balance of steam input and well spacing. When combined with a bench test, sustainability can be further improved as seen at the UK site.

Onsite ex-situ washing of multi-contaminated soils: design and implementation for the remediation of a large industrial site

Thomas Perrier¹; Franck Guerra²; Aurélien Triger²; Adnan Sefer³

¹ Ramboll Environ; ² Sol Environment; ³ Clariant, FR

In the context of the closure of a large chemical site in eastern France, a remedial action plan was developed to define the most appropriate management of the contaminated areas and assess the expected outcomes. Due to the various contaminants of concerns present at distinct site areas and their geographical repartition, excavation was determined to be the sole effective technique to reach the targeted mass removal in the timeframe of the project.

Considering the extension of the contaminated areas (total volume of 65,000 m³) and the nature of the subsoil composed of alluvial deposits, technical solutions of soil washing were studied in details to maximize onsite soil recycling and prevent offsite disposal to the extent possible and associated prohibitive costs.

Initial on-site pilot tests demonstrated that soil washing (with wet sieving) was efficient to clean coarse fractions (> 4 mm) independently of the contamination type and that visual impacts removal was a good tracer of the treatment efficiency. Further washing tests demonstrated that the use of a washing drum, vibratory screens, a hydrocyclone and a water treatment unit could allow the cleaning of fractions greater than 1 mm in a single washing run and of 0.1 to 1 mm sand fractions after additional washing runs, as well as the recycling of water.

Waste water treatment is also critical considering the large volume of water that will be required for the washing (300,000 m³), the high flow rate (200 m³/h) and the required target quality (low turbidity and low residual dissolved concentrations). To ensure full recycling of the washing water, additional treatment and sludge dewatering tests were thus performed using the innovative Clariant Invoque[®] dewatering technology, that showed fast sedimentation and filtration rates, good supernatant turbidity and suspended solid content, press cake with high dryness (80%) and good mechanical properties after filter pressing.

Major technical and operational learnings were also obtained from the tests, valuable for the remedial works bidding process.

It is now expected that future treatment installation will be installed and operated on the site and will allow the washing of 130,000 tons of excavated impacted materials with a reuse as backfill of cleaned materials from >30 cm gravels to 0.1 mm sands, treatment of waste water for full recycling and optimized sludge dewatering.

In addition to the high goals targeted for the cleaning of soils, these works will take place in a challenging context with the demolition of more than 10,000 m³ of underground concrete structures, excavation of a total of 190,000 m³ of materials, with more than 70% being performed under large confinement tents to avoid any nuisances to neighbourhood and the use of retaining structures for 10-meter deep excavation works, and the management of rain and infiltration water to avoid remobilization of contamination to groundwater.

After a period of preparation of several months, the remedial works will start in mid-2017 for two years. These works should lead to the removal of more than 80% of the soil contamination with a soil and water recycling rate greater than 90%.

Development of active capping materials for oil spill contaminated sediment remediation

Ludovica Silvanj¹; Adriano Rossi; Paolo Di Palma; Carmela Riccardi; Sarah Hale; Paolo Viotti; Marco Petrangeli Papini

¹ NGI, NO

Petroleum is extensively used for making oil-based chemical and energy; its daily consume is on average 20 million tons and it is not destined to decrease. The increasing in the use of the petroleum is inevitably connected to an oil spills increasing. Oil spills can occur for many reasons such as human error or equipment failure; anyway, whenever an oil spill occurs it may represent a worldwide environmental problem, thus an effective remediation strategy is required.

The herein work is carried out in the frame of the Kill Spill Project (EU FP 7) designed to develop integrated biotechnological solutions for oil spill remediation and management.

The aim of this study is to develop different sorbent materials for the active capping of oil spill contaminated sea-sediment.

The experimental investigation was performed on a sediment from Messina Harbor (Italy), contaminated with 1% Crude Oil and 0.1% of a mixture of polycyclic aromatic hydrocarbons (PAHs). Different sorbent materials were tested for the active capping: a commercial Activated Carbon (AC) Carbonitalia, an organophilic clays (OC) CETCO Inc. and a biochar (BC). The sorption property of the materials was first investigated in aqueous solution by performing equilibrium tests (isotherm) using a mixture of PAHs as target contaminants. The data were obtained from batch characterization and the equilibrium PAHs concentration were evaluated by using Polyethylene (PE) foil (26 µm) as passive samplers.

Capping experiments were performed in glass cylinder (20 x 7 cm) and box models (25x18x21 cm), where a layer of contaminated sediment (7,5 cm) was capped with a layer of 3 cm of sand mixed with the different tested materials (AC, OC and BC) and synthetic sea water (4 cm) on top. The capping efficiency was assessed by using PolyDimehylSyloxane (PDMS) fibers as passive samplers. The fibers were inserted into the sediment and the capping layer; after fixed times the fibers were retrieved, cut (1 cm resolution), extracted and analysed in order to have the PAHs profile concentration. The PAHs profiles in the different capping systems were thus compared in order to assess the capping efficiency.

Batch tests showed that BC has comparable capping performance with AC and OC after 6 months of monitoring. The experimental properties are used to simulate the long-term behavior of various cap configurations.

Ex-situ Thermal Desorption of TPH contaminated soil

Hatem Saadaoui¹; Jan Haemers²; Teddy Derooy³

¹ Haemers Technologies; ² HAEMERS-TECH; ³ Perenco Rep, BE

Introduction

Petroleum extraction usually results in the contamination of significant amounts of soil due to leaks from oil pipes or accidents during drilling and extraction operations. The pollutant is composed of variable chain hydrocarbons (short and long) and is a short-term hazard to the environment and human.

The application of TPS's on-pile Ex-Situ Thermal Desorption (on-pile ESTD) process as a means of performing thorough on-site thermal desorption provides a definitive solution to this problem, while recovering 72 % of the spilled oil, and destroying the other 28 %.

On-pile ESTD treatment

The current project is located in the territory of Low-Congo near the town of Muanda. The contaminated soil (mainly sand) is stored on site. The amount of contaminated soil is estimated at 16,000 m³ with an average and a maximum hydrocarbon (C10-C40) concentrations of 3.7% and 7.5% (wt.). The objective of the treatment is to reach Louisiana 29-B standards (less than 1% of oils and fats).

The proposed ESTD treatment design utilises the thermal conductive heating (TCH) method. TCH is carried out by placing heating pipes and perforated tubes in a specific pattern throughout the soil pile. A soil vapour extraction unit (SVE unit) is used to maintain negative pressure in the pile during the heating process. The extracted vapour is routed to a cooling system prior to oxidising the non-condensable gases in a thermal oxidiser.

Results

30,243 tons of contaminated soil with high concentration of TPH were treated in 10 piles of different sizes (between 800 and 2,000 m³). The treatment took 12 months.

Based on the preliminary analysis carried out by various accredited laboratories on different collected samples, the total hydrocarbons concentration in the soil varied from 1% (10,000 mg/kg) to 7.5% (75,000 mg/kg).

The average post-treatment concentrations ranged from 757 to 7,410 mg/kg, and were well below the typical remedial goal of 10,000 mg/kg (Louisiana 29-B standards), with more than 96% destruction and removal efficiency. The project met the regulatory emission standards.

The BS&W (Basic Sediment & Water) of recovered pure products (condensed products) is very low (0,05%) and therefore contain very little water. With a °API of 30, which corresponds to the average of the quality of the crude oil harvested on the site field, the extracted products are characterised as medium oil and were sold as crude oil.

Over the last five batches, 72 % of recovered oil (758 m³) was re-injected into the site's production.

TPS carried out the treatment without producing any environmental disturbance (atmospheric, aqueous, dust, etc.) and transparently (process-related data available to all stakeholders on a daily basis).

Conclusion

TPS's ex-situ thermal desorption treatment is able to extract TPH contaminants from highly polluted soils with an efficiency above 95%. Moreover, 72 % of recovered oil can be considered as a clear value-added product. These results show the efficiency of the ESTD remediation and therefore its economic, technologic and environmental interest.

3d. Phytoremediation and ecological engineering

Single and intercropping cultivation of aquatic macrophytes in barium-affected soil phytoremediation.

*Fernando Barboza Egreja Filho*¹; *Cássio Francisco Carvalho*²; *Douglas Gomes Viana*²; *Fábio Pires*²; *Robson Bonomo*²; *Alberto Cargnelutti Filho*³; *Luiz Fernando Martins*⁴; *Leila Beatriz Silva Cruz*⁵; *Mauro Nascimento*⁵

¹ Federal University of Minas Gerais; ² Federal University of Espírito Santo; ³ Federal University of Santa Maria; ⁴ PETROBRAS/CENPES; ⁵ Petrobras, BR

Aquatic macrophytes are plant species that have morphological characteristics that pose themselves as candidates for phytoremediation programs in flooded areas. A field study in southeastern Brazil was conducted to evaluate the ability of three species of aquatic macrophytes, in single cropping and intercropping, to phytoremediate an area under flooded soil, contaminated with barium (Ba), a highly neurotoxic metal. The soil (Aquent according to Soil Taxonomy) is quite heterogeneous regarding the attributes along the soil profile, especially the superficial organic layer of approximately 5 cm, buried by sediments in part of the area. The experiment was performed from December 2014 to July 2015, in randomized blocks with three replications. The treatments were species *Eleocharis acutangula* (E), *Cyperus cf. papyrus* (C) and *Typha domingensis* (T) single cultivated, double intercropping (EC, ET and CT) and triple intercropping (ECT). Evaluations were based on height, stand of plants, fresh and dry biomass measurements in addition to chemical analysis of soil and plant tissues to quantify barium content. None of the treatments showed toxicity symptoms in plants in the 180-day during the experiment. The results showed, with exception of EC intercropping, that all other intercropping treatments produced greater amounts of fresh and dry matter of plants and higher soil Ba extraction when compared to single species treatments. The total fresh matter production decreased in the following order: CT>ET>ECT>T>C>E>EC. In relation to Ba amount extracted by the plants, the order was ET>TC>TCE>T>C>E>EC. *T. domingensis* had been involved in the top four treatments, either intercropped or single. The translocation factor (TF), which estimates the efficiency of plants to translocate the absorbed metal from roots to shoots was calculated as the ratio between the amount of barium accumulated in shoot and the amount accumulated in roots. TF>1 indicate more Ba in shoot. Higher TF is desirable for the improvement of the phytoremediation process. Among the plants in monocropping, *T. domingensis* was the only one that showed TF> 1, reaching 2.75. On the other hand, all intercropping treatments with the participation of this plant showed TF> 1, and the highest value was obtained in ET treatment (TF = 2.03). Due to the large TF, large production of fresh and dry matter and its greater ability to extract Ba, the intercropping *E. acutangula* and *T. domingensis* (ET) proved to have the greatest potential for removal of Ba in the studied area.

Acknowledgements: The authors acknowledge PETROBRAS S.A. and Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) for financial support.

Coupling lead phytoextraction by indian mustard and soil bioaugmentation: stains selection and comparison of the coupling efficiency with phytoextraction associated with EDTA

*Dorine Bouquet*¹; *Armelle Braud*; *Thierry Lebeau*²

¹ LPG-Nantes; ² Université de Nantes, FR

Lead (Pb) phytoextraction has been studied for several decades as a “gentle” alternative for soil cleaning-up. Yet, it has not been applied because of the duration of the process. To improve its efficiency, phytoextraction can be associated with soil bioaugmentation. This study aimed at firstly selecting potentially interesting bacterial strains for phytoextraction, and then at evaluating Pb-phytoextraction efficiency of plant/bacteria couple(s) developed on non-point source contaminated soils (geogenic or anthropogenic Pb).

From a bank of 181 bacterial strains isolated from contaminated sediments, the best one were selected based on i) their growing capacity in soil extracts, ii) the production of interesting molecules involved in lead mobilization (siderophores especially pyoverdine and phosphatase) and iii) their Plant Growth Promoting Rhizobacteria (PGPR) properties (ACC desaminase and AIA production). According to the results, a score was attributed to each stain and bacteria with the highest scores were tested for the soil bioaugmentation experiment. Two soils were used, one naturally rich in Pb (soil E) and one contaminated by human activities (soil M).

Seven stains with the highest score (10 out of 12) were used for soil bioaugmentation. Like EDTA at 2.5 mmol/kg, the bacterial strains had no significant effect on soil pH. EDTA increases by more than 1500 times the phytoavailable lead in soil compared to control. Lead mobilization with bioaugmentation was by far less efficient. On average, phytoavailable lead was 1.2 times higher than control. EDTA addition increased by a factor of 26 (E) lead phytoextraction efficiency (maximum of 45 mg Pb/kg in shoots of Indian Mustard). Although lead mobilization by bacteria was shown to be very low as compared to EDTA, a persistent effect can be assumed with bioaugmentation during all the length of the cultivation cycle of Indian mustard with, as a result a non-negligible phytoextraction efficiency. Work is in progress.

Potential of *Pistia stratiotes* for phytoremediation of arsenic: influence of nitric oxide on absorption and tolerance to the pollutant

Fernanda Farnese¹; Juraci Alves de Oliveira; Paulo Eduardo Menezes-Silva; Gutenberg Almeida

¹ Federal Institute of Science and Technology, BR

Arsenic (As) is a metalloid naturally occurring in the environment. High As concentrations are toxic to all living organisms and occur as a result of human activities. Arsenate, the most common form of As in oxygenated environments, is a chemical analogue of phosphate and can be absorbed by plants through high-affinity phosphate transporters in the roots. This ability of plants to absorb arsenate makes them interesting organisms for the removal of the pollutant from the environment, a process called phytoremediation. Among plants with potential for phytoremediation of aquatic environments, it is possible to highlight *Pistia stratiotes*, an aquatic macrophyte that presents rapid growth and biomass gain, associated with intense absorption of toxic compounds.

Although *P. stratiotes* is able to accumulate As, the severe damages caused by this pollutant compromise its growth and metabolism, which limit its use in phytoremediation. In this context, the search for strategies capable of mitigating damages and increasing the phytoremediative capacity of aquatic macrophytes becomes a necessity. The aim of the work was to evaluate the effect of nitric oxide (NO), signaling molecule in response to abiotic stresses, in the processes of arsenic absorption and tolerance of *P. stratiotes* plants. In order to evaluate the effect of NO on the absorption of the pollutant, absorption kinetics traits were determined, with the plants being submitted to six As concentrations (0.0, 0.25, 0.5, 0.75, 1.0 and 1.5 mg L⁻¹), in the presence or absence of NO (supplied as sodium nitroprusside (SNP), 0.1 mg L⁻¹). To evaluate the effect of NO on plant tolerance to As were measured the growth rate, photosynthesis, respiration, photorespiration, and hormonal profile.

The influx of As showed a linear increase with the enhance of As concentration in the solution. The absorption kinetics of As was adequately described by the Michaelis-Menten equation. Based on the characteristics of the absorption kinetics, *P. stratiotes* revealed a phytoremediation potential for As, since the observed Km was much lower than that recorded for other plant species, indicating an efficient absorption system of As. Km and Vmax were not modified by the presence of NO.

The absorption of As by the plants decreased the growth rate and triggered changes in the primary processes of the plants. While photosynthesis and photorespiration showed sharp decrease, the respiration process increased, probably due to chemical similarity between arsenate and phosphate. The damages were attenuated by NO, which was able to reprogram the hormonal profile of the plants, with changes in the levels of auxin, ethylene, ABA and salicylic acid. Hormonal reprogramming was reflected on plant physiology with restoration of photosynthetic rate and growth, while the photorespiration rate decreased. Thus, although NO did not alter As absorption patterns, it was able to increase tolerance of the plant to the pollutant. The higher growth rate and tolerance might allow the plants to maintain the systems of As absorption active for longer periods, with a consequent increase efficiency in the phytoremediation process.

Barium tolerance, phytoextraction capacity and resprouting ability of aquatic macrophytes in barium polluted flooded soils

*Douglas Gomes Viana*¹; *Cássio Francisco Moreira de Carvalho*; *Fábio Ribeiro Pires*; *Robson Bonomo*; *Fernando Barboza Egreja Filho*; *Alberto Cargnelutti Filho*; *Luiz Fernando Martins*²; *Mauro César Pinto Nascimento*³; *Leila Beatriz Silva Cruz*³

¹ Federal University of Espírito Santo; ² PETROBRAS/CENPES|Biotechnology Management; ³ Petrobras|Environmental Engineering area, BR

Barium (Ba) is very common in effluents from petroleum industry, including water associated with oil production and drilling liquid wastes. In the first case, Ba comes from the oil reservoir, while in the latter its presence derives from the use of barite (BaSO₄) to adjust drilling fluid density. Thus, inappropriate disposal or spills of such effluents may cause the soil to become barium polluted. Because barite solubility in water is very low, its presence in soil is generally supposed not to pose critical environmental risk. In case of flooded soils, however, there is concern because anoxic conditions may increase barite solubility and, consequently, favor Ba²⁺ releasing. For reclamation in this scenario, a phytoremediation approach based on Ba accumulator macrophytes could be very advantageous since it would provide Ba removal avoiding economic and environmental issues with soil excavation and disposal. The purpose of this study was to evaluate Ba tolerance, Ba phytoextraction capacity and resprouting ability of three aquatic macrophytes: *Eleocharis acutangula* (Roxb.) Schult. *Cyperus* cf. *papyrus* L. and *Typha domingensis* Pers. The experiment was carried out in a greenhouse, completely randomized, with four replicates. Plantlets were transferred to pots with 15 kg soil each and exposed to five Ba concentrations (established with BaCl₂): 0; 150; 500; 1000 e 2000 mg kg⁻¹. Every pot was maintained with a thin water film over soil surface to simulate a flooded area. The plants were cultivated over three successive 120-day growth cycles; at the end of each cycle, shoots were harvested and allowed to resprout. Barium content was determined in harvested plant shoots from every growth cycle and in plant roots and soil at the end of the experiment. Biometric analyses were performed as well. Plant biomass production was expressively affected only at 1000 and 2000 mg kg⁻¹ Ba, but inhibition magnitude was unequal for every plant species. For *C. cf. papyrus*, there was almost no growth at the highest Ba dose; *T. domingensis* was more Ba sensitive than *E. acutangula* at the first growth cycle. In the last *T. domingensis* growth cycle, the difference between dry biomass results at 1000-2000 mg.kg⁻¹ Ba and 500 mg.kg⁻¹ Ba was lower than the ones observed in the previous cycles. This was probably a consequence of the efficiency of *T. domingensis* to extract Ba from soil and translocate it to the shoot; indeed, *T. domingensis* reached the highest Ba translocation factor. Therefore, as *T. domingensis* aerial biomass was being harvested, more Ba was being removed from soil. *E. acutangula* showed the highest Ba extraction value, but it was not efficient as *T. domingensis* in exporting Ba to the shoots. *E. acutangula* was the most Ba tolerant and the one with highest resprouting ability, while *C. cf. papyrus* hardly produced some biomass at the last growth cycle. In conclusion, *T. domingensis* and *E. acutangula* are tolerant to high Ba concentrations in soil and have potential to remediate Ba polluted soils with a phytoremediation strategy based on periodic shoot harvest and resprouting.

Use of cereal crops in phytoremediation of As-polluted soils. Effect on plant physiology

Agueda González; Mar Gil-Díaz; Juan Alonso; MC. Lobo

IMIDRA, ES

Soil contamination due to the present of metals and metalloids such as As is a concern of increasing importance due to its high toxicity to biota. Phytoremediation is an emerging green technology for soil remediation which uses the ability of plants to extract soil pollutant and translocate them to harvestable parts. Using crop plants for phytoremediation takes advantage of their ability to produce large amounts of biomass, rapid growth, and adaptability to different environmental conditions. However, to be effective the plants must be tolerant to pollutants and accumulate significant amounts of toxic elements in their tissues. Cereal crops, as wheat and barley, produce a lot of biomass, have a quick and easy crop growth, and so are increasingly interesting for moderately contaminated soil remediation.

To evaluate the potential phytoremediation ability of cereal crops, a greenhouse experiment was carried out, using plants of barley (var. Pedrezuela) and wheat (var. Albares) at different As concentrations: 0, 40 and 80 mg/kg. Ten pots per treatment and two plants per pot were used. The biomass and As concentration in the different parts of the plant were determined at the end of the growing cycle. In addition, chlorophyll content, chlorophyll fluorescence, and relative water content (RWC) were analyzed during the plant-growing period.

The obtained results showed that As was mainly accumulated in roots for both cultivars, being the As concentration dose-dependent. The metalloid affected plant physiology, decreasing its photosynthetic activity and growth. The plant water content, biomass, chlorophyll content and chlorophyll fluorescence were also reduced at increasing As doses. A significant correlation ($p < 0.001$) between the chlorophyll content and chlorophyll fluorescence and the dry biomass was found.

Both cultivars could be used for soil phytoremediation when As concentration was below 80 mg/kg, since the plants were able to complete their growing period at the experimental conditions. The tolerance index of Albares was higher than the Pedrezuela one, although Pedrezuela showed a higher osmotic adjustment and produced more biomass. In this sense, barley would be more effective in As-polluted soil remediation.

Keywords: Barley, wheat, chlorophyll, biomass, tolerance.

Acknowledgements. Projects FP-16-RESIDUA (IMIDRA, Comunidad de Madrid, Spain), CTM2016-78222-C2-1-R (MINECO).

Phytoremediation of aquatic environments contaminated with arsenic: is it possible to increase the tolerance of plants to the pollutant?

Paulo Eduardo Menezes-Silva¹; Juraci Alves de Oliveira; Fernanda Farnese; Adinan Alves da Silva; Fernanda Vidal de Campos

¹ Instituto Federal Goiano, BR

Contamination of water used for human consumption with arsenic (As) is a problem of global proportions, with implications for biodiversity conservation and human health. The increase of As concentrations in the aquatic environment results from the direct dumping of residues in the water courses or the anthropic activities that release the As present in the soil, thus allowing the element to be drained and reach water bodies. Among the several methods that aim to remove As from the environment, one of the most promising is phytoremediation, an efficient low cost technique which does not lead to environmental damages.

Recent studies have indicated that *Pistia stratiotes* presents the ability to accumulate high concentrations of As. However, the intense damage caused by the pollutant, such as the increase in the generation of reactive oxygen species (ROS), leads the roots to fall and render the phytoremediation process unfeasible. Based on these facts, the present work aimed to evaluate the influence of a signaling molecule, the nitric oxide (NO), on the tolerance of plants to As. For this, *P. stratiotes* plants were exposed to four treatments: control (nutrient solution); NO (supplied as sodium nitroprusside (SNP); 0.1 mg L⁻¹); As (1.5 mg L⁻¹) and As + NO (1.5 and 0.1 mg L⁻¹, respectively). The rate of As uptake, ROS generation, antioxidant enzymes activity and the metabolic profile of the plants were evaluated.

The plants exposed to As were able to absorb, translocate and accumulate large amounts of the pollutant in the leaves, essential characteristics for phytoremediation programs. The plants submitted only to As, however, presented high levels of ROS. The NO was able to attenuate this damaging effect of the pollutant, and no changes were observed in ROS concentration, although the plants accumulated the same amount of pollutant. The elimination of excess ROS resulted from the effect of NO on the antioxidant metabolism of *P. stratiotes*, with increases in the activity of superoxide dismutase, catalases, glutathione peroxidases, glutathione reductase and glutathione sulfotransferases. The analysis of the metabolic profile of *P. stratiotes*, in turn, showed a marked metabolic reprogramming of the plants in response to As and NO, as 82.22% of the analyzed metabolites had their levels changed in As + SNP treatment. The most significant responses were the reductions in the levels of amino acids and polyols, indicating the consumption of these molecules during cellular defense reactions. Alterations were also observed in the levels of intermediates of the citric acid cycle and in several antioxidants, such as 4-hydroxybenzoic (4-HBA) and hexadecanoic acids. This metabolic reprogramming resulted in an increase of 47% in the tolerance index to As when the plant were exposed to the pollutant in combination with NO. Based on these results it is possible to conclude that NO had a global action on the metabolism of *P. stratiotes*, allowing the reprogramming and integration of primary and secondary metabolism. These data are important as they provide the basis for the development of methodologies aimed at improving As phytoremediation programs.

Assessment of two rice cultivars (*Oryza sativa* L.) for phytoremediation of barium polluted flooded soils

*Fábio Ribeiro Pires*¹; *Paulo Roberto Cleyton de Castro Ribeiro*; *Douglas Gomes Viana*; *Fernando Barboza Egreja Filho*; *Robson Bonomo*; *Alberto Cargnelutti Filho*; *Luiz Fernando Martins*²; *Mauro César Pinto Nascimento*³; *Leila Beatriz Silva Cruz*³

¹ Federal University of Espírito Santo; ² Petrobras Research and Development Center (CENPES); ³ Environmental Engineering area of Petrobras (E&P-UO-ES/SMS/MA), BR

Barite (BaSO₄) is a key component in oil well drilling fluids. Thus, inappropriate disposal of such fluids could increase barium (Ba) concentration in soils. The low water solubility of barite (2,47 mg L⁻¹ at 25 °C) would make environmental risks practically negligible, however, low redox potential (-200 mV) in soil may change barite solubility due to several electrochemical, physical and biological processes. Therefore, flooding conditions can favor Ba²⁺ releasing from barite in soils, increasing Ba bioavailability. In this scenario, an intervention to remove Ba might be necessary and a phytoremediation scheme with Ba accumulator plants could be suitable to reach that goal. The objective of this study was evaluating two rice genotypes on Ba tolerance and capacity of extracting Ba from flooded soils. The two genotypes – *Oryza sativa* IRGA 424 and *O. sativa* BRS Tropical – were grown in pots with 13 kg soil each and exposed to six Ba concentrations (established with BaCl₂): 0,0; 2,5; 5,0; 15,0; 30,0 e 65,0 mg kg⁻¹. The experimental design was completely randomized, with three replications. A thin water film (~1.0 cm) was maintained over soil surface along the whole experiment, which lasted for four months. Biometric and chemical analyses were performed throughout the experiment, including Ba²⁺ accumulation in shoots and roots (USEPA 3051 - ICP OES). Results were submitted to Analysis of Variance, followed by Scott Knott test ($p < 0,05$), using the software SISVAR 5.3 Build 77. Both rice genotypes presented similar plant height and foliar area results and showed no severe symptoms of phytotoxicity, even at the highest Ba dose. Moreover, the higher the Ba dose in soil, the higher the Ba content in the plants (either shoot or roots) of both genotypes. Nonetheless, such increase in plant Ba content was not great enough to consider them as hyperaccumulators. Shoot dry matter did not differ between the two genotypes, as well as shoot Ba content. However, BRS Tropical produced more roots dry matter than IRGA 424, which probably explained the higher amount of Ba in BRS Tropical roots than in IRGA 424 ones. In conclusion, both rice genotypes showed to be tolerant to the Ba levels applied in this study, yet their Ba extraction capacity make them unfeasible to be used in a phytoremediation process.

Effect of reduced graphene oxide on *Pseudomonas putida*, microorganisms in activated sludge and human lung epithelial cells

*Nhung H. A. Nguyen*¹, *Petra Rosická*¹, *Valentina Castagnola*², *Margarita Esquivel-Gaón*², *Tomáš Lederer*¹, *Alena Ševců*¹

¹Technical University of Liberec, Institute for Nanomaterials, Advanced Technologies and Innovation, Liberec, Czech Republic,

²University College Dublin, School of Chemistry and Chemical Biology, CBNI - Centre for BioNano Interactions, Dublin, Ireland

Graphene oxide (GO) and reduced graphene oxide (rGO) have attracted interest in many applications such as in electronic devices, energy storage devices, biosensors, biomedical applications, coating technologies, composites and paper-like materials. Due to their widespread application, toxicity of the materials should be evaluated before releasing them into the environment or to users. We studied the toxicity of rGO in different dispersants: deionized water (DI), Fetal Bovine Serum and Petronas based oil (ETRO4). We tested effect of 100 mg L⁻¹ of rGO on 1) soil bacterium *Pseudomonas putida* (growth rate, morphology and apoptotic DNA fragmentation); 2) natural microbial community from activated sludge (respiration activity of nitrifying microorganisms) and on 3) human lung epithelial cells A549 (cell viability, lysosomal activation, membrane integrity). We exposed *P. putida* to rGO for 6h and 24h, nitrifying microorganisms for 48h and lung epithelial cells for 24 and 72h. Behaviour of rGO particles in a bacterial growth medium was analysed using differential centrifugal sedimentation. rGO particles originally dispersed in serum were more stable in bacterial growth media than particles originally dispersed in DI. The commercial oil ETRO4 alone slightly affected *P. putida* at concentration of 0.34 mg L⁻¹ and caused problems with exchanging of the gases between microorganisms from activated sludge and air during respirometry measurement. There was neither found significant negative effect of rGO on *P. putida* nor on nitrifying microorganisms at 100 mg L⁻¹. Similarly, no significant decrease was observed in the viability of the human lung epithelial cells up to 100 mg L⁻¹, lysosomal activity was increased in a concentration dependent manner suggesting the activation of endocytic pathways.

3e. Nanoremediation

Impact of the presence of a natural biofilm on mobility and reactivity towards tetrachloroethylene (PCE) of nZVI used for Nanoremediation

Marc Crampon¹; Jennifer Hellal; Caroline Michel; Christophe Mouvet; Guillaume Wille; Patrick Ollivier

¹ BRGM, FR

Remediation techniques for toxic/persistent contaminants in groundwater are often technologically difficult. Nanoparticles (NP) like nZVI (Zero-Valent Iron) applicable as in-situ reduction or oxidation agents for groundwater treatment give promising results. This study aims to evaluate the mobility and the reactivity towards PCE, a frequent groundwater contaminant, of nZVI in the presence or absence of biofilm by column assays mimicking aquifer conditions.

Biofilms were grown on sand using environmental groundwater samples as inoculum in nitrate reducing conditions. For mobility assays, suspensions of nZVI were injected into the columns and the outlet Fe concentrations monitored. Biofilm-nZVI interactions were characterized using SEM/STEM observations of sand after the NP breakthrough. Biofilms were further characterized using molecular approaches. For reactivity experiments, three columns were used to study the impact of the presence of a biofilm and of nZVI on the dechlorination of PCE in the nZVI reactive zone.

The predicted travel distances of nZVI are found to be 1.5 to 25 m for a 10 m d⁻¹ flow. The presence of biofilm in the column decreased the total porosity of column from around 30% to around 15%. Though the recoveries of nZVI at the column outlet in the presence or absence of biofilm were similar, the analysis of the sand suggested nZVI-biofilm interactions (correlation TOC vs Fe concentrations, presence of aggregates). These interactions are confirmed by the SEM/STEM observations. Concerning reactivity experiments, it appeared that the dechlorination of PCE was slightly higher in the absence of biofilm (65% of PCE transformed into Cl⁻ vs 60% in the presence of biofilm), but anaerobic corrosion, characterized by evaluating the formation of H₂ within the porous media, was greatly diminished in the presence of biofilm, suggesting (i) interactions between nZVI and biofilm, and (ii) a better longevity of nZVI in the presence of biofilm, and thus a better reactivity towards contaminant over time.

It appears finally that reactive NP, even if they can represent a source of emerging contamination, are very useful for in situ groundwater treatment. However, the presence of biofilm in the porous media could modify the mobility and reactivity of nZVI and should be considered when designing a nanoremediation treatment.

In situ application of nano zero-valent iron (nZVI) for reducing mobility of As and Hg in a brownfield.

Mar Gil-Diaz¹; Juan Alonso¹; Eduardo Rodríguez-Valdés²; José Luis R. Gallego³; MC. Lobo¹

¹ IMIDRA; ² Universidad de Oviedo; ³ Universidad de Oviedo, ES

Mining and metallurgy are important sources of anthropogenic soil pollution. The mine "El Terronal" (Asturias, Spain) was the second largest Spanish Hg producer between the 1960s and the early 1970s, and it also produced As compounds. The environmental effects of site pollution are considerable after 40 years of weathering, which came to the attention of EU environmental bodies. Mining waste occupies the bottom of a valley, with the risk of diffusion of As and Hg by infiltration and leaching. In the last few years, the use of nanoscale zero-valent iron (nZVI) to immobilize metal(loid)s in contaminated water and soil samples has resulted effective. Studies at lab scale have shown that nZVI can reduce As availability in polluted soil. Therefore, long term studies at field scale which evaluate the effectiveness of the nanoremediation process, its stability and the potential adverse effects are lacking. This work aims to evaluate the effectiveness of nZVI to immobilize As and Hg in two zones of the "El Terronal" brownfield at field conditions, as well as, the stability of the immobilization. Two zones inside the brownfield were studied (A, B) because of the heterogeneity of metal(loid) concentration, especially for As. Arsenic and Hg mean concentrations in A zone were 25,900 and 2,900 mg/kg, respectively, and in zone B, 70,200 and 2,800 mg/kg. Plots of 5 m² were treated with nZVI (Nanofer 25S, NANO IRON, Czech Republic) at the dose of 2.5%. Soil samples at 0, 72 hours, 1, 2 and 8 months were collected. The availability of As and Hg was evaluated according to the TCLP test (USEPA 1311) and the most bioavailable fractions of the Tessier sequential extraction procedure (exchangeable (EX) and carbonates (CB) fractions).

Arsenic and Hg were mainly in RS fraction. The nanoremediation treatment decreased the As and Hg availability in both zones of the brownfield after 72 hours of the treatment. The immobilization remained stable at least for 8 months. The best immobilization results were obtained in zone A, whereas in the zone B, which showed the highest concentration of As, the application of nZVI showed less immobilization percentages. This fact suggests the need to apply a higher dose of nZVI in this zone. Thus, the effectiveness of the metal(loid)s immobilization with nZVI strongly depends on pollutant concentration and soil properties. In the study conditions, the application of nZVI could be an adequate remediation strategy for this brownfield.

Keywords: nanoremediation, iron nanoparticles, availability, field experiment

Acknowledgements. Projects CTM2016-78222-C2-1-R (MINECO), FP-16-NANOREMED (IMIDRA, Comunidad de Madrid, Spain).

Testing of an in situ adsorptive barrier of iron oxide nanoparticles for dissolved arsenic removal, in Asturias, Spain

Nerea Otaegi¹; Ekain Cagigal¹; Rainer Meckenstock²; Vitor Correia³

¹ Tecnalia Research & Innovation; ² Universitaet Duisburg-Essen; ³ Geoplano - Consultores, SA, ES

The efficiency of a novel water nanogeotechnology for the immobilization of toxic metals in groundwater is currently being tested under real scale conditions, as part of the REGROUND “Colloidal iron oxide nanoparticles for the reclamation of toxic metal contaminated groundwater aquifers, drinking water wells, and river bank filtrations” project (funded by European Union’s H2020 research and innovation programme, project no641768). The basic concept of the technology is the creation of adsorptive in situ barriers for the immobilization of heavy metals contamination in groundwater. This barrier is made of customized iron oxide nanoparticles (NPs), which are injected into the aquifer as colloidal suspension, forming stable deposits there. In contrast to previously used nanoparticles (e.g. nZVI NPs), which have low mobility and often are transformed and lose their capacity to adsorb contaminants, Reground NPs are fairly mobile and have shown great transport and adsorption potential in aquifer materials in laboratory. Now, two industrial sites have been selected for the field-scale application of the technology; one in Portugal and one in Spain. The Spanish test site is an abandoned 20Has brownfield in Asturias (Northern Spain), used historically for the production of fertilizers during 48 years (1950 – 1998). Contaminants include predominantly heavy metals both in soil and groundwater. Metals are associated to fill materials, pyrite ashes and furnace slags used historically to level the ground; whereas in groundwater, leaching processes from contaminated fill result in high levels of dissolved arsenic, lead, copper, cadmium and zinc. Solved arsenic has been selected as the target contaminant to be treated with NPs, given its high groundwater concentration at this particular site and the global environmental and health impact associated to it, particularly in developing countries. Still, the study also considers the effects of the treatment on the other metals. On the 25th June 2016 a first small scale field application was performed at the Spanish test site. In total, 30m³ of 1:10 diluted NPs suspension were injected at a low pressure (<2bars) and a general flow rate of 30l/min. The injection is followed by a 6 months period of detailed groundwater monitoring (June - December 2016). Groundwater monitoring is currently ongoing and includes hydraulic-slug tests, periodic sampling and water levels and basic geochemical parameters measurement. Results, including technology’s effectiveness and NPs migration, obtained from the first small-scale application will be made available at the beginning of 2017 and they will serve as the basis for the in situ adsorptive barrier design and implementation expected in April 2017. At final stages of the project the technology assessment will consider its overall sustainability, including not only technical but also economic and social aspects evaluation. This is of particular importance taking into account the market readiness of the technology. The REGROUND project started on the 1st September 2015 and has a total duration of 36 months.

Magnetic Porous Carbon Materials Derived from Biomass With High Remediation Ability

Eleni Petala^{1,2}, Yiannis Georgiou³, Vasilis Kostas², Konstantinos Dimos², Michael A. Karakassides², Yiannis Deligiannakis³, Claudia Aparicio¹, Jiří Tuček¹, Jan Filip¹, Radek Zbořil¹

¹ Regional Centre of Advanced Technologies and Materials, Departments of Physical Chemistry and Experimental Physics, CZ,

² Department of Materials Science and Engineering, University of Ioannina, GR, ³ Physics Department, University of Ioannina, GR

In the present work, an investigation of the iron-catalyzed graphitization of various kind of biomass was performed. The mechanism of the gradual conversion of biomass into magnetic porous carbon materials was thoroughly studied. Magnetic porous carbon materials (MPCs) have been synthesized via a simple, cost-effective and environmentally friendly way using biomass, e.g. pine resin and sawdust, and iron nitrate salt as a carbon and iron source, respectively. The materials were prepared by carbonization of biomass and iron nitrate at 1000 °C in inert atmosphere (iron acts both as a precursor for magnetic species and as a catalyst for the graphitization process). The mechanism of formation of such materials was revealed by analyzing all the intermediate steps (there were obtained and investigated various materials involving heating of the same precursors at different temperatures below 1000 °C). MPCs have significant surface area (177 m²/g) with both micro and mesoporosity. It has been noticed a homogeneous distribution of core-shell-type magnetic nanoparticles surrounded by few graphitic layers-walls, dispersed within the carbon matrix. Magnetic nanoparticles of 20-100 nm found to consist of iron carbide and metallic iron while carbon is in graphitic form as it was estimated by means of microscopy and spectroscopic techniques. MPCs materials were tested on various water treatment scenarios. They have exhibited a significant remediation ability towards various pollutants, e.g. towards arsenite, hexavalent chromium and methylene blue in a fast and simple route. For instance, it has estimated a maximum capacity of more than 200 mg of arsenite per gram of MPCs within 24 hours. Hence, MPCs exhibits the potential of converting biomass into advanced materials in an easy and environmentally friendly way with superior toxic compounds removal capacity. They can be considered as excellent candidates for a wide range field of water treatment technologies.

Methodology of laboratory tests for the support of the reactive properties of zero-valent iron nanoparticles by the application of direct current

Kristýna Pešková¹; Jaroslav Nosek; Lucie Cádrová

¹ Technical University in Liberec, CZ

The submitted paper presents the methodology of laboratory tests for the increasing of effectivity of the reactive properties of zero-valent iron nanoparticles (nZVI) by the application of direct current (DC). The saving of reactive agent and prolongation of longevity of nanoparticles in the subsurface are the main advantages of DC application, which make the in-situ chemical reduction by nZVI considerably more economical. For the purpose of reactivity monitoring were chosen the tests in the continual reactors and were performed with real water from sites contaminated mainly by chlorinated ethenes. The advantage of these reactors arrangement is the possibility to continuously monitor the course of chemical reaction after the application of a remediation agent. The reactors with contaminated water are directly connected with the gas chromatograph with flame ionization detector. This experimental set-up enables to measure the intermediates and the end products of dehalogenation of chlorinated hydrocarbons, as ethen, ethan. The direct measurement enables the process optimization and understanding of degradation mechanism by using of the process of reductive dehalogenation by nZVI and DC.

The application and behaviour of nZVI during the treatment of chlorinated hydrocarbons in the field test at Spolchemie site

Vojtech Stejskal¹; Jan Slunský²; Tomáš Lederer³; Jürgen Braun⁴

¹ Technical University of Liberec, CZ; ² NANO IRON, s.r.o.; ³ Aquatest a.s.; ⁴ University of Stuttgart, DE

The main aim of this study is a verification of migration characteristics and remedial efficiency of the new type of nZVI using advanced procedures for monitoring both ZVI nanoparticles and vertical stratification of contamination, including detail water and soil sampling after infiltration.

The Spolchemie site was chosen as one of the NanoRem project case study sites, to test zerovalent iron nanoparticles (nZVI) for in situ remediation of chlorinated hydrocarbons. Spolchemie is one of the leading synthetic resin manufacturers in Europe, located at Usti nad Labem (Czech Republic) in the heart of Europe. The production, treatment, storage and distribution of various raw materials and products has led to extensive contamination by chlorinated ethenes and methanes, which in many cases have dispersed widely from the original source areas.

The test site is contaminated only by chlorinated hydrocarbons installed permeable reactive barrier, but recent part of contamination overflowed this wall is solved by nZVI application. This new contamination is the subject of Nanorem field test using two different types of ZVI NPs as crucial agents (NANOFER 25S – 200 kg in November 2014 and NANOFER STAR – 300 kg in October 2015, both NANO IRON, s.r.o., Czech Republic).

A number of groundwater monitoring campaigns has been undertaken followed by a preliminary site investigation. Based on this work a conceptual site model (CSM) has been developed detailing the subsurface conditions followed by a preliminary risk analysis. This initial CSM was refined by further targeted investigation and subsequent updating of the risk analysis. This work indicated that remediation requirements would be complex. With further funding being secured, the CSM was expanded following delineation of the contamination, geological and hydrogeological surveys, well logging, development of a hydrogeological model of the site and a remediation feasibility study. Exploration of the site is still ongoing to further improve the conceptual site model and review further the most appropriate overall remedial strategy.

At Spolchemie, injection equipment, particle suspensions preparation and procedures have been set up; injections into six depths (contaminated horizons) by direct push were performed after detail monitoring using newly developed micropumps (VEGAS Stuttgart) installed into 5 position (5 depths). The pilot trials have been up and are running and the results were collected. The NanoRem partners involved in this trial are AQUATEST, NANO IRON, VEGAS Stuttgart, Technical university of Liberec and Palacky university in Olomouc.

nZVI nanoparticles are characterised with regard to their physical and chemical properties, their mobility and migration potential in the subsurface and their potential to cause harm (ecotoxicology).

Presented poster will summarize very positive results (e.g. 277 days lasting decrease of ORP or 222 days lasting contaminant reduction) from the first field test with NANOFER 25S and will present also results of the second nZVI injection (NANOFER STAR).

Simulation of the NAPL source zone remediation by injecting nZVI suspensions: application to PCE remediation

Christos Tsakiroglou¹; Alexandra Sikinioti-Lock; Katerina Terzi

¹ Foundation for Research and Technology, GR

Among the various nano-materials explored for remediation, the nanoscale zero-valent iron (nZVI) is currently used widely for the in situ remediation of aquifers from a variety of toxic pollutants (e.g. reduction of chlorinated hydrocarbons, and nitro-aromatics, sorption/geochemical trapping of heavy metals/metalloids). The macroscopic modeling of nanoparticle transport during their injection in porous media is of key importance for the interpretation of lab-scale tests and design of efficient field-scale applications. Although extensive work has been done on the simulation of nZVI transport and immobilized nZVI interactions with NAPL and dissolved species, there is a lack of numerical models coupling the multiphase transport with reactive processes during the continuous injection of nZVI in porous media partly saturated with NAPL (chlorinated hydrocarbons) ganglia. In the present work, a macroscopic numerical model of reactive nZVI flow in porous media is developed by using the software platform of ATHENA Visual Studio.

First, the nano-colloid transport in a porous medium is simulated by using the model of Tosco et al., (2014). The model is based on a modified advection-dispersion equation by accounting for chemically (attachment/detachment, blocking, and ripening), physically (mechanical filtration), and physicochemically (straining) induced mass transfer between the liquid (suspended nZVI particles) and solid (porous medium grains) phases. The numerical code is used to perform a sensitivity analysis, and elucidate the effects of process dimensionless parameters (Peclet number, Dimensionless velocity, Damköhler number for particle deposition) on the transient response of nZVI concentration in effluent. With inverse modeling of experimental results, the parameters describing the kinetics of nanoparticle attachment / detachment in a glass-etched pore network are estimated.

Afterwards, the transport model is extended to reactive flows by including mass balances for residual NAPL saturation (source zone), and dissolved pollutant concentration (aqueous phase), and accounting for NAPL dissolution and nZVI/dissolved pollutant reactions. The kinetics of reactions in aqueous phase is provided by an analytic phenomenological model, resulting from the fitting of a statistical shrinking-core model to batch reactivity tests, and expressing the overall reaction rate of dissolved tetrachloro-ethylene (PCE) as a function of PCE and nZVI concentrations. A sensitivity analysis is performed with the extended model to clarify the effects of dimensionless parameters (Sherwood number, Dimensionless velocity, Damköhler number for reactions), quantifying the interactions of nZVIs with dissolved PCE and NAPL ganglia, on remediation efficiency. Experiments of nZVI injection in a glass-etched pore network and a soil column partially saturated with trapped ganglia of tetrachloro-ethylene (PCE) are employed to evaluate and calibrate the model.

Literature

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The impact of nano-scale and micro-scale zero-valent iron particles on planktonic microorganisms in reservoir water

Nhung H.A. Nguyen¹, David Ribas², Iva Dolinova¹, Denisa Vlková¹, Roman Špánek¹, Hana Řeháková¹, Hana Pohlreichová¹, Daniela Myšáková¹, Pavel Kejzlar¹, Alena Ševců¹

¹Institute for Nanomaterials, Advanced Technologies and Innovation, Technical University of Liberec (TUL), Czech Republic,
²Department of Chemical Engineering, Technical University of Catalonia (UPC), Spain.

Nano-scale and micro-scale zero-valent iron (nZVI and mZVI) materials have shown high potential for the remediation of polluted soil aquifers and groundwaters. However, these particles have been reported to be toxic to bacteria and other microorganisms in cell cultures. The objective of this study was to assess the impact of 100 mg/L of nZVI and mZVI on the planktonic microorganisms from Harcov reservoir. Concretely, bacterial biomass was determined using 16S rRNA gene and the number of cultivable cells and the dominant species of phytoplankton along with cell counting were determined after 0, 1, 3, 7, 14 and 21 days. In addition, the bacterial community structure was also investigated by Next-Generation Sequencing (NGS). Changes in the reservoir water chemistry were also monitored. nZVI particles caused a rapid decrease in oxidative reductive potential (from +200 to – 136 mV) and dissolved oxygen concentration (from 9.2 to 2.3 mg/L) after 1 day. Both gradually increased after 3 days and stabilized during the experiment. Interestingly, the number of cultivable bacteria increased significantly after 3 days and even more after 7 days ($P < 0.0001$), while the total bacterial abundance was comparable to the control. The NGS results are still being analysed. The algae were slightly affected by nZVI only at day 7 ($P = 0.04$), while the cyanobacteria were stable over 21 days. Surprisingly, mZVI did not have any effect on bacteria or algae, but the number of cyanobacteria doubled after 7 days. We also observed that nZVI was oxidized after 3 days and mZVI after 7 days. Bacteria and cyanobacteria might profit from the bioavailable oxidized iron and increase their abundance.

3f. Stabilization techniques

Assessing natural clays of a contaminated site to stabilize and reduce the ecotoxicity of a coal tar

Nicolas Fatin-Rouge¹; Julie Brand²; Annette de Vaufleury³; Rachida Bamze Attoumani³; Nadia Crini³; Stefan Dragos Gaitanaru⁴; Ioan Bica⁴

¹ University of Bourgogne Franche-Comté; ² Université de Franche-Comté, UMR 6213-UTINAM; ³ Université de Bourgogne Franche-Comté; ⁴ University of Bucharest, FR

Coal tars are waste materials originate from various industrial activities. They are hazardous and persistent liquid substances that contain a high fraction of toxic compounds such as polycyclic aromatic hydrocarbons (PAHs), benzene derivatives and phenols. Pollutions are often the result of accidental spills from tanks resulting in non-aqueous phase liquids (NAPLs). On the ground, unconfined tars represent a risk for health by physical contact and the release of toxic volatile compounds. These NAPLs are also a permanent threat for groundwater.

Possible management options are limited because of the restricting regulation on PAH containing wastes. The most obvious are incineration above 800°C for energy production in cement kilns, disposal in landfills and on-site oxidation. Their management often requires their handling and thus their solidification/stabilization (S/S). Sawdust is largely used when incineration is selected, but it does not reduce the emissions of hydrocarbons in the atmosphere. Then, huge volumes of foul-smelling and highly contaminated material must be transported. Since the immobilization of liquids occurs mainly through capillary trapping and adsorption, the use of pulverulent natural materials like clays is a way to be explored.

Contaminant mobility and their toxicity are critical points when considering management options of coal tars. S/S is a fast process that uses additives to prevent the release in the environment of contaminants from hazardous wastes. S/S has been found the best remediation strategy for source zones of PAHs contamination on the basis of sustainability of technologies. Therefore, it is known that S/S is less compatible with organic liquid wastes as they are held by physical mechanisms. Moreover, they may prevent reaction between binder's particles to make hard materials because of dewatering their surfaces. It was shown that the use of hydraulic binders used to develop strength, like Portland cement, are unable to prevent PAHs leaching when directly mixed with contaminated materials. The use of hydrophobic clays to immobilize hydrophobic compounds is expensive because of the costs of surfactants used to change their surface properties.

The present work aims investigating the possibility of using natural clay widely available onto a contaminated former site to stabilize the liquid coal tar. The effect of clay addition on stabilization of the waste was studied considering mobility of the pure phase, leaching and evaporation. The ecotoxicity of the coal tar and coal tar-clay mixture was assessed using aquatic and terrestrial molluscs. Effect of the coal tar at various stages, i.e. crude or mixed with clays, after evaporation or incineration, was assessed with an ex situ bioassay using the land snail *Helix aspersa aspersa*. Measured endpoints were survival, fresh mass variation, behaviour. At the end of exposure, internal have been analysed to characterize bioaccumulation potential of PAHs in snails and possible mechanisms involved in toxicity. Finally several management modes of the stabilized wastes are discussed considering their physicochemical and ecotoxicological properties and site conditions.

Innovative Formulations for Reductive Adsorption and Precipitation of Heavy Metals using Elemental Iron, Iron Sulfides, and Related Reactive Minerals

Michael Mueller

PeroxyChem, AT

New applications of in situ chemical reduction (ISCR) have been developed for treatment of heavy metals. ISCR has been broadly applied to treat soil and groundwater contaminated with chlorinated organics. The mechanisms involved are well understood and widely recognized in the environmental remediation community. ISCR is defined as a category of in situ soil and groundwater remediation technologies in which treatment occurs primarily by chemical reduction of contaminants, and mediated primarily by abiotic processes.

More recently, it has been recognized that innovative forms of ISCR can be effective for removal of soluble heavy metals from soil and groundwater. The major groups of reductants operative in such treatments include (a) elemental or zero-valent iron (ZVI), (b) minerals that derive reducing power from Fe⁺² (magnetite and ferrous clays), (c) minerals that derive reducing power from reduced S⁻ or S⁻² either alone or in combination with Fe⁺² (iron sulfides), and (d) organic matter containing redox-active functional groups (quinines). A significant advantage of the ISCR approach is that it can be effective in applications where both chlorinated solvents and heavy metals must be treated.

The authors will present a survey of ISCR materials and mechanisms as applied to treatment of a wide range of common heavy metal impacts found in soil and groundwater. Content will focus on the evolution of scientific concept over the past 3 years, including short case studies which address Chromium, Lead, Mercury and Nickel impacts.

3g. Combined treatment technologies and technology trains

Advanced Oxidation Processes for Wastewater Reclamation and Reuse

Feryal Akbal; Emre Burcu Özkaraova; Ayşe Kuleyin; Seda Çoruhlu; Ayşe Ceylan

Textile industry is one of the major consumers of water and largest sectors causing intense water pollution. Textile effluents contain a large variety of raw materials and reagents: synthetic dyes, pigments, biocides, oils, heavy metals, salts, nutrients and organic compounds. Consequently, these effluents are characterized by high values of chemical oxygen demand (COD), temperature, colour, changeable pH, suspended solids and organic chlorine compounds. The physical, chemical and mostly biological technologies have been widely used to treat textile effluents. Afterwards, they are normally discharged into the sewer system. However, most of the organic matter in the effluent is not biodegradable and/or toxic, so that a biological treatment is inefficient. Moreover, physical and chemical treatment techniques are effective for colour removal but consisting only in a phase transfer of pollutants that requires additional treatment or disposal.

The advanced oxidation processes (AOPs) are a good alternative to treat the colored effluents, having the ability to decolorize the effluent completely and mineralize (total or partially) complex molecules in a relatively short reaction time. The AOPs are based on the generation of highly reactive species, which indiscriminately react with a large amount of compounds, at a high reaction rate. The most widely studied AOPs include: heterogeneous photocatalytic oxidation, treatment with ozone/H₂O₂ or ozone/UV, H₂O₂/UV process, Fenton and photo-Fenton type reactions. Among the different existing AOPs, the Fenton process arises as very promising and alternative wastewater technique that can be applied to the remediation of textile wastewaters, either alone or in combination with pre or post biological treatment. Persulfate oxidation (PS) has also proven to be a promising technique for the removal of refractory organic pollutants. The PS process is based on the production of strong reactive sulfate radicals (SO₄^{•-}) from peroxydisulfate, which is a strong and stable oxidizing agent and it has high aqueous solubility and high stability at room temperature as compared to hydrogen peroxide.

In the present study, the post-treatment of a biological treated real textile wastewater was carried out by means of Fenton and PS processes. The effect of the operating variables such as H₂O₂ and Fe²⁺ concentrations in the Fenton process and persulfate and Fe²⁺ concentrations in PS process has been studied. The effectiveness of the Fenton and PS processes were evaluated based on decolorization and COD reduction. It was observed that decolorization of textile wastewater was higher than mineralization, in terms of COD reduction. Both decolorization and mineralization, increased with increasing oxidant concentrations and oxidation times. The comparison between both processes was also performed in terms of remediation effectiveness.

Retention soil filter – an effective nature based technique for removal of micropollutants from wastewater treatment plant effluents

Andrea Brunsch¹; Ekkehard Christoffels; Thomas Ter Laak; Huub Rijnaarts

¹ Ertverband, DE

A Retention soil filter (RSF) is a vertical flow constructed wetland with event specific feeding. RSFs are used in parts of Germany to treat precipitation related overflows of combined sewer systems (diluted sewage) or of separate sewer systems (rain- and surface runoff water) to reduce emissions of N, P, C and heavy metals to surface water. In this study we present RSF as an additional treatment step at conventional wastewater treatment to remove micropollutants. Three pilot scale columns were installed at the outlet of a wastewater treatment plant and were fed with effluent. The reduction capacities of 147 micropollutants were monitored.

Each column has a filter surface of 1.5 m² and a volume of 1.4 m³. Two of the columns contain material from two different full-scale RSF, both in operation since 2005. Filter material is sand supplemented with CaCO₃ and organic matter material. Content values of organic matter of the full scale RSF initial material were 3 % (Filter 1) and 14 % (Filter 2) respectively. The third column (Filter 3) contains filter material and two extra additives: Biochar in the upper layer (0-10 cm) as well as granulated activated carbon (GAC) in the lower layer (60-90 cm). All three filters are planted with phragmites australis. Hydraulic retention time is 3.25 h. Operation of Filters 1 and 2 started in September 2014, of Filter 3 in April 2015. For aerobic conditions within the filter, feeding is set in alternating cycles of 28 h feeding and 56 h non-feeding. The feeding rate is 45 ml/s/m². Samples were taken regularly (Filter 1, 2 n = 37; Filter 3 n = 22) at inflow, outflows and in three depths within the filters. Additionally, the filter material itself was analysed for micropollutants in order to investigate accumulation and loads in the filter material.

Median reduction rates for 74 micropollutants were 39 % for Filter 1 and 50 % for Filter 2, as determined for each sampling campaign. Concentrations measured at the outflow of Filter 3 were in 99 % below limit of quantification. After one year of operation only Metformin and Amidotrizoic acid were measured regularly in the outflow. DOC reduction was 21 % at Filter 1, 24 % at Filter 2 and 96 % at Filter 3. Organic matter in the Filters 1 and 2, which is most present in the upper layers, was found to be positively related to the reduction rates. Measured concentrations in the material of the upper layer of Filter 1 were for Metoprolol 27 times and for 1H-Benzotriazole 15 times lower than weekly loading rates. This indicates that removal of Metoprolol and 1H-Benzotriazole in these filters is largely determined by transformation and not by sorption.

Reduction of micropollutants was best in Filter 3 containing biochar and GAC. Due to the high removal rates after 1.5 years of operation, long lifetime of this system is anticipated. Sorption and biodegradation contributions need to be further elucidated. The filters with conventional material (Filter 1 and 2) are attractive in removing micropollutants from effluents because biodegradation is the major removal mechanism of most of the substances. Therefore, the systems can be run for long times before renewing the filter material.

Treatment Train Targeting Chlorinated Solvents at an Active Pharmaceutical Site in the UK

Chris Evans

HBR Limited, GB

A treatment train approach was employed to address chlorinated hydrocarbons in challenging soil conditions, whilst working on an operational top-tier Control of Major Accident Hazards (COMAH) pharmaceutical facility. Remediation was undertaken to avoid off-site disposal as a means to minimise the client's carbon footprint and avoid importation of quarried material. Circa 11,500m³ of impacted soil was successfully remediated on-site using a combination of Anaerobic and Aerobic Bioremediation and Chemical Oxidation. Sustainability was maximised with 100% of excavated and treated soil reused on-site, providing a flexible development platform for site expansion of the facility. Works were undertaken on a voluntary basis to meet the client's exemplary Corporate Social Responsibility policy and to mitigate potential liabilities associated with future site development plans. Works were conducted between July 2015 and May 2016. AECOM acted as Principal Designer and Principal Contractor under Construction Design and Management Regulations 2015 and deployed works on the site under their Environmental Permit. HBR acted as specialist remediation sub-contractor. The ethos of the project was to form a collaborative project team operating under mutual trust and cooperation between all parties. PEROXYCHEM acted as remediation technology provider, delivering >110 tonnes of DARAMEND to affect a combination of abiotic chemical reduction, using micro-scale zero valent iron (ZVI), coupled with anaerobic bioremediation, and 10 tonnes of KLOZUR alkaline activated sodium persulfate as a chemical oxidation reagent. Key challenges were a function of the complex combination of contaminants, their differing catabolic pathways (VC – anaerobic/aerobic; 1,2 DCA – anaerobic, co-metabolic aerobic; Chloroform – anaerobic; Chlorobenzene – mainly aerobic; 1,3 DCB – anaerobic), order of magnitude reductions required to meet remediation goals, and the nature of soils requiring treatment. HBR's lab trials optimised amendment addition rates to achieve maximum contaminant mineralisation, transformation and mass reduction at all stages of the treatment train approach. Prior to treatment, excavated stiff clay materials were processed to expose the Contaminants of Concern to various amendments. This was accomplished by breaking up the material using a batch mixer to ensure sufficient blending with the reagents. The next step was an initial anaerobic period which involved creating large sealed static biopile cells suitably amended. Aerobic conditions were subsequently created with amendments and aeration using a closed SVE system embedded within each cell. Close monitoring ensured optimisation was achieved and maintained. Lastly, geotechnical modification was engineered via a lime stabilisation stage prior to final placement. All soil was successfully treated to meet stringent re-use criteria, no longer posing an unacceptable risk to human health or the environment for commercial end use.

Remediation of an As-Hg polluted soil by means of enhanced soil washing with ZVI nanoparticles

Carlos Boente; Carlos Sierra; Juan María Menéndez-Aguado; Eduardo Rodríguez-Valdés; Diego Baragaño; José Luis R. Gallego¹

¹ University of Oviedo, ES

Soil with medium-high concentrations of As and Hg (up to 250 ppm for both elements) as the main contaminants of concern was studied to test (physical) soil washing remediation approaches. Samples for pilot-scale tests were obtained in a former mining and metallurgy area devoted to cinnabar exploitation between the 1950s and the 1970s. An initial geochemical and pedological characterization revealed a mixture of silty soil and waste of the mining activities, and therefore soil washing was considered for a feasibility study. The procedures used included, firstly, grain-size fractioning and then, for the classified batches, gravity separation by shaking tables, multigravimetric separation (MGS) or hydrocycloning depending on the fraction, whereas the main alternative tested was magnetic separation by wet-HIMS (high-intensity magnetic separation) at different levels of magnetic field intensity. In both cases no application of usual co-adjuvants such as quelating agents was done.

Grain-size classification revealed a significant fraction of silty-clayey particles, with a preferential accumulation of contaminants when compared with coarser fractions. In this context, gravity separation showed acceptable performances in shaking table for the fraction between 2000-500 μm , for the MGS device in the 500-125 μm interval, and for the fraction below 125 μm in hydrocycloning at high pressures (>130 kPa). Nevertheless wet-HIMS presented a better performance for all the fractions, therefore indicating the relevant differential magnetic susceptibility between mineral waste and natural soil aggregates. The results of the experiments were compared through the novel approach of attributive analysis, and the findings indicated that the separation procedures for pollutants yielded repeatable results. Moreover, an intuitive method of evaluating the performance of the separation techniques recently developed ("success score") was used. This procedure takes into account not only the various scenarios contemplated by legislation (threshold levels and soil uses) but also the performance of each washing method for each element.

In a second step of this work, an attempt to improve the yield of the separation technologies described above has been carried out by means of application of nZVI (zero-valent iron nanoparticles). In brief, additional batch trials were carefully prepared with a mixture of the soil fractions previously studied and 10% w/w of nZVI. The changes observed in the magnetic and gravimetric properties were significant, and therefore, enhanced treatments using nanoparticles as an additive can be considered a promising alternative to the use of chemicals in enhanced soil washing.

Investigation of geochemical long-term Processes by flooding of the former Königstein uranium mine

Michaela Hache¹; Ulf Jenk²; Andrea Kassahun²

¹ GFI Grundwasser-Consulting-Institut GmbH Dresden in the Grundwasser-Zentrum Dresden, ² Wismut GmbH, DE

At the former uranium ore mine 'Königstein'/ Saxony (Germany) geochemical long-term processes were investigated as relevant results from flooding during 4 years. To understand geochemical, biochemical and microbiological processes in the mine, different flood scenarios were simulated at pilot scale using column experiments and a multiphase system 'alternating-layer mineral - sandstone - iron sludge - flooding water'. For this purpose besides to water and rock analysis were also investigated the composition of microbial population and the produced gas phase. The experimental flooding scenario "washing" is already being carried out as accompanying remediation: Contaminated flooding water is purified by water treatment and after that re-infiltrated for washing. The previous flooding on a stable impounding depth shows a decrease in pollutant concentrations in flooding water.

The applications for the final flooding approval includes recommendations of supporting chemical measures for the elimination of acid and oxidizing agents from the flooding water by adding appropriate reactive solutions. Dissolved pollutants could be immobilized by sorption or co-precipitation of iron hydroxides by adding alkaline and other reactive media in the flooded mine area.

The long-term stability of these precipitations depends on the alteration degree of iron hydroxide sludge and the nature of the flooding water. The microbial sulphate reduction is therefore seen as an aspired sustainable long-term process and can be stimulated by adapted substrates. Sulphide-bound heavy metals are well immobilized due to their low solubility. The current flooding regime is simulated in pilot scale in column TV2. For this purpose, the complete mobile aqueous phase was exchanged periodically during 2 years by purified flooding water. Then followed a year of status quo ('washing' stop).

Experiment TV3 includes the treatment with an alkaline solution to increase the pH from 3.2 to 5.5 to eliminate acid and oxidants by discontinuous adding of alkalinity.

A third experiment TV4 focussed on the microbial processes by enrichment with different substrates to stimulate the microbial sulphate reduction rate using alcohol as an easily available carbon source.

The investigations allow to consider the behaviour of retention and re-dissolution of the relevant pollutants arsenic, cadmium, uranium, zinc, and furthermore also manganese and aluminium under flooding conditions arising from the treatment with alkalinity, reactive solutions or the addition of substrate. The microbial population changed their composition depending on boundary conditions of the experiments. The results give a further understanding of geochemical and microbiological long-term processes that occur in the flooded mine area and the connected aquifers to establish a self-regulating, semi-natural system.

Combining thermal treatment with ISCO and bio for reduced cost and more sustainable implementation

Gorm Heron¹; Seth Pitkin²; Eliot Cooper²

¹ TerraTherm; ² Cascade Technical Services, US

Thermal treatment has been used successfully at close to 200 sites - mostly for source zones with a lot of chemical mass. In order to make solutions as sustainable and cost efficient as possible, Cascade Technical Services and TerraTherm provide combined remedy solutions, where thermal treatment costs and impacts are minimized by using less intensive technologies in tandem with thermal. Eleven completed projects form the basis of our offerings. These will be reviewed with lessons learned from each site, and the most promising combinations will be presented. In addition, high-resolution site characterization tools are used to track progress and to optimize the remedies - examples of how interim data was used to greatly enhance performance will be presented. These tools include Waterloo Profiling, Membrane Interface Probe, and Laser Induced Fluorescence. The resulting tools lays the foundation for a future with more cost effective and sustainable treatment of the most difficult sites.

Enhancement of recovery of chlorinated volatile organic compounds from a complex interbedded aquifer

Jake Hurst; Jonathan Miles; Mark Webb; Katy Baker

Arcadis UK, GB

The process of remediating a site using in situ techniques should be seen as iterative and flexible, with system performance monitored and evaluated regularly. This can help identify opportunities for system optimisation, or even enhancement, to enable remediation objectives to be met in the most cost effective manner – whether technically, economically or environmentally. The concept of a “treatment train” has been used for a number of years, but it is generally only recently that the concept of continual remediation design review and adaptation has become more prevalent in the successful remediation of contaminated sites. A case study demonstrating the use of adaptive design, enhancing the efficacy of residual source removal via application of thermal treatment to a clay-rich geology will be described.

The site under assessment is located in the centre of England, used historically as an automotive component supply site. Chlorinated volatile organic compounds (CVOCs) had been used at the site, with an initial investigation highlighting the presence of concentrations of trichloroethene in groundwater above 100 milligrams per litre (mg/l), requiring more detailed evaluation. The groundwater rests approximately 4 metres below ground level. In 2013, the multi-technique investigation approach used to assess the site and determine remediation needs was introduced. In 2017, an overview of the remediation strategy which has been successfully implemented at the site will be explained, including enhancement to the recovery of CVOCs as a result of continual review and optimisation of the system performance.

The remediation system comprised dual phase extraction targeting the source mass zones, combined with soil vapour extraction along one of the site boundaries protective of neighbouring residents. The performance of the system was monitored weekly and the system optimised during each performance visit to ensure that recovery rates were maintained as high as reasonably practicable using the existing infrastructure. This continual review and adaptation of the system resulted in an average TCE monthly recovery of 589kg in 2013, 264kg in 2014, 207kg in 2015 reducing to 87kg in 2016. By 2016, the data clearly indicated that mass was being recovered primarily from areas of the site with the highest clay content and close to the original source of the contamination. These were targeted for more aggressive remediation. To achieve the remediation objectives, the system was subsequently enhanced to comprise DPE with in situ thermal remediation in the identified areas of the site. The data collected during implementation of the enhanced solution will be presented, including lateral and vertical temperature profiles and the increase in contaminant recovery, alongside the plan to complete remediation – including verification works – in 2017.

Reusable iron-composites as heterogeneous catalysts in the electro-Fenton degradation of Diclofenac

Emilio Rosales Villanueva¹; Silvia Diaz²; Marta Pazos Currás¹; M. Angeles Sanroman Braga¹

¹ University of Vigo; ² Instituto Politécnico Nacional, ES

In the last decades, the consumption of pharmaceutical products is increasing among the population. Thousands of pharmaceutical drugs are in use and their release to the environment is a subject of concern. Pharmaceuticals are disposed mainly via domestic wastewater and can eventually reach the environment surface and groundwater generating harmful effects. For this reason, much attention has recently been paid to these compounds. The removal efficiency of pharmaceuticals in the wastewater treatment plants is low and new alternative technologies are required.

Advanced oxidation processes have been lately proposed as alternatives to those conventional treatments. Among them, electro-Fenton process has demonstrated to be an efficient alternative in the removal of emerging pollutants due to the generation of $\cdot\text{OH}$ radicals powerful oxidants. However, this technique has difficulty operating in continuous mode because the catalyst, Fe(II), is released into the treated stream and it should be continuously added. In order to overcome this drawback, the use of heterogeneous catalysts could be considered as a viable alternative.

The aim of this study is the development of new iron-base heterogeneous catalysts for the treatment of emerging pollutants such as diclofenac. Five new iron-composite catalysts were developed based on the iron immobilisation into hydrogels: entrapment (CE, AE), co-precipitation (CP, AP) and iron impregnation (CI). The synthesized catalysts were characterized in deep by different techniques such as infrared spectroscopy, electronic microscopy, etc. The performance of the different prepared catalysts in the heterogeneous electro-Fenton system was screened achieving high removal values (85-95%) in short periods of time (120 min) without structural modification. The highest values were achieved when CE catalyst was used. Then, the working parameters related to the electro-Fenton process were optimized for this catalyst (applied intensity, amount of catalyst). Moreover, the reuse of the catalyst was also confirmed after three batches reaching total degradation of the pollutant. Finally, the mineralization process of the pollutant was verified and several degradation intermediates including carboxylic acids such as oxalic, formic, glycolic and succinic acids were identified.

This heterogeneous electro-Fenton treatment has demonstrated to be effective for the removal of the selected pollutant and consequent mineralization. Therefore, new prospects have been opened and the necessity of further studies in their application to the removal of the emerging pollutants are required.

Acknowledgments

This research has been funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and ERDF Funds (Projects CTM2014-52471-R). The authors are grateful to MINECO for the financial support of Emilio Rosales under Juan de la Cierva program.

ISTD & ISCO technologies combination: experimental study of persulfate heat activation

Hatem Saadaoui¹; Jan Haemers²; Thibaut D'hondt²; Michael Mueller³

¹ Haemers Technologies; ² HAEMERS-TECH; ³ PeroxyChem Environmental Solutions, BE

Introduction

To stay at the cutting-edge of the technology, TPS, world leader in the thermal desorption, always improves his treatment methods. To reduce the cost of remediation, one of the current research consists to have a better understanding of the heat-activation process of persulfate (S₂O₈)²⁻. A good understanding of the mechanism and the kinetics of the process could lead to optimised coupling of thermal treatment – in-situ or ex-situ thermal desorption (ESTD/ISTD) – with chemical treatment – in-situ or ex-situ chemical oxidation (ISCO/ESCO); a promising way to treat plume in vadose zone and groundwater.

The main benefit of the coupled method is that the heat resulting from the thermal treatment may be use to activated the persulfate. That activation increases the reactivity and the reaction rate (i.e. a wider range of pollutants is faster removed). That new method could be used for various chemicals products in contaminated soil or water.

Principle

ISCO is an oxidation method where strong oxidants are introduced to destroy the contaminants of concern into water (H₂O) and carbon dioxide (CO₂).

Several oxidants are available for the ISCO process; their strength is characterised by the potential of oxidation. Higher the potential, higher the oxidant. Once activated, the potential of persulfate seems high enough to break all types of carbon-carbon bonds from organic contaminant.

Activated persulfate is a product widely used and accepted for remedial strategy. The activation generates radical species and may either be chemical (using alkaline, iron or hydrogen peroxide solutions) or physical (light or heat). Most of the time, activation process is made using ferrous solution but the drawback is that it requires several injections.

On the other hand, if persulfate is heat-activated only the injection of persulfate is required as the heat is supplied by conduction through the soil and/or water.

A study about the heat activation and the influence of temperature on the persulfate behaviour in contaminated soil and water leads TPS to join forces to collaborate jointly with PeroxyChem; a world leader in ISCO technologies and a leading global manufacturer and supplier of persulfates and adjacent technologies.

Methods

At first, laboratory tests will study the kinetics of persulfate activation: a well know amount of persulfate is injected into a reaction chamber under different experimental conditions (such as temperature and persulfate concentration). Regarding the remaining concentration over time, the kinetics may be studied for high temperature reaction (at the moment, the experimental studies are limited to temperature lower than 70°C). Those data will be use to optimise the diffusion and reaction simulations made with FLUENT®.

The second step of laboratory tests will study the behaviour of persulfate for different soil composition (such as sand and sand polluted by Diesel).

Conclusion

All those studies will be used to define the optimal conditions (injection rate, temperature, concentration...) for a pilot test. A confirmation of the result will lead to a full scale project such as the treatment of the plume in vadose zone and groundwater.

Engineering the Treatment Train: Implementing Biological Remediation in Soil after Smouldering Remediation of Heavy Hydrocarbon Contamination

Christine Switzer; Neil McCosh; Amy Curtis-Hamilton; Andrew Pape; Charles Knapp

University of Strathclyde, GB

Smouldering remediation is capable of removing 99.9% of heavy hydrocarbon contamination from soil using self-sustaining flameless combustion. In cases where operation may not yield as high removal rates, the use of biological remediation processes such as bioremediation or phytoremediation may be desirable as a polishing step. As a result of contamination and smouldering remediation, soil loses some of the essential nutrients for supporting biological activity. Changes to soil texture and geochemistry alter how the soil interacts with water and its ability to store nutrients. Adapting to and overcoming these changes is essential to the successful implementation of biological remediation.

Changes in nutrient content and availability are related to the temperature experienced during remediation and thus hydrocarbon contaminant. Smouldering of coal tar yields temperatures of 900-1100°C whereas smouldering of light and heavy oils yields temperatures of 500-800°C. Soil organic matter is destroyed by the combustion reactions at all temperatures. Nitrogen is typically lost by 500-750°C. Phosphorous availability changes and some phosphorous is lost from 750°C. Strategic reintroduction of balanced nutrients can be used to overcome these changes and support microbial and plant growth.

Phytoremediation potential was investigated by growing *Sinapsis alba* (white mustard) in soil that had been contaminated with coal tar and remediated with smouldering. Coal tar contained potentially toxic elements, including lead, as part of its composition. To investigate nutrient replacement, supplementation regimes followed the Redfield ratio (106C:16N:1P) or the Redfield ratio with 1 key nutrient removed. Plants grown with the C:N and C:N:P treatments reached maturity and developed characteristics consistent with *Sinapsis alba* grown in uncontaminated soils. Plants grown with N:P, C:P, and water were slower to grow, smaller, and exhibited less chlorophyll a than the plants receiving the C:N and C:N:P treatments. Lead uptake was observed in plants receiving C:N and C:N:P treatments, demonstrating potential for phytoremediation in smouldered soils.

Bioremediation potential was investigated by introducing *Pseudomonas* and *Burkholderia* species to soil after remediation independently and in competition with each other. Limited supplies of nutrients were introduced and allowed to deplete over time, creating a finite duration of the experiment and a source of stress (limited resources) for the microbes. Rapid initial growth was observed in all microcosms followed by biofilm formation as nutrients depleted. Some competition between microbes was observed, but nitrogen fixation was not observed. Similar to the *Sinapsis alba* experiment, this work demonstrated that nutrient supply is critical to support initial growth.

These experiments demonstrate the feasibility of biological remediation after smouldering remediation. Further work is underway on supporting microbes and plants through the transition from nutrient dependence to independence. Future work involving successive plantings of *Sinapsis alba* and other plants is also planned.

3h. Other technologies

A 20-Site Review: Groundwater pH Effects of An Electron Donor Microemulsion

Kris Maerten¹; Craig Sandifur²; Joy Gravitt²

¹ REGENESIS Remediation Solutions, Europe; ² REGENESIS, USA, IE

Enhanced bioremediation can be an effective technology for cleaning up sites contaminated with anaerobically biodegradable chlorinated hydrocarbons. Fermentable organic substrates, which serve as electron donors, are commonly used to enhance natural biological dechlorination. This process releases hydrogen which increases the rate of contaminant dechlorination. This multi-step process is termed ERD or enhanced reductive dechlorination. Electron donors release acids upon their fermentation. For example, oleic acid, a C18 fatty acid, is degraded in the presence of water to a C16 fatty acid, acetic acid and two equivalents of hydrogen.

In addition to the organic acids produced due to fermentation, a primary product of reductive dechlorination is hydrochloric acid. The production of organic acids and HCl in the subsurface causes concern over the pH effects of ERD. Various laboratory studies have suggested that primary dehalogenating bacteria, such as dehalococcoides ethenogenes, are sensitive to pH and may be inhibited under acidic conditions below the range of pH 5.2-6.2, depending upon the specific bacteria community.

This study analyzes trends in groundwater pH over time in aquifer zones where an emulsified electron donor, 3-D Microemulsion[®] has been applied. Organic acids are formed in the subsurface as 3-D Microemulsion hydrolyzes and ferments. It is possible that the formation of these acids could cause a decrease in site pH during the life of the electron donor in the subsurface. The aim of this work is to quantify the average effect of the emulsified donor and emulsion has been injected.

3-D Microemulsion was developed and is manufactured by REGENESIS, San Clemente, CA for enhanced anaerobic bioremediation. This electron donor has a novel molecular structure which enables the formula to distribute widely in the subsurface and provide a three-stage (immediate, mid-range and long-term) controlled release of hydrogen into contaminated groundwater for two or more years per application.

In this study, the average observed decrease in pH due to fermentation of 3-D Microemulsion was less than or equal to 0.25 pH units. No strong trend in groundwater pH was observed over the course of the first year after the electron donor emulsion was applied. Changes in pH within aquifer treatment zones after donor application averaged between -0.14 and -0.25 pH units. Baseline and post-application average pH values measured at this set of sites ranged between 5.91 and 6.33. These data suggest that typical aquifer material has the capacity to buffer much of the acids generated by reductive dechlorination and fermentation of the emulsified donor. Exceptions to this would include sites with very low buffering capacity, such as fractured bedrock.

Future work will include collection of more detailed site data to expand on these results and elucidate any further trends. In particular, mineral and soil type information will be examined to determine if and when these might be predictive of significant pH changes as a result of the application of 3-D Microemulsion.

International Advanced Master® "Management of polluted sites and mineral waste processing/recycling"

Fernando Pereira¹; Virginie Bruyas; Jean-Michel Herri; Karine Rottier; Didier Graillot; Cyril Faure

¹ Mines Saint-Etienne, FR

The area of depollution is undergoing significant growth since 2000. The rehabilitation of polluted sites and soils was worth some 200 M€ in 2000, approached 500 M€ in 2010 and reached 560 M€ in 2012 (ADEME, 2013). After a two-year economic slowdown, a market analysis study (Xerfi institute, 2015) projected that the turnover of the companies concerned should grow by respectively 6 % in 2016 and 4 % in 2017. The regulatory backgrounds (in perpetual evolution) of the cutting back of raw materials (especially, metals) and the land resource (often situated in urban areas) optimization bring real growth opportunities to the sector.

Although the growth outlook is considerably stronger, the sustainable management of contaminated sites and soils remains an important challenge despite the significant progress identified in the last fifteen years. Processing techniques are constantly evolving and improving (to meet new legislation and new environmental challenges), as well as their implementation, with in particular more and more remediation activities conducted on site.

The training program will be specifically designed to answer to an identified expertise demand regarding mineral waste treatment schemes. It will provide tools to solve any shortcoming or challenge linked to the processing and recycling of contaminated mineral matrices (soils, sludge, sediments, excavated soil, by-products and waste) and will be aimed at developing teachings useful in proposing sustainable, integrated and economically rational solutions that address the full range issues posed by these materials since their on-site management until their evacuation, treatment and reuse. All this taking into account the environmental and sanitary impacts that their implementation, treatment and reuse cause.

The specificity of the SPIN ("Sciences des Processus Industriels et Naturels") centre of Mines Saint-Étienne lies in its multidisciplinary approach and orientation towards industrial processes. Under that feature, SPIN can propose an integrated, pragmatic and economically rational approach to the mineral waste concern covering the:

- expertise of existing processes and the proposal of alternative solutions that really fit the contamination type and local conditions through regular knowledge exchange and coordinated action with its clients;
- mineral waste characterization (development of diagnosis and monitoring tools) both in terms of heavy metals and organics to facilitate the most effective processing technologies choices;
- combination of treatment techniques (chemical, physico-chemical, hydrometallurgical, phytomanagement, etc.), which allow to widen the range of mineral matrices to process.

The proposed poster will underline the four teaching units of the Advanced Master® planned, that are devoted to the:

- characterization methods of contaminated sites and mineral matrices and diagnoses of pollution;
- existing processing/recycling techniques for sites and mineral waste;
- risks study (pollution transfers, environmental impacts, etc.);
- regulatory territorial, social and economic approaches intended to assist the rehabilitation of a contaminated site.

Modelling of Air Flow in the Capillary Break Layer of Buildings at Polluted Sites

Jakob Skovsgaard; Hans Bengtsson

Ramboll Environ, DK

In Denmark the threshold values for volatile pollutants (e.g. chlorinated solvents) in indoor climate are low. At many polluted sites remediation or technical building measures are being conducted to lower the indoor concentration. Within recent years there has been an increased focus on developing improved methods for design and documentation of sub floor ventilation solutions on contaminated sites. Many of the solutions applied are based on ventilation of the capillary break layer or a ventilation layer under the floors.

Ventilation systems in these layers can be provided with electrically driven blowers (active ventilation) or passive ventilation systems driven by wind. By using a gas permeable medium in the capillary break layer (e.g. Leca) and a combination of drain pipes, it is possible to control the air flow, and thereby ensure that even edges and corners of the ventilated layer are covered. To apply ventilation systems in the capillary break layer successfully, a range of design parameters must be described in detail, and documentation must be provided in order to ensure, that the solution applied meets the requirements for sufficient air exchange rates in all spaces of the layer.

Efforts to predict the effect of different designs of ventilation systems has until today proven to be difficult, and the few simple designing guidelines that are usually followed, are still subject to debate.

In order to get a better understanding of how to design and apply ventilation systems successfully, it is necessary to gain insight into the mechanisms that control the distribution of air flow in the ventilated zone, and there is a need to develop methods and tools that can support the design and documentation of subfloor ventilation systems.

The aim of the project is to develop and describe a concept for modelling air flow in capillary break layers that can help to provide the documentation needed to apply ventilation systems successfully. With the modelling concept, different designs of sub floor ventilation systems can be analysed, and documentation can be provided when proposals are presented to authorities for approval. Estimates of the cost of using a modeling tool for design and optimization of a ventilation system is also part of the project. The modelling will be performed in a freeware program as well as by CFD (Computational Fluid Dynamics).

The project is divided into four phases: 1) searching and selecting suitable software tools 2) describing essential design parameters in order to identify variables and boundary conditions for the modelling of air flow in capillary break layers 3) designing and conducting modelling with two different modelling tools 4) describing the results including the pros and cons of the tools applied.

Phase 1, 2, and 3 of the project will be completed November 2016. Phase 4 will be completed in December 2016 and the results will be presented at the conference.

Topic 4. Strategies and policies for pollution management and remediation

4a. Remediation goals and strategies

Shut-down criteria for in-situ thermal remediation (ISTR) based on hot vapor concentration

Laura Bieber¹; Uwe Hiester

¹ reconsite GmbH, DE

At some sites with volatile organic compounds (VOC), partial source removal can be an efficient strategy to reduce environmental hazard risks economically. Final shut-down criteria for in-situ thermal remediation (ISTR) during heating system operation are important to ensure an economically remediation. The application of conventional clean-up goals for natural temperatures to ISTR might cause an increase of the remediation costs, energy consumption and CO₂ footprint.

In-situ thermal remediation (ISTR) is operating at high temperatures, which leads to another contaminant distribution in the environmental media as "cold" remediation operations. An application of "normal" clean-up goals is therefore not recommended, because it leads to wrong interpretations of the contaminant development.

Therefore final shut-down criteria for ISTR must be defined and applied during the remediation process, also because the energetic effort to heat the soil to remediation temperature is higher than holding the temperature after heating. The cooling down of soil and groundwater to a delta less than 5 K to natural, ambient temperatures takes about several months, sometimes even more than a year. This period is too long to apply conventional clean-up goals as final shut-down criteria for ISTR. To bridge this gap, a conceptual model has been developed to predict remaining concentrations after ISTR shut-down and cooling of soil and groundwater to ambient temperatures from soil vapour concentrations with temperatures above 50°C. The developed model enables an easier, cost-effective, and efficient evaluation of the remediation process. By applying this model an increase of ISTR costs, energy consumption and CO₂ footprint can be avoided.

The model is applied after most of the contaminant is removed and the mass flux curve of the remediation operation had reached its inflexion point after the mass discharge peak. Basis of the model is the contaminant distribution between soil matrix, pore water and soil vapour. All three media are connected through the temperature dependent Henry coefficient and soil-water distribution coefficient. Next to the temperature dependence also facility depending correcting factors are included into the model. Soil vapour concentrations are measured during thermal soil vapour extraction (SVE). To generate steady-state conditions the concentration is multiplied by a minimal and maximal validation factor. Calculation of the remaining contaminant mass is possible as well as the contaminant mass flux in seepage and groundwater. A prognosis of the development of contaminant concentration, remaining contaminant mass in soil and risk of contaminant migration in the unsaturated and saturated zone is also included. That can help to predict contaminant development and risk assessment after ISTR and forecast the most beneficial ISTR shut-down taking into account economic and environmental aspects.

The model can not replace project and remediation management and has to be adapted to the site conditions but its application leads to an adequate, ecological, economical and sustainable remediation.

In situ management with a secure cropping system for moderately lead contaminated allotment gardens

*Dorine Bouquet*¹; *Alexandra Lépinay*²; *Pierre Gaudin*²; *Liliane Jean-Soro*³; *Cécile Le Guern*⁴; *Thierry Lebeau*²

¹ LPG-Nantes; ² Université de Nantes; ³ IFSTTAR; ⁴ BRGM Nantes, FR

The maintenance of the agronomic quality of soils in case of allotment garden rehabilitation is of great concern. Considered as an environmental-friendly solution, phytoextraction may be adapted to this issue. Nonetheless this method requires sometimes many years to achieve the cleaning-up of soils. For this reason phytoremediation hardly develops. To circumvent this problem, this study aimed at developing a secured cropping system in allotment gardens including the authorization to cultivate vegetables unable to accumulate lead (Pb) and phytoextracting crops simultaneously.

To achieve this goal, an in situ and participative 3-year experiment has been launched since July 2015 on an allotment garden soil (Nantes, France) contaminated by geogenic Pb. Pb in topsoil is 170 mg/kg on average. Vegetables (tomato, winter cabbage or potatoes) and Indian mustard (*Brassica juncea*), used for phytoextraction, were cultivated in rotation or as crop co-cultures and were compared to a control (without phytoextraction process).

The two first seasons of culture showed that Pb concentrations in edible parts of tomatoes and winter cabbages were under the EEC regulatory threshold set at 0.1 and 0.3 mg/kg of fresh matter. For the "co-culture", Pb in Indian mustard shoots was around 0.9 mg/kg dry matter (DM) with a translocation factor (TF) of 1.5 in average and 0.2 mg/kg DM with a mean TF of 0.03, respectively for the season 1 (Tomato) and the season 2 (Cabbage). Then, phytoextraction efficiency was very low. But, compared to previous experiment realized in laboratory, in situ phytoextraction associated with tomato and cabbage is respectively 83 and 18 times more efficient than phytoextraction by itself. For the "rotation" growing method, lead concentration in *Brassica juncea* shoots, ca. 0.5 mg/kg DM with a mean TF of 0.2, was significantly lower than what was recorded with co-culture. Analysis of Pb in potatoes are in progress.

After three growing crops, the culture of tomatoes and cabbages could be maintained on this site in association with phytoextraction, expecting nevertheless higher performances for this latter. In such a prospect, the regulation could pay attention to this secure cropping system.

Development of a simplified method for the assessment of the environmental impacts of groundwater remediation processes

Francesco Caridej¹; Sarah Bonvicini²; Vicens Martí³; Costanza Martina²; Roger Midence¹; Roger Midence¹

¹ Ecosurvey[®]; ² Alma Mater Studiorum Università di Bologna; ³ EEBE, IT

A simplified method is described for the assessment of the environmental impacts caused by groundwater remediation process. This new tool for environmental impact analysis considers, among others, specific indicators related to greenhouse gases, air pollution, energy use, resources consumption, and water pollution, not neglecting safety issues and cost figures. The methodology takes also into account some specific indicators useful for Life Cycle Assessment and for the evaluation of the environmental footprint of different remediation strategies, so to allow the analysis of innovative "green" solutions in comparison with traditional current practices of remediation.

In order to work out the procedure, different methods to calculate the environmental impacts are studied and compared, including the SiteWiseTM and SEFA-USEPA codes. At the end the method will be detailed step by step and will be furthermore validated by means of real-life data from groundwater remediation processes, in collaboration with researchers of ISPRA (Italian Environmental Minister) and SEFA-US_EPA.

The new tool will be fully developed during a three year project and will become available for free use on the web "portal for a simplified assessment of the environmental impacts". This research project will be co-funded by the Italian Government of Instruction, University and Research (MIUR), Confindustria and CRUI Foundation under the Italian PhD ITalents program and lead by Ecosurvey[®]. Moreover, the project has already been awarded by the "Seal of Excellence" from the European Commission in the framework of the H2020 highlighting: "The proposal was successful in a highly competitive evaluation process as an innovative project".

A preliminary study was already performed by applying the SiteWiseTM tool to an Italian case study, represented by an active industrial area polluted with hydrocarbons and chlorinated compounds. The subsoil of the site is characterized by the presence of two continuous clay layers, at the scale of the site, that separates two aquifers, at a depth of 6 m and 18 m respectively. Both aquifers are contaminated and the presence of a former site production well is probably the cause of the transfer of contamination from the upper aquifer to the lower one. Remediation has the objective of respecting the contamination thresholds fixed by the Italian law. The remediation strategies suitable for the site that were examined in a comparative environmental impacts assessment are Pump & Treat (P&T), In-Situ Chemical Oxidation (ISCO) and Monitored Natural Attenuation (MNA). The study, among other results, pointed out the normalized values of environmental impacts and the costs of each strategy, allowing to rank them. The evaluation of the applicability of bioremediation to the examined site is currently under way.

The present abstracts related to a poster presentation about the description of the research project and the main phases of the new procedure for environmental impact analysis, as well as on the presentation of the intermediate results actually available.

Westward Expansion to Urban Remediation and Watershed Reclamation: US EPA Superfund Optimization Lessons Learned at Legacy Mining and Smelter Sites in the American West.

Stephen Dymont; Carlos Pachon

US EPA, US

Westward expansion and development in the American West includes a history rich in mining and smelting operations. This same legacy has resulted in tens of thousands of historical and abandoned hard rock mine and smelter sites throughout the Western United States. The most contaminated and dangerous sites are often addressed through EPA's Superfund removal and remedial programs. These large remote mining sites and historical smelters in populated areas can each present unique and significant challenges to characterization, risk assessment, and remediation. Smelter sites in residential settings often focus on metals exposures from soil and dust while mining sites and districts can present challenges from metals contamination in groundwater, surface water, soil, and sediment.

This 90 minute session will explore the evolution of addressing mine and smelter sites in the US EPA Superfund program and present a series of best practices identified through recent optimization reviews of existing remedies. Collectively, the best practices presented in this session highlight the latest strategies being employed to address mine and smelter sites in the US EPA Superfund program.

large mining sites and districts, the best practices presented will reflect programmatic challenges as well as opportunities to approach these sites from a watershed perspective seeking to characterize and remediate these sites using a holistic approach. This session will identify characterization strategies, tools, and techniques along with passive/active remediation technologies currently operated in the Superfund program, soil amendments, and other techniques that highlight EPA's efforts to address mining sites in the most sustainable and protective manner. For smelter related sites the session will discuss historical efforts to address lead, arsenic and other smelter related metals in residential soil while providing the latest findings and best practices associated with the use of x-ray fluorescence (XRF) analysis and incremental sampling for residential soil and indoor dust at Superfund sites.

Applying geostatistics to assign waste ownership and waste management responsibilities

Caroline Le Boulch; Anne Delos

A pit has been filled with industrial wastes originating from two industrial facilities over a 20-year period. After closure of the pit in the early 90's, initial investigations showed potential stratification of wastes. In anticipation of the need to remediate the pit, both facilities wanted to identify the location of their respective wastes in the pit, the corresponding waste endpoints and the quantities needing to be dealt with, when excavating the pit.

The initial investigations indicated that each facility waste could be characterized by two tracers. This, combined with the potential presence of stratification of waste revealed by the initial investigations, inspired the use of geostatistics to interpret both in situ and laboratory results. It allowed:

- the correlation between in situ measurements and laboratory analysis, reducing time and costs of laboratory analysis.
- waste type mapping based on the tracers' distribution considering uncertainty,
- the estimation of waste type volumes to be treated based on a defined threshold.

Exploratory Data Analysis confirmed a data set with more numerous low concentrations than high concentrations. The EDA also identified a "background noise" for every parameter, demonstrating a certain amount of waste types mixing had taken place.

Sophisticated visual representation of the findings was made through the process of kriging, which is a data interpolation method using geostatistics. This method captures the spatial structure of the data set and, based on measurements points, predicts a likely value on each map point while also quantifying the associated uncertainty. A 3-Dimensional geostatistical study was conducted on each tracer, following the drilling of 15 boreholes in the pit. It was based on analysis results in 75 samples taken from the 15 boreholes.

The geostatistical simulation methods, which will be described alongside the results, enabled:

- the approximate distribution of wastes from each industry to be estimated, by visualization of each tracer distribution in the pit;
- visualization of the degree of mixing between the wastes through review of the tracer cross-over, helping to define industrial ownership
- the quantification of volume of wastes that were likely to exceed the relevant threshold values
- estimation of the associated treatment costs, including calculation of the uncertainty associated with the costs of treatment after excavation.

Challenges in investigation and remediation of Chlorinated Compounds

Karin Birn Nielsen

Central Denmark Region, DK

Background: For many years there has been a special focus on chlorinated compounds (VOCs) in indoor air in Denmark. Particular drycleaners have induced contamination of soil, groundwater, soil and indoor air.

In this case the apartment with indoor air problems was unoccupied and the Central Denmark Region (CDR) got a unique opportunity to try out different sampling and remediation meth-ods.

Case study:

A former drycleaner is contaminated with VOCs. Investigations from the 1990's showed a contamination in both soil and groundwater. Back then only soil and groundwater samples were analyzed.

The CDR performed an additional investigation during the period 2011-2015 to detect wheth-er or not the contamination at the site had an impact on the indoor air in the buildings on site and at the neighbors and to find the perfect remediation technic to secure the indoor air.

CDR performed different sampling technics to determine the intrusion pathways to the build-ing; among others are sampling of air from the sewer system on activated carbon; behind wa-ter traps, in sewage wells and in the sewer strings. Different ways of accumulating VC on ac-tivated carbon in soil air.

Furthermore CDR tried depressurization of the sewer system, implementation of a radon well and seven drains under the buildings on the site and one of the neighbors.

Lessons learned

At first CDR were sure that the source were two septic tanks placed just outside the apart-ment with the highest indoor air concentrations. In the light of that a depressurization of the sewer system were establish. The results were satisfactory – only smaller exceeding's in con-centrations of PCE in indoor air were detected after depressurization of the sewer. However further investigations showed that the source was placed under the apartment and a radon well and seven drains were established. To day the depressurization of the sewer system is turned of.

Important factors: Produce a profound historic report of the activities on site, the changes in buildings and tv-inspections of the sewer systems. These factors are necessary to detect the source and thereby choose the best remediation technic.

Presentation: At the conference, the case will be presented with special focus on the steps in an investigation, from sampling to remediation and how the unexpected results can induce a total change in choice of investigation or remediation.

Tackling non-point source lead contaminated soils

Piet Otte; Martine Bakker; Johannes Lijzen; Ellen Brand; Arjen Wintersen; Marco Zeilmaker

National Institute for Public Health and the Environment RIVM, NL

Man has for centuries been exposed to lead. Nowadays the level of exposure is significantly reduced by the use of unleaded petrol and paint, and the replacement of lead water pipes. Moreover, many cases of soil contamination have been cleaned up, but in some neighborhoods of Dutch cities, the presence of lead in the soil is still an issue.

RIVM brought together the current knowledge about the health risks of lead exposure. Lead affects children's brain development and is associated with a reduced intelligence quotient score. The European Food Safety Authority (EFSA) concluded that there is no evidence for a threshold for critical lead-induced effects. Using the IEUBK model from the USEPA in combination with the RIVM CSOIL exposure model the calculated external exposure to lead originating from contaminated soils from inner cities was related to an estimated loss of a few IQ-points. Calculations were made for different uses of the soil (i.e. vegetable garden, living with (vegetable) garden and places where children play). Small children are exposed to lead from contaminated soil mainly through ingestion of soil particles while playing in the garden or on playgrounds.

It is not possible to indicate the level of IQ loss for an individual. That depends, amongst other factors, on the level and frequency of exposure. However, for reasons of safety, it is recommended that the competent authorities, municipalities and residents take measures to reduce exposure to a level as low as possible. RIVM recommends undertaking the following steps:

- Locate peak concentrations within the neighborhood;
- Match peak concentrations with actual use of soil and label so called 'focus spots'. Focus spots are intensively used areas with high soil lead concentrations;
- With relevant authorities and residents, arrangements can be made on the refurbishment of these "focus spots". The redesign should be realized in such a way that contact with soil and ingestion of soil particles with lead is minimized. Possible measures can include the application of a clean top layer, a grass cover and sandboxes with clean sand;
- Backyards and kitchen gardens are potential focus spots. It is recommended that the municipality and the Public Health Service inform residents about possible health risks and on measures, residents can take by themselves. For parents it is important to know that with relatively simple measures they can reduce children's exposure to lead.

At this time, Dutch competent authorities develop a common approach based on the recommendations. Some municipalities started to inform their citizens.

The Danish way to registration, exchange, reporting and publication of data from contaminated sites.

John Ryan Pedersen

Central Denmark Region, DK

Background: In connection with the investigation and remediation of contaminated sites, large amounts of valuable data are generated. These data are collected and stored electronically mainly by the regional authorities in Denmark. In accordance with the legislation the five regions report selected data annually to the Danish EPA. The data describes the regions activity mapping, surveys, remediation and monitoring. At the same time, the regions provide consultancy to thousands of citizen inquiries regarding soil contamination. In addition, there is a great need at municipal level to have an easy access to the regional soil contamination data as these are of great importance in their daily administration and planning. Collecting, storing, sharing and distribution of data from contaminated sites have long been time-consuming and costly, but today an effective and cross-sectorial system has been developed to the benefit environmental authorities and the public.

Activities: The Danish regions have developed a common contaminated soil database named JAR "Jordforureningslovens Areal Register" with three clear goals in mind: 1) It had to be Web-based, so that everyone could access it, 2) there should be an integrated GIS, so that data was automatically geocoded and 3) the regions should own the system (open source). The system is designed so that all partners (e.g. municipalities and consultants) can have access and view all the data in the system. Thereby, the municipal groundwater experts have online access to updated soil data. For consultants, it is part of the contract with the region to update the JAR with the data they produce during investigation and remedial action made on behalf of the region. JAR contains a public online certificate feature that allows anyone to check and see if the region has knowledge about contamination or suspect soil contamination on a property. In Denmark there is a "National Environmental Portal" (DMP), a collection of environmental data from many disciplines. Data in DMP are primarily produced by the state, regions and municipalities. Data are available within the topics of: Soil contamination, surface water, ground water and nature. DMP is the one central place where all Danish authorities seek data maintained and produced by other authorities. DMP also presents selected soil data on a GIS platform where the public can view, e.g. where contaminated and potential contaminated sites are located.

Lessons Learned: During the last 7 years the collection, storage and distribution of data on contaminated sites, have been intensively digitalized in Denmark, to the benefit of all authorities and the public. The Regions, that have fully implemented JAR's public self-service solution, answers almost exclusively inquiries electronically. In Central Denmark Region alone it is about 33,000 responses per year. It has obviously been a huge administrative relief, as these responses previously were made manually.

The poster will illustrate the data flows in Denmark. In the manned poster session a laptop will online demonstrate: JAR, DMP, and the public access to data.

National risk management strategy for contaminated land in Finland

Outi Pyy¹; Anna-Maija Pajukallio²; Sarianne Tikkanen²

¹ Finnish Environmental Insitute; ² Finnish Environment Institute (SYKE), FI

Background

National strategies are one important instrument for governments to steer contaminated land management (CLM) policy by creating a comprehensive framework for the risk management of contaminated sites. Ministry of the Environment defined general objectives for soil protection in the report in 1998. In many ways the conclusions and recommendations of the report are out of date. Re-evaluation of the key objectives and the identification of development needs and principles became a topical issue. There was a need for a comprehensive policy framework for promoting sustainable contaminated land management in Finland.

Aim

The main aim of the PISARA working group appointed by the Ministry of the Environment (from October 2014 to October 2015) was to define a future vision, main goals and principles for a national CLM policy. In addition, the strategy should contain recommendations for policy means and instruments together with a plan for the organization of the risk management of contaminated land areas in Finland. The task was divided into the following actions:

- defining objectives and goals for different CLM policy fields,
- making recommendations for policy means and instruments to achieve the policy goals,
- presenting a groundwork proposal concerning the reform of the State Waste Management System for contaminated soil sites and
- preparing The National Investigation ja Remediation Programme.

The preparation process included close interaction with various stakeholders e.g. the working group organized workshops, meetings, interviews and commentaries. Thus various stakeholders were engaged in establishing a comprehensive view of the current state. Based on this, the working group formulated the goal, objectives, and recommendations for policy means and measures.

Conclusion

The main aim of the strategy is: Significant risks of contaminated land to human health and the environment are managed in a sustainable way by the year 2040. This goal can be achieved by meeting the following six objectives:

- Risk sites are identified, investigated and remediated systematically.
- Spatial planning and risk management in contaminated land support each in order to achieve sustainable and comprehensive solutions.
- Data management systems support planning and decision-making in a user-friendly way.
- Remediation methods are cost-efficient, save natural resources, minimize adverse environmental effects and promote circular economy.
- Procedures are interactive and the roles, responsibilities, and liabilities of the actors are explicit.
- Practices and communication are open, transparent, and interactive.

The strategy contains recommendations for policy means and measures to achieve the objectives in an efficient and feasible way. The responsible actors for the measures and actions are identified as well. The purpose of the National Investigation and Remediation Programme for Contaminated Sites is to identify significant contaminated areas and promote research on these and the implementation of necessary risk management measures.

Conceptual Site Models for Niger Delta Ecozones

Jonathon Smith¹; Stephen Truchon²; George DeVauall²; Kim Bye Bruun³

¹ Shell Global Solutions (UK) Ltd; ² Shell Global Solutions US Inc.; ³ Shell Petroleum Development Company of Nigeria Ltd, NL

The Niger Delta has experienced 60 years of oil exploration and production. Throughout this period the Delta's environment and population have been affected by spills from oil operations.

Since 2012, the Shell Petroleum Development Company of Nigeria Ltd (SPDC), as operator of the SPDC joint venture has been working with the International Union for Conservation of Nature and its Niger Delta Panel (IUCN-NDP) to explore ways to better rehabilitate the delta environment and its biodiversity.

This poster presents Conceptual Site Models (CSMs) for the different eco-zones found in the Niger Delta. Five eco-zones are identified: (1) Lowland Forest, (2) Flood Forest, (3) Swamp Forest, (4) Mangrove Swamps, and (5) Coastal Barrier Islands. The CSMs include identification of the stressors at a site (specifically, in this case, release of crude oil); qualitative description of the fate and transport of crude oil under the varied eco-zone conditions; the mechanisms of toxicity associated with the crude oil; evaluation of both complete and incomplete exposure pathways from source (point and nature of oil release into the environment) to a receptor; and identification of the likely receptors.

The potential ecological receptors are identified for each of the eco-zones. Similarly, for human exposure, potentially applicable exposure pathways and exposure routes are also presented.

The CSM for each of the eco-zones was developed for each of two broadly identified crude oil source types: [1] mobile crude oil, and [2] immobile 'residual' crude oil. The intent of using separate CSMs for [1] mobile oil and [2] residual oil is that different mitigation, remediation, and restoration options are viable for the different oil conditions. The CSMs shown in this poster provide the foundation for working these various options towards more successful site risk management within different eco-zones.

Soil and Groundwater Visualization Tool for spills in the Niger Delta: LORAX-Nigeria

Jonathon Smith¹; Andy Lee²

¹ Shell Global Solutions (UK) Ltd; ² Shell Petroleum Development Company of Nigeria Ltd, NL

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As part of a broader effort to develop effective processes and practices in the Niger Delta, and to help communicate soil and groundwater issues to key stakeholders, including regulators and communities, a visualization tool, 'LORAX-Nigeria' has been developed that helps risk assessors and remediation practitioners more clearly explain their approaches and objectives to regulator and lay audiences.

The tool is a powerful and interactive piece of software that can be used to help communicate important aspects relating to all aspects of risk assessment and management.

This poster presents the LORAX-Nigeria tool, and (space permitting) the visualization tool will be demonstrated in real time.

Remediation Industry Best Practice Guidance: An Illustrated Handbook of LNAPL Transport and Fate in the Subsurface

Rob Sweeney

CL:AIRE, GB

The aim of the 'LNAPL Illustrated Handbook' is to provide a clear and concise, best-practice guidance document that will be a valuable decision support tool for use in discussions and negotiations regarding light non-aqueous phase liquid (LNAPL) impacted sites. LNAPLs notably include fuels and oils, and are amongst the most commonly encountered organic contaminants in the subsurface environment due to their ubiquitous use, accidental release and, perhaps, poor (historical) disposal. The LNAPL Illustrated Handbook is the sister document to the well-known and highly regarded 'An illustrated handbook of DNAPL transport and fate in the subsurface' (aka, 'DNAPL handbook'), published by the Environment Agency in 2003. Similar to its sister document, the LNAPL Illustrated Handbook is a user-friendly overview of the nature of LNAPL contamination in various geological settings including unconsolidated, consolidated and fractured rock environments to best understand its fate and behavior leading to the appropriate management and/or remedial approach.

The LNAPL Illustrated Handbook is intended to assist site investigators, site owners and regulators in conducting site investigations and risk assessments, and in selecting remediation approaches. There have been significant developments in recent years on the understanding of LNAPL behaviour and the associated groundwater and vapour plumes; however, the state of practice has often lagged behind these improvements in knowledge. This gap can result in resources being spent on sites and conditions that may not warrant them. The LNAPL Illustrated Handbook will support:

- Better conceptual understanding of LNAPLs in the subsurface, on which risk-management strategies can be built;
- More effective site characterization and risk-prediction.
- More sustainable and risk-based management of LNAPL releases.
- Better understanding of where/when specific LNAPL remedial techniques can/should be applied.

The LNAPL Illustrated Handbook was prepared by leading practitioners from Europe and North America, Academics from the UK and Site Owners with LNAPL liabilities. The publication of the handbook was facilitated by CL:AIRE with funding from Shell Global Solutions. The LNAPL Illustrated Handbook is available to download free of charge at: <http://www.claire.co.uk/LNAPL>.

Inventory of potential contaminated sites as keystone of soil policy

Nathalie Van Trier¹; Bruno Billiaert; Johan Ceenaeme; Eddy Van Dyck

¹ OVAM, BE

The Soil Decree is an important tool for the Flemish government, not only to counter the contamination of land, but also to prevent such contamination. Prevention begins with sufficient information. The preliminary soil investigation is the first source of information for soil quality. It examines whether there are serious indications of soil contamination on a given site.

In order to facilitate the identification of the contaminated sites, the Soil Decree devotes specific attention to activities and facilities that can cause soil contamination. These activities or facilities are listed in the VLAREBO implementation order. Land, on which a facility is or was established or on which an activity is being conducted or was conducted that is included in this list, is required to undergo a preliminary soil investigation at the moment of property transfer, on a periodical base or by closure of certain installations that can or could cause soil contamination. Through the identification of these 'risk-sites', it will be clear how many potential contaminated sites still need to be investigated.

The OVAM has compiled a land information register. This is an inventory of:

- the parcels of which data on soil quality are known at the OVAM (data from reports and records of soil investigations and remediations);
- the parcels on which facilities and activities with a relatively higher risk for soil contamination are/were carried out (data from potential contaminated sites listed by each municipality in the 'local inventory').

This land information register serves as a database for policy decisions and also functions as an instrument to protect and inform potential buyers of contaminated sites. One of the key-issues of the Soil Decree is the possibility to request a soil certificate, an extract of this register for a specified cadastral parcel.

The land information register is being updated on an ongoing basis, but is not completed yet. Each municipality has to identify the 'risk-sites' that are located on their territory in a local inventory. The OVAM assumes that information about 40.000 'risk-sites' from the local inventory still need to be exchanged with the land information register. The local inventories must be completed by the end of 2017.

The OVAM provides maximum support to the 308 Flemish municipalities for the composition and management of their local inventory. In November 2012 the OVAM launched a new web tool, such that the municipalities can exchange the necessary data of 'risk-sites' from their various data management systems more efficiently. Because most of the archive information is not digitized yet, a large proportion of information of older activities currently lacks in the local inventories. Since 2015, the OVAM provides a made-to-measure approach with each municipality. Together with external experts we determine the most practical and most effective method in every municipality to complete their local inventory.

In addition the OVAM provides general and infrastructural support so that local authorities are encouraged to continue to complete their local inventory with sufficient priority.

Assessment of effects of PAHs on soils functions in contaminated soils

Jana Weiss¹; Pär-Erik Back²; Dan Berggren Kleja²; Anja Enell²; Magnus Engwall³; Malin Fransson⁴; Sara Hallin¹; Christopher Jones¹; Sarah Josefsson⁵; Maria Larsson³; Lars Rosén⁶; Astrid Taylor¹; Maria Viketoft¹; Yevheniya Volchko⁶; Annika Åberg²; Karin Wib

¹ Swedish University of Agricultural Sciences; ² Swedish Geotechnical Institute; ³ Örebro University; ⁴ Swedish Transport Administration; ⁵ The Geological Survey of Sweden (SGU); ⁶ Chalmers University of Technology, SE

APPLICERA is a 3-year project aiming to develop a site-specific environmental risk assessment (ERA) methodology of contaminated soils, where effects on relevant soil functions (SFs) are included. Current ERA tools suffer from a limited understanding on how contaminants affect the soil ecosystem and its soil functions (Volchko et al. 2014. *Sci Tot Env* 485:785). This frequently leads to expensive dig-and-dump, where all soil masses with levels above guideline values are removed, but with largely unknown benefits for the soil ecosystem and its functions.

Within APPLICERA, one aim is to investigate a contaminated site in situ and to explore how biotic and abiotic indicators can be used to express SFs. The selected site is a railway yard in southern Sweden, close to the city Mjölby. The area is a property of the Swedish Transport Administration, and human activities have been ongoing there for more than 150 years. In a previous survey (2010), potentially contaminated areas were identified on the basis of various anthropogenic land-use, such as a depot for cross-ties, loading docks and a locomotive stable. In 2015, soil was sampled from two areas (North and South) at the railway yard within APPLICERA. The selection of sampling points covered an area where a former traction power network station was located (S), which is an electricity grid for the supply of electrified rail networks, and a contaminated area (N) with diffuse source. Soil was sampled from different soil layers independently on the soil structure and characteristics.

The samples were analyzed for a selection of chemical, ecological and eco-toxicological indicators. These indicators were selected either as potentially regulating SFs or being indicative of SF activity. The soil was characterized in terms of basic abiotic parameters (texture, pH, etc.) and PAH contamination levels. Bulk levels in the soil and pore-water concentrations of three groups of PAHs (PAH16, alkyl-PAHs and oxy-PAHs) were determined. The pore water concentration represents the bioavailable level of PAHs and is a more relevant measurement for correlation to potential toxicological effect on the micro-macro fauna (Arp et al. 2014. *ES&T* 48:11187). In addition to the abiotic characterization, micro- (nematodes), meso- (springtails and mites), and macrofauna (earthworms) were counted and identified (organism families). For relevant microbiological indicators, the enzyme coding genes present in groups of microorganisms performing specific functions were analyzed. These functions are key elements in e.g. the N-cycles, and can therefore potentially serve as functional indicators.

On the basis of results from the current field study and an on-going lysimeter experiment, a methodology for site-specific ERA will be developed, where SF rather than biodiversity is in focus. The most promising microbiological SF indicators found will be used together with other ecological, chemical, and ecotoxicological indicators in a site-specific risk assessment using the TRIAD approach (SE EPA report 5928 2009). Finally, consequences of a shift towards site-specific SF-based ERA methodology will be evaluated versus traditional approaches.

4b. Sustainability and socio-economic appraisal of remediation technologies and strategies

Strategies for rehabilitating brownfield land in emerging economies for renewable energy and other self-sustaining re-use strategies

Paul Bardos¹; Frederic Coulon; Alfonso Rodriguez; Quing Hu; Yongguan Zhu

¹ University of Brighton, Brighton, UK, r3 Environmental Technology Ltd., GB

The opportunities of rehabilitation of brownfield land in support of low carbon / renewable energy policy goals in China and Colombia will be presented and discussed. These are based on the completion of two recent strategic partnership fund (SPF) projects where a series of case studies have been undertaken in the two countries. Specifically, the Colombian project focused on the opportunity of soft-reuses to rehabilitate land affected by soil mercury pollution which are often located in disadvantaged areas; in contrast the Chinese's project focused on the rehabilitation and the opportunity of soft-reuses of land affected by the closure and relocation of industrial facilities that are along the edge of or within the city boundaries. The value-based approach taken to identify and optimise the services will be discussed and the tools used to identify and prioritise the soft-reuses opportunities will be described. Similarity and differences between the two countries will be further highlighted and compared to other European case studies. The main driver for both projects was to bring back the impacted areas into productive use focusing on renewable energy opportunities and/or other services as appropriate and therefore supporting the goals of increasing regional stability, facilitating sustainable economic growth, harnessing innovation in particular for low carbon development, supporting OECD accession, and identifying possibilities for new community enterprise.

Leveraging Big Data and Cognitive Computing for Remediation Selection, Benchmarking, and Environmental Portfolio Optimization

Craig Divine

Arcadis US, US

Environmental experts are challenged with the extremely rapid growth of information across the planet (Big Data), making it impossible for an individual to assimilate knowledge available and quickly integrate it to his or her expertise. While traditional information systems allow experts to have access to a wide variety of information sources, a detailed review of the scientific literature is a complex and laborious task. In addition, the information is generally complex and available in different formats; both structured (data tables) and unstructured (text reports). Therefore, integration, synthesis and use of all information remains very difficult and requires a significant amount of time. Obtaining and fully analyzing all appropriate information to identify all variables required to select the most efficient solution with high level of confidence is key to an economic and efficient remediation of contaminated sites. Furthermore, environmental portfolio managers are challenged with the optimization problem – how to make use of all their project data, assess the performance of their current remediation projects, and maximize the return on the resources applied to restoration.

A new evolutive technological tool is underdevelopment to support site remediation selection and design by integrating and leveraging all available technical, regulatory and financial information. Specifically, this application incorporates the new machine learning and cognitive processing technology created by IBM/Watson. This technology allows experts to exploit very quickly and efficiently environment Big Data. Current cognitive tools are used to develop an access to different sources of structured and unstructured massive data to make their assimilation and treatment very quickly. In addition, this tool has the ability to enrich its knowledge exponentially by integrating the information, as soon as it is available. Consequently, the uncertainty related to the selection of the remediation technology is continually improving and is determined dynamically. Additionally, the use of this tool allows the professional to work in natural language environment. The application's outcome is based on the search of benefits at different level: user, business, financial, environment and society by increasing and sharing the knowledge and the information related to development of remediation technologies for contaminated sites.

The application has been trained, with a current focus on petroleum hydrocarbon sites, by reading hundreds of site reports representing several hundred mature remediation sites. Based on that, the application can extract most relevant site information from a report, such as contaminant type and levels and geologic conditions in order to develop recommend site-specific remedial approaches with anticipated performance and cost range estimates. This capability is currently being used to support remedy selection and performance benchmark for current remediation projects for clients in the oil and gas and rail sectors. The application will be further expanded to address other contaminant types, including chlorinated solvents, in the next development phases.

The advantage of thermally enhanced bio-stimulation for sustainable land use

Yasuhide Furukawa¹; Takaaki Shimizu¹; Takeshi Kobayashi²

¹ Takenaka corporation; ² Yokohama National University, JP

[Background]

In Japan, there seems to be over 28,000 hectares of brownfield sites, which was used for commerce that has been used for industry and might be contaminated. Sustainable land management has received attention due to its importance for redevelopment of brownfields. One option to use brown field is to apply low-energy consumption system through remediation, which can make some benefit for land users. We have developed the new thermal enhanced bio stimulation system for CVOC-contaminated aquifer which can use the waste heat from the on-going factories. We conducted the field test of this unique system with automatic injections and pumping, and compared the other remediation techniques from the three aspects of sustainable remediation.

[Approach/Activities]

Pre pilot tests were conducted by the small amount of table tests and water treatment test of 300 little per day. By applying these results, the injection and pumping system with thermally enhanced aeration, which can treat 30 m3 of contaminated ground water per day, was designed. At the pilot test, we used the water soluble materials which consist of source of energy, macro-nutrients, micro-nutrients, vitamins, and components of nucleic acids for bio-stimulation. All system was controlled with sequencers and via Wi-fi, therefore it was possible to change the pumping or injection rate in the distant place. This system has been operated over one year and the amount of energy consumption and the changing of water quality of ground water has been measured.

[Results/Lessons Learned]

From the economic aspects, the cost of thermally enhanced bio-stimulation seems to be lower than that of excavation or long term pump and treat. And from the environmental aspects, the energy for remediation was almost same as in-situ bio-stimulation, because the duration of remediation could be reduced. Furthermore, from the social aspects, the number of the workers in the site was dramatically decreased by this automatic system. It also seems to be easy to announce the situation of on-going remediation, by using alarm system, which could send the alert-mail to PC or mobile phone when some warning situation. This means that when the volume of reagents has been decreased, or water level becomes higher than the planed level, some of the stake holder can easily know it and share the important information.

Remediation techniques decision making tool GAMMA

Stéphane Muguet¹; Jean-Marc Aldric; Lambert Jean-Marc²; Sabine Radas³; Bénédicte Dusart⁴

¹ Almadius; ² ABV Environment; ³ SBS Environnement; ⁴ Public Services of Wallonia, BE

The GAMMA project consisted in the development of a tool aiming to facilitate the selection of the most sustainable remediation techniques in the framework of remediation works in the Walloon Region.

The projects included the following phases:

- Synthesis and critical analysis of the legal and technical framework, including an extensive review of existing regulation worldwide;
- Proposition of the methodology ;
- Development of an multi-criteria grid integrating selected sustainable criteria's
- Consultation work involving industrial representative, consultant groups, remedial actors and the public sector;
- Application to real cases
- Drafting of the reference guide
- Amendments to CWBP [Guide for Good Practices in the Walloon Region]

The final tool [GAMMA] consists in a user-friendly Excel-based software using the PROMETHEE method and supporting 5 main sustainable criteria's, each of them being subdivided into sub-criteria:

- Local environmental impacts;
- Global environmental impacts;
- Local Social impacts;
- Global social impacts;
- Economical impacts;

A guide has been developed to support the utilization of the GAMMA tool.

Development of a Sustainable Remediation Evaluation Tool in Japan

Makoto Nakashima; Ray Hidaka; Tetsuro Sato; Hiroto Yamaguchi; Ray Hidaka

Kokusai Kogyo Co.,Ltd., JP

In the past five years sustainability has become a major topic in the field of remediation. Compared to green remediation which solely considers the impact of the remediation project on the environment, sustainable remediation (SR) also includes the impact on the economy and society from a local and regional perspective. SURF-UK is one of the leading international forums regarding the implementation of SR practice into remediation projects. Japan is still in its infancy regarding the development of decision making tools for SR. Tools, such as LIME for CO₂ emission gas calculation during general construction projects, are commonly used in Japan. However, due to the ongoing international efforts to develop new methods and tools to support SR decision-making, various groups in Japan are developing tailored evaluation methods and tools to address unique aspects of the Japanese economy and society.

Our group has developed an easily applicable tabular evaluation method for decision making in order to incorporate SR aspects into the project design and minimize, not only the impact on the environment of a remediation project, but also minimize negative impact and maximize positive impact on the economy and the local society. Compared to other available tools, ours unifies all three aspects of sustainability (ecology, economy, and society) in one evaluation sheet and makes it possible to compare different remediation methods through a standardized evaluation process. This evaluation method allows the user to separately rate and evaluate each remediation practice applicable to a project under the aspect of SR. Based on SR criteria from a list of impact factors published by SURF-UK., 15 categories with a total of 91 subcategories were chosen as main impact factors for Japan. Each category has been thoroughly defined in order to ensure a standardized evaluation from user to user and to make results comparable from case to case.

In total, there are 5 categories regarding ecology with 38 subcategories, 5 categories for economy with 23 subcategories, and 5 categories for social impact factors with 30 subcategories. The evaluation is based on the experience of the remediation professional but supported by a list of examples and a clear definition for each subcategory. Each factor is rated on a scale of 1 to 5, depending whether the impact is evaluated as positive (1), neutral (3), or negative (5). Each subcategory can be individually weighted. All evaluation levels (1-5) are explained in the evaluation matrix in order to help the user in the decision making process. Average scores for ecological, economical, and social factors help the remediation professional decide which remediation method will have least negative impact and the greatest benefit under SR aspects.

The evaluation matrix will be assessed and applied (tested?) in a stakeholder discussion in order to finalize the tool. The development of this universal and comparable evaluation tool for SR will hopefully lead to faster implication and greater general acceptance of sustainability practices in remediation projects by all stakeholders.

Means to attain sustainable risk management of contaminated sites in Finland

Jaana Sorvari¹; Meri Nihtilä; Jussi Reinikainen²; Outi Pyy³

¹ Aalto University; ² Finnish Environment Institute (SYKE); ³ Finnish Environmental Institute, FI

Around 250 contaminated sites are annually remediated in Finland, excavation and off-site disposal still being the most common method. According to a common understanding, the current remediation practices do not really comply with the principle of sustainable risk management (RM). To identify the most sustainable RM methods in a particular case we need tools. These are already available and include, i.a. computational tools based on different methodologies. Besides the tools, we need policy instruments to promote the application of sustainability appraisal as part of RM.

In our study we first surveyed the tools for sustainability appraisal available abroad. Then we selected some tools for studying their applicability in Finland. Current Finnish practices to assess sustainability and needs for method development were discussed in a workshop. With the support of several stakeholder groups, we also identified and analysed the policy instruments needed to support the adoption of sustainable RM practices. Our survey on the available tools showed variation from complicated, quantitative multi-criteria analysis tools to simple qualitative matrixes. So far, only a limited number of tools are available for a wide use as many tools were developed for research purposes.

We selected two quantitative tools, GoldSET and PIRTU, for testing with four different contaminated sites typical to Finland, i.e. gas station, shooting range, sawmill and market garden, and considered several, feasible remediation options for these. Our study showed that both tools need to be further developed to be suitable for common use in Finland. Lack of a component to consider the uncertainty of input values is a shortcoming of both tools. PIRTU runs in Excel, so it is actually possible to add this element in it. Both tools require a considerable amount of data and are thus most suitable for large and challenging remediation projects. For small sites, common in Finland, the advantages gained with the assessment may not outweigh the amount of work needed for gathering the data.

The representatives from consultancy, authorities, research and expert institutes and environmental administration, who participated in our workshop, brought forward that sustainability appraisal is not yet a common practice in the planning of remediation. They also highlighted that the tools should be clear, transparent and easily available in order to be widely adopted. There is also a need for tools of different levels varying from simple qualitative checklists to more complicated quantitative tools, and for instruments both at a regional and site level. The participants also acknowledged the necessity of policy and economic instruments, research on new remediation methods, education and clear communication.

Based on our results, in the development of policy instruments, we recommend focusing on the following topics: criteria, instructions, education and communication of sustainable remediation; restriction of landfill disposal of recyclable excavated soils; national database on the state of soil; and procedures for public procurement and spatial planning

Sustainable management of anthropic backfill materials: a technical proposal to overcome the impracticability of the new Italian rules

Daniele Susanni; Sara Ceccon

Ramboll, IT

Materials deriving from demolition of buildings, such as concrete or debris, have been historically used as backfill materials to level soil surface, mixed with native soils. Large industrial and residential areas in Northern Italy reveal the presence of backfill materials, below existing buildings or foundations.

In Italy new legislations, issued in 2012-2013, require the application of a leaching test for the characterization of backfill materials – according to standard UNI 10802, method UNI-EN 12457-2 – to evaluate the potential leakage of contaminants. Concentrations in the leachate are compared against threshold values for groundwater. In case of exceedance, the material should be removed, or treated, or encapsulated by means of permanent safety measures.

If concentrations in the leachate are below the applicable limits, the backfill material should be additionally characterized as a native soil, according to standard EPA methods.

While for native soils a human health and environmental risk assessment procedure can be applied, to determine risk-based target levels, risk assessment is not allowed on backfill materials exceeding the leaching test.

The following technical and procedural issues are highlighted:

- It is not clear how to distinguish an anthropic backfill material from native soil;
- The leaching test is specifically designed for metals and other inorganics, while the Regulators require to analyze also organic chemicals;
- The leaching test procedure is not representative of actual leaching phenomena at the site (where pavements reduce infiltration, contact time may be limited, mixing is not forced);
- Backfill materials may vary abruptly over short distance, thus making their thorough characterization very expensive; groundwater quality may represent a better indicator of actual release of contaminants over a larger scale;
- The threshold values applied to leachate are very stringent;
- Results from the leaching test cannot be used as input data for risk assessment, as applied to native soil;
- At several sites, analytical results from the different procedures (leaching test, soil and groundwater samples) do not provide a coherent picture;
- Leaching tests usually overestimate the concentration expected in groundwater, since depth to groundwater is not taken into account;
- Large remediation costs are expected to remove or encapsulate the backfill materials, with no or little benefits to the groundwater quality.

The presentation will discuss the consequences of applying the new legislation to the large scale, by demonstrating that the required approach is not sustainable, and proposing a different technical approach, based on human health and environmental risk assessment. Only materials actually posing risks should be addressed, while others would be managed as long as native soils.

Sustainability assessment tool of soil remediation and redevelopment projects

Peter Van den bossche¹; Maarten Schöffner¹; Griet Van Gestel²; Johan Ceenaeme²

¹ Witteveen+Bos; ² OVAM - Public Waste Agency of Flanders, BE

The Public Waste Agency of Flanders (OVAM) aims to make soil remediation in Flanders greener and more sustainable. In order to evaluate and quantify the sustainability of projects regarding land development, soil remediation and land use, an assessment tool was developed. This tool combines development alternatives with remediation options in order to evaluate their sustainability. In addition, sustainability of a selected remediation strategy can be optimized using this tool.

The assessment tool is web-based and contains approximately 30 criteria grouped into five themes: Economic costs & Benefits, Society & Social aspects, Sustainable Soil Management, Environment & Climate and Ecology & Biodiversity. The criteria and themes were selected based on experience of Witteveen+Bos regarding sustainability, stakeholder management and international criteria, e.g. SuRF and NICOLE Roadmap. Finally the tool was further optimized using case studies. During development of the assessment tool, the relevant stakeholders on soil remediation and development in Flanders were involved using bilateral conversations, workshops and conferences.

The tool is developed for soil remediation experts, contractors, project developers, the OVAM and other governments. The instrument can be used in a flexible way and on a voluntary basis to evaluate the sustainability of projects regarding land development, soil remediation and land use. Furthermore, the instrument is applicable in a general way but can also handle project specific aspects to sustainability.

The instrument can be applied to different phases of soil remediation and development: from investigation and design to execution and evaluation phase. The ambition level of the project is determined at the start in a well motivated and transparent way using stakeholder involvement. Several phases of the project are then evaluated and the criteria are scored based on phase specific themes and criteria.

4c. Managing large scale industrial pollution

Taking sustainable risk based land management to petrochemical impacted sites in Libya

Salahadein Alzien¹; Paul Bardos²; Uwe Schneidewind¹; Rafiq Azzam¹; Claudia Post¹

¹ RWTH Aachen University, DE; ² University of Brighton, Brighton, UK, r3 Environmental Technology Ltd., GB

Contamination with petroleum hydrocarbons (PHCs) is found in many countries and can cause widespread problems as PHCs can be easily leached into the environment. As such, adverse impacts can occur on human health, ecosystems or soil and water resources. Also, PHC-contamination might cause severe problems for a national or regional economy. Therefore, several contaminated land management approaches have been developed in the past that have proven beneficial to the restoration of contaminated sites. However, not all countries have managed such progress. While contaminated site management approaches now exist in many developed countries, Libya still lacks such a management system and it is important to develop and implement an effective regulatory system in a systematic manner to improve conditions in the affected areas. In recent years, sustainability also has become an integral part of many remediation studies. The idea behind sustainable remediation (SuR) is to perform contaminated site management in a sustainable manner (i.e. a balanced outcome in terms of the environmental, social, and economic elements of sustainable development) by taking into account risk-based land management, stakeholder participation and ensure sufficient transparency in the decision-making process.

In Libya, environmental problems resulting from PHC-contamination can ultimately be linked to NOC (National Oil Corporation of Libya) that was established to control Libya's oil industry through its fully-owned companies or in partnership with foreign entities. Although NOC desires to solve PHC-related environmental problems in an adequate and sustainable manner, no environmental management procedure to handle contaminated sites has been put into place. This is certainly for the most part due to a general lack or shortage of laws and regulations, difficulties in implementing such laws, and often low environmental awareness among the stakeholders.

Here, we propose a management guideline applicable to Libya that takes into account specific local social, environmental and economic conditions. This guideline is tailored to the specific environmental and socio-economic conditions of Libya and is based on approaches from the UK (CLR11), the US (CERCLA 1980, ASTM E1739-95) and Germany (BBodSchV 1999) as well as on ISO 31000, 31010 and ISO Guide 73. The issue of sustainability is addressed based on documents from SuRF-UK. Special attention is paid to the delineation of threshold values for soils at PHC-contaminated sites in Libya.

In this study, data from the Oases area (Al Wahat) in NE Libya is used. This site contains three oases, Jalu, Awjila and Jakharrah and the local population is about 50,000. The area is also the biggest producer of dates in Libya. The three oases are situated in a sub-region of the Libyan Desert with one of the highest oil records in the world and are surrounded by many oil fields. Oil production has led to the creation of at least 19 old big lagoons containing contaminated water, oil residues and various heavy metals.

Evaluation, Remediation and Long-Term Management of a Large Comingled Dilute VOC Plume

Craig Cox

Cox-Colvin & Associates, Inc., US

Background/Objectives. In 1998, the detection of chlorinated volatile organic compounds (CVOCs) in a public well field led Ohio EPA to begin a search for potential sources. By 2002, as many as four different consultants, representing local industries, had identified a comingled plume extending a distance of four miles. The highly permeable, well oxygenated, federally-designated sole source aquifer has a hydraulic conductivity on the order of 1200 feet/day and a horizontal flow velocity estimated at 10 feet/day. By chance, most of the industries lay along a common groundwater flow path and had tended to use similar CVOCs. This situation complicated the issue of source identification and potential responsibility. The objective soon became source area identification and dissection of the comingled plume to assign ownership. Following plume delineation, the sources of CVOCs were addressed through a variety of source area remedial actions (some of which are still proceeding). Public water was supplied to affected domestic well owners, and the public water supply was treated prior to delivery. The current objective is to return the groundwater quality to drinking water standards throughout the length of the plume.

Approach/Activities. Working in cooperation, the consultants shared analytical results from monitor wells, domestic wells, production wells, temporary wells, and surface water to form a regional database on groundwater and surface water quality. This database is still in use and updated frequently. Based on contaminant ratios of tetrachloroethene, trichloroethene, cis-1,2-dichloroethene, and 1,1,1-trichloroethane coupled with groundwater flow data the comingled plume was found to be sourced from at least six separate areas. Each industry chose remedial options based on their particular goals. The options included: excavation, in-situ chemox (potassium permanganate) injection, in-situ emulsified zero-valent iron injections, in-situ thermal desorption, and air sparge/soil vapor extraction. The treatment option for the public well field was granular activated carbon. Monitoring of the plumes, which have responded positively to the source removal, continues.

Results/Lessons Learned. To date, four sources have been remediated and groundwater quality has improved dramatically. Periodic regional plume updates are performed to monitor progress. The use of contaminant ratios proved to be a very powerful tool in plume delineation. Other characterization techniques including compound specific isotope analysis are being used to learn more about the plumes before they are gone. The presence of cis-1,2-dichloroethene was key to locating source areas where anerobic conditions existed locally. Due to the very high hydraulic conductivity and associated groundwater flow velocities, in-plume groundwater treatment options including permeable reactive barriers, containment (pump and treat), recirculating wells, and the like proved infeasible.

Improving management and rehabilitation of contaminated soils at the Sudoe region (project soil take care)

Montse Calderer¹; Irene Jubany¹; M.Inmaculada Álvarez-Fernández²; Celestino González-Nicieza²; Marilynne Soubrand³; Emmanuel Joussein³; M.Teresa Condesso de Melo⁴; Myriam Schmutz⁵; Michel Franceschi⁵; Xavier Boespflug⁶; Silvia Martinez⁷; Angel Faz⁷; Christ

¹ Fundacio CTM Centre Tecnologic; ² Universidad de Oviedo; ³ Université de Limoges; ⁴ Instituto Superior Técnico, Universidade de Lisboa; ⁵ Géoresources et Environnement; ⁶ CIMES; ⁷ Technical University of Cartagena; ⁸ Irstea; ⁹ CNRS, ES

Soils are a vital part of the natural environment and they are essential to human life. However, soils are subject to frequent attacks that might cause irreversible damage to them.

In particular, many regions from Southwest Europe are affected by soil contamination due to metals and/or petroleum hydrocarbons. This pollution not only affects the soils and they functions, but also to surface water and groundwater, atmosphere and human life (through breathing and ingestion).

Public authorities responsible for environmental management face two major problems in terms of economic costs: establishing accurate inventories of contaminated sites and defining the appropriate remediation process.

In this context, the project SOIL TAKE CARE aims at offering diagnostic tools, soil remediation technics and efficiency in political and social management of contaminated places. Specific objectives of the project are:

- To develop experimental devices and innovative methodologies to achieve fast and cheap soil diagnosis in terms of metal and petroleum hydrocarbons contamination.
- To develop monitoring tools for air and water contamination from soil by using cheap devices and modelling.
- To improve the technical development of two soil remediation strategies: in situ oxidation of petroleum hydrocarbons impacted soils and phytoremediation of metal contaminated sites.
- To identify strengths, weaknesses and motor elements in society (government and population) who face soil pollution.

The SOIL TAKE CARE is an international project co-financed by the European Regional Development Fund (ERDF) through the Interreg initiative SUDOE. The project started in July 2016 and will last until June 2019.

This work will introduce the goals of the project, the study sites and will show the results of the first year of the project.

Technical fact sheets on the relevance of industrial groundwater monitoring network: A tool for priority actions and pollution management

Susanne Schomburgk; Hubert Leprond

BRGM, FR

The water department of the French geological survey (BRGM1)) supports the local authorities with advices, local studies and tools in order to control groundwater quality in environmentally-sensitive facilities, supervised by the French the Ministry's environmental departments (DREAL). Prefectural orders regulate the industrial groundwater monitoring network, the frequency and the list of substances and types of analyses. Nevertheless, a frequent supervision is asked by the numerous analyses reports. To take into account a global perspective on groundwater good chemical status, we need to answer the question: Is the actual monitoring relevant with the environment and the present or former contamination? In order to find an efficient answer to this question, the DREAL of Alsace region and the BRGM water division decided to develop a technical fact sheet on the relevance of industrial groundwater monitoring network.

The fact sheets have been developed with environmentally-sensitive facilities of different environments and monitoring networks. They propose to gather with the standardization environmental information including industrial background information, local hydrogeology, environmental issues, the availability of analyses data as well as the cartography of the monitoring network distribution. Long term monitoring with an appropriate monitoring network points out the evolution of contamination in space and time by means of the national groundwater database (ADES 2)) providing water quality data of various providers in France. This data gathering enables the view on the relevance of specific groundwater monitoring network and the adequacy of the actual monitoring frequency and the prescribed substances. Data statistics enable to highlight missing data or a lack of available data.

The crossed viewpoints of hydrogeology and contaminated sites and soil provide fact sheets with an indicator of monitoring relevance, quality and comprehensiveness. It is designed for the regional authorities to define further priority actions in collaboration with the environmentally-sensitive facilities in terms of new prefectural orders and to prioritize the monitoring of environmentally-sensitive facilities with environmental issues.

1) Bureau de recherche géologique et minière (BRGM)

2) Banque nationale d'Accès aux Données sur les Eaux Souterraines (ADES) www.ad.es.eaufrance.fr

Monitoring of soil salinities in an irrigated area

Harun Kaman¹; Ahmet Kurunç; Mahmut Çetin

¹ Akdeniz University, TR

Salinity, which is one of the most important factors limiting agricultural production, decreases plant growth and yield. Additionally, it also causes serious damage to plants. Therefore, soil salinity is an important and significant risk for sustainability of agricultural production. Salt accumulation in plant root zone can reach significant levels, particularly in irrigated areas, over time. It is not possible to determine the soil salinity quickly by conventional methods since they requires too many of soil sampling especially in large areas. Therefore, new methodologies have been developed in recent years for easy and quick assessment of soil salinity in agricultural areas. One of these methods is the electromagnetic induction (EM38) technique. In the field, salinity can be measured by using EM38 tool in horizontal- and vertical-dipole orientation. Average apparent salinities of 1 and 2 m of the soil profile can be determined by positioning the EM38 instrument in horizontal and vertical orientations, respectively. This research was carried out in Serik Plain irrigation area which is located in Antalya, south of Turkey. In the study, it was aimed at determining changes in soil salinity in the irrigation area by EM38 instrument readings. To this end, salinity readings were done at 125 different points in the pre- and post-irrigation season. At the pre-irrigation (in June), the average soil salinities were determined as 5.52 ± 5.4 and 7.42 ± 5.49 dS/m for 0-1 and 0-2 m of soil profiles, respectively whereas they were 7.66 ± 6.80 dS/m for 0-1 m depth and 8.58 ± 6.72 dS/m for 0-2 m of soil depth at the post-irrigation (November). The results indicate that soil salinity is higher in the post-irrigation than that of pre-irrigation period. Additionally, results lead us to conclude that the EM38 device might be promisingly used to determine soil salinity in a quick and safe manner in large scale areas.

Evaluation of soil salinity and alkalinity in low-lying irrigated areas

Harun Kaman¹; Mahmut Çetin; Cevat Kırdı

¹ Akdeniz University, TR

Alkalinisation of soil resources is more critical than salinization. Reclamation of alkali soils needs more time and money, compared to the salinity amendment. This study was conducted in Yemişli Irrigation District of Lower Seyhan Plain, prone to both alkalinity and salinity development, located in the Mediterranean region of Turkey. There has been irrigation and drainage system in Lower Seyhan Plain for almost 50 years. Lower Seyhan Plain (LSP) covers about 213 200 ha area and 174 088 ha of it is arable for irrigated farming. A pilot area of Yemişli Irrigation District with 7100 ha was chosen in the LSP for this study. The farmers in the District have no other alternatives to use irrigation return flows of inferior quality for irrigation. Therefore, salinity and alkalinity has been an extremely important and increasing problem in the region year by year. Considering the degradation by salinity and sodicity, this study investigated to figure out the extent and severity of sodium adsorption ratio (SAR) and soil salinity in the lands where irrigation return flows have been used in irrigation for a long time. Study results showed that the salinity development and the severity of salinity are almost null in the areas where fresh water has been used for irrigation. However, non-saline areas have exhibited a patchy distribution pattern when the fresh water and irrigation water has been jointly used, indicating the natural effect of dilution mechanism of environment. It was also found out that there has been severe sodicity problem in Yemişli Irrigation District. The more salinity development in the profile is, the more sodicity is in the area, suggesting that severe salinity development should be prevented by taking measures such as more fresh water use in irrigation, supplementary drainage actions, creating opportunities for leaching salts from the root-zone.

Evaluation of Irrigation Performance in an Irrigated Area

Harun Kaman¹; Mahmut Çetin; Cevat Kırdı

¹ Akdeniz University, TR

Global warming and climate changes have caused unfavorable changes for availability of water resources. Climate changes have caused increases in temperatures and remarkable decreases in the availability water resources, to the detriment of demand of water by all sectors. On the other hand, increased population and industrial development cause additional strain on availability of water. Therefore, it is important to determine water use efficiency in irrigated agriculture which is the largest user of available water resources. If water use efficiency is found to be low, the management options, which would increase water use efficiency, must be sought and investigated. The low water use efficiency implies wasting of water resources, suggesting that there is a room for saving water in favor of other water demanding sectors. The work undertaken here investigates water use efficiency under an existing irrigation management through evaluating all terms of water balance equation in a large scale irrigation district by following the basic hydrologic water balance approach. The study was carried out in the Akarsu Irrigation District of Lower Seyhan Plain in the Mediterranean coastal plain in Southern Turkey. There were four water inlet and one water outlet sites in the study area where irrigation water inflows to the agricultural basin and outflows from the basin were measured with automatic water level recorders. Mean hourly water depths at the canal cross-sections were obtained by averaging measurements done at 10-minute intervals, then, mean hourly water depths were converted to flow rates by using stage-discharge rating curves developed exclusively for the gauging sites. Similarly, drainage in- and out-flow measurements were also made at sites to assess the net drainage flows generated by the command area. Rainfall data was also recorded at the meteorological station located in the research catchment during the study period. Crop coverage in the area was mainly corn as first and second crops, wheat, cotton and citrus orchards. The results showed that the irrigation efficiency in study area was as low as 29%. Surface irrigation methods were common in the catchment, and this kind of irrigation technique under Mediterranean climate caused an adverse effect and reduced irrigation efficiency; whereas, increased drainage fraction. Therefore, sprinkler and drip irrigation methods which are considered as the water saving methods must be promoted to replace traditional surface methods. Additionally, deficit irrigation methods should also be considered as means of increasing crop water use efficiency. In this regard, our suggestion is that partial-root-zone drying (PRD) irrigation technique is worth trying to adopt in the region for saving irrigation water and increasing both water use and irrigation efficiency.

4d. Managing large scale agricultural pollution

A preliminary study on the technical system of land consolidation integrated with soil remediation

Xiaoming Wan

Chaoyang District, CN

Action Plan on Soil Pollution Prevention and Control released recently set a timetable for the prevention and control of soil pollution in China, and built a working pattern of 36 departments to work together. It is required by the current pollution status for all the administration units to work together, especially for the environmental protection department and the land and resources department. In order to make clear the technical route of soil consolidation when the agricultural land is contaminated, the current paper carried out a preliminary study on the technology system of land consolidation in the integration of soil remediation.

Through literature collection, expert interviews, a comprehensive analysis was conducted of the problems existing in the system of farmland consolidation, and the potential integration directions with soil remediation. First of all, the concept and technical points of farmland reconsolidation and soil remediation were discussed. Then the problems brought in by the lack of effective convergence of farmland reconsolidation and soil remediation in China were analyzed. Finally, the PRP system (Planning-Remediation-Policy) of integrated farmland reconsolidation technology is proposed. The PRP system includes farmland consolidation project Planning with the integration of soil environmental quality survey and evaluation, the integrated Remediation technology for contaminated soil, and the farmland reconsolidation incentive Policy for the integration of soil remediation. The PRP system will provide an important way for the land and resources department to realize the safe use of agricultural land.

Topic 5. Reuse and upgrading of land, water and sediment in the circular economy

5a. Brownfield regeneration and redevelopment of former industrial areas

Goal setting of groundwater remediation in an old INDUSTRIAL AREA - case Härmälänranta in Tampere

Juha Parviainen

Ramboll Finland Oy, FI

Background

Härmälänranta area is an old industrial area in Tampere, Finland. There were industrial operations from 1936 until 2013. Over the following decades versatile workshop and assembly industry was in operation. Industrial activities included use of oils, metal cleansers, coating chemicals, paints and also fuel storing and distribution, and heating oil storing. Due to the heavy industrial history, numerous soil, groundwater (GW) and porous/indoor air investigations have been carried out from 2005 until today to find out if the area is environmentally legitimate and applicable for future residential use. Ramboll has been involved with the case since the beginning. Investigations have showed that especially the soil is, at many places, contaminated with petroleum hydrocarbons, heavy metals, volatile organic compounds (VOCs) and waste. In GW there have also been detected organic contaminants, mainly chlorinated compounds (CVOCs). CVOCs (especially tetrachloroethene, PCE) have been used as degreasing agent broadly in the area. PCE has likely ended up to the GW through processing and storage basins.

PCE is heavier than water and has low viscosity. Because of these characteristics, after reaching the soil, it has descended to GW and further downwards. Industrially used PCE often includes trichloroethene (TCE) as an impurity which is also a breakdown product of PCE. In anoxic GW conditions TCE further breaks down to dichloroethene (DCE) and vinyl chloride (VC). VC needs oxic conditions to break down to ethane. Due to this and to the anoxic quality of the GW, there are still high VC concentrations (max 1 900 µg/l) in many parts of the old industrial area (area of VC > 43 µg/l = 6 ha). Breakdown of PCE has started when it has reached the GW. The natural breakdown process of PCE and TCE is normally slow and it can even stop when it reaches the form of VC. The concentration of VC has been clearly higher than the concentration of TCE or PCE. This indicates that the natural breakdown process has already occurred. VC is the most harmful compound in the area because it is very transmissible in soil and carcinogenic.

Aim

Primary aim of the work is to find out what are the necessary remedial and/or structural means to enable healthy living in the future residential area. In addition to modelling the transfer risk of VOCs in the soil, Ramboll will continue investigations on GW and porous and indoor air to clarify if there is an actual risk of VOCs transferring from GW to porous air and further to indoor air of the future buildings. Installations used in the measurements will imitate actual groundwork structures of a residential high-rise. Another aim is to define what is the most cost-efficient remediation design for contaminated GW in the area. To identify the best available technologies a pilot project was started in August 2016 with 3 independent pilot zones which are operated by 3 different GW remediation constructors.

Conclusions

By June 2017 we intend to have found the best remediation method to be able to lower the VC concentrations to acceptable and safe level. Simultaneously, the risk assessment modelling will be improved via on site measurements of VOCs.

Redevelopment of a former industrial area: do willows like Heavy Metal

Cirsten Zwaagstra¹; Marlea Wagelmans

¹ Bioclear, NL

The province of Groningen has started the redevelopment of the site of a former industrial area. The site will be turned into a housing area with a part recreational area for cycling and walking. A part of the site is polluted with heavy metals. At this part willows have been planted in 2012. Due to dense willow plantation people cannot access the site and direct human contact with the pollution is not possible. Bioclear investigates the possibilities for risk management at this site and the possibilities to use the wood from this site for sustainable production.

The soil is polluted with heavy metals. Planting trees has an effect on soil properties. In the root zone of trees a population of bacteria and fungi will develop and oxygen will be transported through the soil. The soil structure can improve due to the root system and also a healthy soil ecosystem can be developed. This might also improve the water holding capacity of the soil. This means that the soil ecosystem services can also be improved at a polluted site. All the beneficiary effects of a willow plantation to soil can also have various effects on the heavy metals:

- Heavy metals can be precipitated and stabilised in the root zone. They are no longer available for uptake by organisms and the (ecological) risk will decrease. This process does not remove pollutants from the soil system but their (potential) effect to the environment will decrease.
- Heavy metals can be uptaken by the root system of plants and can be transported to above ground plant tissues. These plant tissues can be harvested and removed from the location. This decreases the total amount of metals in the soil. Attention should be paid to sustainable use of the harvested material.

In this project we have determined whether the soil quality actually improves by the willows. We have monitored the heavy metals in soil and willows as well as the availability of the metals in soil. This information is used to calculate the removal capacity of the willows. In order to assess and monitor the ecological risks we have used a test with springtails (small soil organisms) that measures the actual exposure of the soil organisms to the pollution.

Based on the concentration of heavy metals in the willows we have also defined possibilities for sustainable use of the wood. The wood can for instance be used for garden fences, extraction of salicine (a pain killer) from bark or for heating.

This combination of redevelopment, remediation, risk management and creation of sustainable, biobased products is a concept that can be used at more former industrial and other polluted sites within the province of Groningen and outside.

5b. Recovery of nutrients and other valuable resources

Cadmium and zinc recovery from soils using hyperaccumulator plants

Marie-Odile Simonnot¹; Claire Hazotte; Baptiste Laubie; Frédéric Rees; Jean-Louis Morel

¹ Université de Lorraine, FR

Plants that hyperaccumulate metals are of potential interest for soil remediation and subsequent metal recovery. Cd and Zn are common contaminants of urban, industrial and agricultural soils. The decontamination of soils where both metals are present is a major challenge, as these elements cannot be easily removed from the soil matrix.

Phytoextraction is the process using plants able to accumulate sufficient quantities of metals in the harvestable parts. Hyperaccumulators can serve this purpose as their shoots reach concentrations higher than 0.1 % metal in dry weight. *Nocca caerulescens* is able to accumulate up to 20 000 mg kg⁻¹ of Zn, 2000 mg kg⁻¹ of cadmium and 10 000 mg kg⁻¹ of Ni. As it can grow on a variety of soils contaminated by metals, it presents a high interest for the decontamination of soils polluted by metals.

To avoid the disposal of the harvested metal-rich plants, physical and chemical processes may be applied to recover selected heavy metals with a high purity, thus enabling the recycling of these elements. This strategy, called agromining, has been proved feasible for nickel, but means of recovering Cd and Zn have rarely been investigated so far.

This work was undertaken to design a new process to recover Cd and Zn from the biomass of *N. caerulescens*. At first, dry plants need to be burnt to concentrate the metals in ashes, which are leached into solution. Then, different techniques are available to extract the metals from the leach liquor: liquid-liquid extraction, ion exchange, Cd electrodeposition or Cd cementation. The latter technique consists of adding Zn powder to a solution containing Cd²⁺ cations to obtain Cd metal and Zn²⁺. It has been selected here, because it is rather simple, effective and cheap.

The objective of this contribution is to present the process that has been developed for Cd and Zn recovery from the biomass of *N. caerulescens*, with the following stages:

1. Plant ashing,
2. Ash washing to remove potassium (K) and leaching to transfer metals into solution,
3. Cd recovery by cementation with Zn powder,
4. Recovery of excess Zn by selective precipitation.

To the best of our knowledge, this is the first time that a hydrometallurgical process is tested for Cd and Zn recovery from *N. caerulescens* to produce purified metal compounds.

5c. Reuse and upgrading of water, soil and sediment products

Effect of using reclaimed water on the development of microbial biofilms on drip irrigation systems

Carmen Biel; Marc Viñas; Miriam Guivernau; Robert Save

Institute of Agrifood Research and Technology (IRTA), ES

According to climate change projections, water scarcity under Mediterranean conditions is promoting the need of using reclaimed water for agricultural irrigation. Drip irrigation is suitable for reclaimed wastewater use because it minimizes the health risk for farmers and consumers minimizing the contact of users and products with reused water. However, emitter clogging and potential microbial infectiousness are the main restrictions for its general use in irrigation. Clogging is tightly related to biofilm formation linked with inorganic mineral precipitation on drip irrigation pipes and emitters. Different parameters such as water quality, pressure and temperature, dripper design and flow rate impact directly on clogging formation.

In this work, groundwater and reclaimed water irrigation system were performed during two years. Groundwater from IRTA facilities was pumped and stored in a lagoon reservoir. Reclaimed water was obtained from a non-disinfected secondary treated wastewater from local Waste Water Treatment Plant (Caldes de Montbui) that collects waste water from the municipality (domestic and industrial effluents). To avoid biofilm and scaling formation two mitigation strategies has been applied: i) nitric acid and ii) CO₂ injection, in the reclaimed water irrigation system. After seventeen and twenty months of continuous irrigation, microbial community established on biofilm inside the drippers, and water inflow and outflow of the drippers was assessed by means of classical and molecular techniques. To distinguish those metabolically active microbial populations from total community, molecular analysis (qPCR and MiSeq) were performed from total genomic DNA and RNA from biomass biofilm and water suspensions. qPCR and high throughput sequencing (MiSeq-Illumina) of 16S rRNA/ITS rRNA genes were assessed both for total (DNA based) and active (cDNA based) eubacterial and total (DNA based) fungal community to distinguish those metabolically active microbial populations. Microbial diversity of water outflow was not affected by the biofilm microbial composition being similar to the inflow. Therefore, the previous treatments applied on reclaimed water were key factors to prevent the growth of microbial pathogens on biofilms. Microbial community structure on the dripper biofilms was dependent on water source. Moreover, the high temperature reach inside the drippers (>37°C during light hours) seems to exert a positive pressure on final microbial population promoting an enrichment of thermophilic microbiota such as *Deinococcus-Thermus*, *Ignavibacteriae*, *Chloroflexi* phyla are outcompeting pathogenic microbes. CO₂ and HNO₃ treatments reduced considerably the presence of the phytopathogen *Cladosporium* spp. Interestingly, known human pathogens such as *Legionella* and *Mycobacterium* were less metabolically active (RNA level) on the biofilms.

To sum up, treated reclaimed water with arises to be a good alternative water source with a low biofouling and scaling formation but we have to take in consideration the high accumulation of sodium and chloride content that could affect soil performance and growth in sensible crops to high water and soil salinity.

Groundwater heat pump : A case study in the city of Lyon

Vincent Gruffat; Aurélie Labastie

ARCADIS France, BE

The shallow aquifer of the Rhône alluvium in the Lyon area is particularly well suited for shallow geothermal systems. It is being used as a heat source since the 60's for buildings heating and cooling.

This poster presents a comprehensive study performed in the framework of a tertiary building construction which complies with High Quality Environmental standards, so geothermal system was a key asset in order to achieve required environmental criteria. The study included feasibility study, permitting and project management. Main difficulties encountered and solutions found are presented. Suggestions for improvement of tools available for overall thermal impact are proposed. The need for a thermal impact assessment at the scale of the urban area is highlighted.

In the past, studies were carried by public or semi-public organisms (ADEME, BRGM...) in order to assess the impact of the groundwater warming since cooling cycles are generally more energy-consuming (many systems present a heat-excess energy balance towards the aquifer. They conclude to a significant increase of biological activity with temperature increase. A state of the thermal situation of the Rhône alluvial aquifer, aimed at better understanding current situation and evolution of groundwater temperature at the scale of the city of Lyon would be very beneficial in order to work towards a better planning and use of the thermal resource.

Alteration of arsenic release from excavated sedimentary mudstone with oxidative weathering in Japan

Akihide Kamata; Toshihiko Miura; Tetsumi Higasayama; Masahiko Katoh

Okubo, Konan-ku Yokohama-shi, Kanagawa, JP

Sedimentary rock naturally occurring contamination with hazardous trace metal and/or metalloid, in particular arsenic, should be treated without its leaching to outer environment. Sedimentary rock naturally contains arsenic at a very low concentration; but, the excavation often makes arsenic more soluble. Understanding the mechanisms of arsenic release from the excavated sedimentary rock is important to design the treatment without its leaching to outer environment; however, little was known regarding the mechanisms. The sedimentary rock is excavated from the redox condition, and placed on the temporary storage site. Thus, the aims of this study was to elucidate the effect of oxidative weathering on the arsenic release mechanisms of excavated sedimentary rock. In this study, the target of sedimentary rock was marine sedimentary mudstone, which is one of the sedimentary rock excavated a huge amounts in Japan.

The mudstone removed the 2-5 cm surface was crushed under 0.5 mm particle size. We believe that the sample prepared by such procedure could be considered as the representative sample just after the excavation. The crushed samples were incubated under room condition maintaining the moisture to the initial content for 0, 7, 14, and 30 days, and after the incubation, the sample was used as oxidative weathered sample. The water-soluble arsenic and other element in the oxidative weathered sample was evaluated by the water extraction with a solid/water ratio of 1:10 for 6 to 720 hrs contact time. A sequential extraction procedure was performed on the sample in accordance with the procedure described by Wentzel et al. (2001).

The amount of water-soluble arsenic at 6 hrs contact time was fluctuated with the increase in the days of oxidative weathering; from days of 0 to 14, the water-soluble arsenic increased, but from days of 14 to 30 it decreased to the same level as the value of 0 day. In all the oxidative weathered sample, the levels of water-soluble arsenic decreased with the increase in the contact time, and reached to the same level at 0.5 mg/kg in the end of experiment (720 hrs). The pH value of oxidative weathered sample decreased with the increase in the contact time despite day of oxidative weathering although the EC value oppositely increased. The sulfate ion increased as the day of oxidative weathering and contact time increased. The iron concentration rapidly decreased at the beginning of shaking, and then stable at the low level. Alteration of water-soluble arsenic would be attributed to the pyrite oxidation, and subsequent iron precipitation. Pyrite oxidation during the oxidative weathering would release arsenic from the pyrite, and subsequent iron precipitation could induce the coprecipitation of arsenic and/or the arsenic sorption on its surface. The alteration of arsenic fraction by the sequential extraction during the oxidative weathering was compatible with that of water-soluble arsenic. These results suggest that the temporary storage without exposing to rain would make the arsenic risk lower in the excavated sedimentary mudstone.

Relationship between arsenic release from excavated soil and sedimentary rock and its phases by sequential extraction

Masahiko Katoh; Mariko Watanabe

Kawasaki City, JP

Many tunnel projects is be planning for next decades in Japan, which will result in generation of a huge amount of excavated soil and/or sedimentary rock. The excavated soil and sedimentary rock naturally contains hazardous trace metal and metalloid, in particular arsenic, and the excavation make arsenic phases soluble. Thus, the level of arsenic release from the soil and sedimentary rock often exceeds the Japanese environmental standard for soil (0.01 mg/L). Therefore, such excavated soil and sedimentary rock expects to be treated appropriately, and be re-used without environmental risk due to limited disposal sites in Japan. In order to reach the goal, it is important to understand the arsenic phases that has potential to be released and readily extract their fractions. In this study, the first fraction of sequential extraction was considered as a potential fraction to be released. The aims of this study were to understand the relationship between the arsenic release from excavated soil and sedimentary rock and its phases by sequential extraction.

The six excavated sedimentary rocks (two mudstones, marine clay, hard shale, black schist, slate) and one excavated soil were provided, and crushed under 0.5 mm particle size. The arsenic release from the sample was evaluated by the water extraction under the different contact time and solid/water ratio. The contact time was set to 3–672 hrs at a constant solid/water ratio of 1:10, and solid/water ratio was done to 1:10–1:1000 at a constant contact time of 24 hrs. After the shaking (200rpm), the arsenic concentration was determined. A sequential extraction procedure was performed on the sample in accordance with the procedure described by Wenzel et al. (2001).

The amount of arsenic release from the excavated rock and soil was highly depended on the contact time. The amount of arsenic release gradually increased to 168 hrs extraction, and then were stable except the black schist and slate samples. In similar to the contact time, the arsenic release was highly depended on the solid/water ratio. The arsenic release from all the excavated rock and soil used in this study increased with the increase in the solid/water ratio. The distribution of arsenic fraction by the sequential extraction greatly differed between the excavated rock and soil. The positive liner relationship between the amount of arsenic release at the contact time of 672 hrs and the amount of arsenic in 1st fraction was observed. This suggests that in equilibrium condition, water would extract the arsenic phases in the 1st fraction of the sequential extraction. In similar, the positive liner relationship between the amount of arsenic release at the solid/water ratio of 1:50 and the amount of arsenic in 1st fraction was observed. Furthermore, the correlation of 1:50 extraction was high as compare with the 672 hrs extraction. Thus, this study suggests that the water extraction at the solid/water ratio of 1:50 and contact time of 24 hrs is suitable to evaluate the arsenic phases that has potential to be released from the excavated rock and soil.

Improvement of excavated materials management by using urban geochemical baseline data – Nantes case study (France)

Cécile Le Guern¹; Baptiste Sauvaget²; Pierre CONIL¹; Vivien Baudouin¹

¹ BRGM; ² BRGM/Mines ParisTech PSL, FR

In France, the reuse of excavated materials is conditioned by their geochemical compatibility with the receiving site, referring to the notion of urban geochemical baseline. To avoid a case by case approach, a more general characterization of urban geochemical baseline has been tested in several quarter of the city of Nantes to anticipate the management of excavated materials from redevelopment projects. The challenges to be faced were numerous, including: 1) No systematic characterization of urban soils and subsoil geochemistry was available, only pollution diagnostics were available; 2) The excavation of materials occurring on several meters of depth, a 3D approach was necessary. We focus here on the reflection carried out on the potential use of geochemical baseline to drive the management of excavated materials.

The methodology consisted in gathering pollution diagnostics results into a georeferenced database, cleaning the data from point source pollutions, assigning the samples to the typology of materials defined on the quarters (including a typology of made-ground according to their intrinsic potential of pollution), calculating statistical distributions of the various geochemical parameters per type of materials, and verifying the coherence. Statistical analysis using box plots were also carried out. The urban geochemical baseline was supposed to correspond to the 90th percentile of the data set available.

A single urban geochemical baseline value would have been very welcome operationally. Nevertheless, it appeared inconsistent with the heterogeneity of the materials encountered in the studied urban areas. In particular, the questionable made-grounds, containing industrial residues, show a poor geochemical quality. They also strongly contrast with some clean sandy anthropogenic deposits. To face this problem of heterogeneity, we considered several geochemical baselines, one per typology of materials.

Nevertheless, using the 90th percentile as reference value conducts to consider that 10 % of the excavated materials are not acceptable for reuse, whereas their geochemical quality correspond to usual values. The notion of level of anomaly appeared operationally more attractive to us. In this frame, we considered the upper whisker. The postulate that the upper whisker is higher than the 90th percentile, verified for the natural geochemical baseline, was not verified for some parameters (Pb, Zn, PAH, ...). This could be related to a more important diffuse pollution by these contaminants on the studied areas. Considering this, we propose to consider the highest value between the 90th percentile and the upper whisker to define geochemical compatibility levels.

The geochemical compatibility levels defined, integrating the notion of anomaly levels, appears more appropriate to manage excavated materials than geochemical baseline values. The statistical approach should however be completed by a spatial approach, especially if the data used were acquired for other purposes (eg., pollution diagnostics) than the calculation of geochemical reference values.

Evaluation of Glauconite Sediments as an Amendment for Sandy Soils in Egypt 1- Preliminary studies

Mahmoud Morsy

Faculty of Agriculture , Minia University, EG

Glauconite ,also known as “green sand” is an iron potassium phyllosilicate (mica group) mineral of characteristic green color with very low weathering resistance and very friable . Preliminary studies were carried out to study the possibility of using the glauconite as an amendment for the sandy soils. Two glauconite sediments were investigated, one was coarse textured (CG) , and the other was fine one (FG). The two glauconite samples were collected from Al-Bahria Oasis, Egypt and analyzed. Two pot experiments using a sandy soil cultivated with broad beans and peas were set up to study the efficiency of using glauconite as a soil amendment. The two glauconites were applied to the sandy soil at six rates (0, 5,10,15,20 and25 ton/hectare). The obtained results of the current study show that the clay + silt % , E.C ,K and Zn contents of the fine glauconite were higher than those of the coarse one; however; the P , Fe and Mn contents of the coarse glauconite were higher than those of the fine one. Application of the two glauconites at the rate of 20 ton/hectare to the sandy soil increased the plant height, fresh and dry weight as well as water use efficiency by broad beans and peas shoots . In general, application of glauconite improves the water use efficiency and enhances the plant growth. It could be recommended to use the glauconite at the rate of 8 ton/ feddan as an amendment for the sandy soils under the conditions of El-Minia Governorate,Egypt.

Key words: Sandy soil, glauconite, amendment ,broad beans and peas .

A new regulation to promote beneficial use of excess soil materials

Jussi Reinikainen

SYKE, FI

Background

Although the Finnish policy approach strive for avoiding unnecessary remediation and using more innovative risk management methods, soil remediation is and will be often based on excavation. This results from the fact that the most typical drivers for remediation in Finland are related to site redevelopment activities where soil excavation, connected with conventional earth construction works, is often a practical solution. Hence, most of the redevelopment and remediation projects also involve management of excess excavated soils. Within the whole construction sector the annual amount of surplus soils that may be classified as waste totals around 20-30 million tons. Promoting environmental and economic sustainability in the soil management practice is therefore a common objective for both regulators and operators.

At present, however, certain regulatory barriers restrict the extensive reuse of surplus soils mainly to large-scale redevelopment projects in the capital region, and hamper it even then. Such barriers include a lack of guidelines and the likely obligation to apply for an environmental permit for reuse due to the somewhat vague definition of waste in terms of surplus soils.

Aim

To tackle the regulatory barriers for sustainable soil management a new government decree on the reuse of soils from construction activities, including remediation, is being prepared in the Finnish environmental administration in collaboration with key stakeholder groups. The objective of the decree is to promote reasonable, but controlled usage of surplus soils in earth construction by the adoption of a simple notification system that would replace the time-consuming environmental permit procedure. The decree is expected to be issued around summer 2017.

The scope of the decree will be restricted to predefined materials, construction applications and site conditions with specific requirements. The materials, included in the decree, cover both contaminated and uncontaminated soils that are or may be classified as waste, soils including small amounts of mineral construction waste, in situ stabilization of clayey soils with certain industrial wastes or by-products, excavated stabilized soils, and dredged sediments when reused on land. The construction applications intended to be included in the decree include e.g. traffic lanes, field structures, noise barriers, and filling applications. The decree will also include new risk-based environmental acceptability criteria for the leaching of contaminants from the soils to be reused. Moreover, required quality assurance protocols covering e.g. leaching tests and the necessary sampling approaches based on representative multi-increment samples will be given in the decree.

Conclusion

We believe that the forthcoming decree with the defined preconditions and the consequent simple notification system will strongly promote and increase the systematic reuse of contaminated and other surplus soils originating from remediation and construction activities nationwide. Hence, it will also contribute to the attainment of more sustainable land management practice and promote the principles of circular economy.

Arsenic phases and its leaching behavior in excavated sedimentary rock and soil by up-flow column leaching test

Shoji Suzuki; Masahiko Katoh

Sobudai, Minami-ku Sagamihara-shi, Kanagawa, JP

Sedimentary rock and soil excavated for tunnel construction is concerned, particularly in Japan because toxic metal and/or metalloid such as arsenic often becomes more soluble by the excavation. The arsenic release from the excavated rock and soil often exceeds over the Japanese environmental standard for soil. Therefore, such excavated rock and soil expects to be treated appropriately, and to be re-used without environmental risk due to limited disposal sites in Japan. Understanding the arsenic phases and arsenic leaching behavior in the excavated sedimentary rock and soil is important to design the countermeasures of such excavated sedimentary rock and soil. The aims of this study were to elucidate the arsenic leaching behavior, and to excavate the amount of arsenic leached relating to the arsenic phases in the excavated sedimentary rock and soil using the up-flow column leaching test.

The four excavated sedimentary rocks (two mudstones, marine clay, black schist) and one excavated soil were provided, and crushed under 0.5 mm particle size. The crushed sample was filled into the glass column at a bulk density of 1.47 g/cm³. Ultra-pure water was flowed from the bottom of column at a rate corresponding to 20 mm precipitation per hour. The leached water was periodically collected, and the test was concentration in percolated water was below 0.01 mg/L. The arsenic concentration in percolated water was determined. The arsenic phases in the samples before and after the leaching test was evaluated by a sequential extraction following the method of Wenzel et al. (2001).

The similar tendency of arsenic leaching behavior was observed despite the type of excavated rock and soil; i.e., the rapid increase of arsenic concentration was observed, and the arsenic concentration gradually decreased with the increase in the water percolation after the peak of arsenic concentration. However, the slope of increase in arsenic concentration, the maximum arsenic concentration, and tailing of arsenic concentration differed depending on the excavated rock and soil type. Comparing with the results of leaching test and arsenic phases by the sequential extraction, the sum total amount of arsenic fraction in the sequential extraction before the leaching test was balanced with the summed amount of arsenic leached during the leaching test and arsenic fractions after the leaching test. Furthermore, the leaching test and sequential extraction demonstrate that the amounts of arsenic leached from the beginning to the maximum arsenic concentration observed and from the maximum arsenic concentration to the end of test was almost equal to the amount of first and second arsenic fractions, respectively. This suggests that the arsenic phases that have a potential to be leached from the excavated rock and soil was consisted of the first two fraction of sequential extraction: the arsenic phases in the first fraction would be readily leachable, and arsenic phases in the second fraction would be leachable after the end of leaching from the first fraction.

Sediments and suspended matter contamination of the dam reservoirs

Gabriela Zemełka

Cracow University of Technology, PL

The aim of this article is to describe the sediments and suspended matter contaminations in selected water dam reservoirs in Poland. The suspended matter was taken in individual water samples and in an integrated way through so-called "time integrated collector". The basis of field research was sediment fingerprinting method commonly used to determine the sources of the suspended matter in the water reservoirs. The proposed methodology can be useful in: a) the description of the differences between the "geochemical profiles" in the different parts of the reservoirs, b) the determination whether there is a direct relationship between "geochemical profiles" of suspended matter and sediment samples in different parts of the reservoirs.

Topic 6. Sustainable use & spatial planning of the subsurface

6a. Ecosystem services and natural capital, socio-economic value of soil-water systems

Site investigation, sustainable remediation, and ecological restoration - a framework for evaluation

J Mark Nielsen

Ramboll Environ, FR

The selection of remediation options should reflect a clear, scientifically-based, defensible, and logical decision process for evaluating possible techniques. Net environmental benefit analysis (NEBA) is one decision making tool that can be applied to evaluate such remedial options. The NEBA seeks to balance the risk, benefits and trade-offs between competing alternatives. This tool can lead to remediation efforts that are more focused, less resource intensive and incorporate sustainable practices, while managing both ecological and human health risk.

The application of NEBA is presented in a case study for a legacy industrial site located within an environmentally sensitive area. The site comprises legacy landfills and uncapped waste piles, with sediment and water quality impacts observed in surrounding wetlands. Remedial options were developed for analysis including capping waste stockpiles, controlling leachate migration, and targeted sediment removal and restorative capping of wetlands.

Site characterization followed conventional techniques to develop a well understood conceptual site model (CSM). Site-specific ecological data were collected to inform the NEBA evaluation. Remediation options included four key components that were each separately evaluated in terms of long and short term effectiveness, implementability, cost and economic resources, and community acceptance. These components were then considered in terms of discrete and quantitative components that included: 1) risks comprising on and off site migration risks; total energy used ; air emissions comprising greenhouse gas emissions and on-site and total NO_x emissions, on-site and total SO_x emissions ; implementation (physical) and chemical ecological risks for upland and wetlands/open water; implementation (physical) and chemical human health risks ; cost and view-shed (changes in human use services).

The use of a quantitative NEBA for the assessment of remediation strategies for a wetland complex is illustrated in this paper. In this case, five remedial options were considered ranging from considered natural recovery (i.e. 'no action' or baseline), capping, and removal of all impacted sediments. Each option was evaluated in terms of the adopted NEBA criteria.

The natural recovery approach (baseline) did not reduce the ecological risk associated with site-related impacts. All other options were demonstrated to reduce the ecological risk relative to the baseline condition; however, each option has different environmental and cost footprints. Overall, the analysis demonstrated that each option achieved acceptable risk reduction with costs and environmental impacts increasing with more intrusive actions.

This analysis illustrated that with this type of evaluation, a break point typically occurs, where further efforts to reduce long-term risks are only achieved through greater environmental impact or cost; these impacts can outweigh the risk reduction that is achieved. NEBA provided a tool that allowed for this trade-off to be quantitatively evaluated and provided a transparent and scientifically defensible basis for remedy selection.

6b. The role of the natural system in climate change adaptation and urban resilience

TopSoil - Resilient soil and water resources, understanding the water beneath your feet

Rolf Johnsen

Central Denmark Region, DK

Background

Climate change affects the hydrological cycle and we all ready now experience more heavy rains and increasing sea levels. The water under our feet is also known to be a major actor when it comes to the

quality and quantity of our water resources. Accros the North Sea in Northern Europe we share different challenges within ground water and climate change. In a 3½ year European project we have identified five shared challenges to be adressed via geological, geophysical and hydrological investigations, stakeholder involvement and changes in management.

The five shared challenges are:

1. Flooding in towns and agricultural areas due to the rising groundwater table caused by
1. changed precipitation patterns.
2. Saltwater intrusion into freshwater reserves due to rising sea levels and changed irrigation,
3. drainage and drinking water demands.
4. The need for a groundwater buffer to store water in periods of excess rainfall. The buffer
5. of fresh water can be used for irrigation purposes during dry periods.
6. 4. Better knowledge and management of soil conditions, which will provide better resilience
7. to extreme rainfall events, improve water quality and improve crop yields.
8. 5. The capacity to break down nutrients and other environmentally hazardous pollutants
9. in the uppermost layers is yet unexplored. By improving our understanding, better land
10. management can be implemented.

Objectives:

The five challenges are addressed in 16 pilot areas, to develop and test solutions for managing uppermost 20-30 m of the subsurface. This will lead to a strong improvement of climate resilience in and across pilot areas, The partnership is strongly committed to bridging science, practice and countries.

The Topsoil Project will explore the possibilities of using the topsoil layers to solve current and future water challenges. It looks beneath the surface of the ground, predicts and finds solutions for climate related threats like flooding during wet periods and droughts during summer seasons. The overall objective of the Topsoil Project is the joint development of methods to describe and manage the uppermost 30 m of the subsurface, in order to improve the climate resilience of the North Sea Region. In addition, the project will demonstrate a practical implementation of solutions in 16 pilot projects.

General information

Duration: 1 December 2015 – 1 February 2020, budget 7.4 mio Euros

24 PARTNERS:

Belgium (1):

Vlaamse Milieumaatschappij

Denmark (6):

Herning and Horsens Municipalities, Aarhus University, GEUS, Central Denmark Region and Region of Southern Denmark

Germany (8):

Bundesanstalt für Geowissenschaften und Rohstoffe; Dachverband Feldberechnung Uelzen; Landesamt für Bergbau, Energie und Geologie; Landesamt für Landwirtschaft, Umwelt und ländliche Räume Schleswig-Holstein; Landwirtschaftskammer Niedersachsen; Leibniz-Institut für Angewandte Geophysik; Oldenburgisch-Ostfriesische Wasserverband; Universität Bremen:

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The Netherlands (3):

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United Kingdom (6):

Durham University, Essex & Suffolk-, Wear- and Norfolk Rivers Trust, Northumbrian Water Limited,

The Rivers Trust,

www.topsoil.eu

6c. Sustainable land use and spatial planning of the subsurface

Soil quality recovery in a chronosequence of abandoned vineyards

*Juan Pedro Martín Sanz*¹; *Cristina Vaquero Perea*¹; *María Inmaculada Valverde Asenjo*¹; *Juan Pedro Martín Sanz*¹; *Ana De Santiago Martín*²; *Concepción González Huecas*¹; *Antonio López Lafuente*¹; *Antonio Vázquez de la Cueva*³; *José Ramón Quintana Nieto*¹

¹ Universidad Complutense de Madrid; ² Laval University; ³ Centro de Investigación Forestal-INIA, ES

During the last decades, there has been a progressive abandonment of large areas of agricultural land throughout Europe caused by socio-economic factors and accelerated by the successive Common Agricultural Policy reforms. Land abandonment and subsequent management strongly affect the carbon cycle and the nutrients that limit plant growth in soils. Understanding of processes controlling both aspects during the secondary succession after abandonment can provide valuable tools for improving the ecosystem management and mitigate greenhouse gas emissions. In this context, the purpose of this work was to determine the environmental and edaphic variables which can control the quantity and quality of the organic matter accumulated in soil during the abandonment. To this end, a chronosequence of abandoned vineyards was used, within an area of 2x2.5 km in the municipality of Navas del Rey (Community of Madrid) dedicated to vineyard cultivation in the 1940s and progressively abandoned from the 60s to the present. Sixty nine plots with different vineyard abandonment were selected through aerial photographs taken on 5 different dates (1957, 1968, 1985, 1998 and 2004). In each plot, the first 5 cm of soil under the influence of each of the dominant species/ communities were sampled to calculate the averages of soil parameters: total organic carbon (COT), total N, available P, the organic fractions Labile Pool I, Labile Pool II and Recalcitrant determined by acid hydrolysis, and the pH, proportion of clay and free-oxides. To observe the environmental variables which determine the quantity and quality of the organic matter accumulated in the studied plots, the analysis of canonical redundancy, RDA, was used. Soil COT showed a rising trend until the end of the chronosequence, although the maximum storage capacity of carbon was not reached. The organic matter fractionation did not show a clear trend with the time elapsed after land abandoned, suggesting that the mineralization/ humification processes do not depend on abandonment age, but on other environmental or soil factors. Total soil N content increased significantly throughout the chronosequence. The concentration of available P did not have a clear evolution, although the maximum content was obtained in the plots of recent abandonment. The first axis of the RDA showed that the age of abandonment is determinant in the COT accumulated during the chronosequence. In the axis 2, it was the slope that determined the dispersion of the accumulated COT in the different age of abandonment. The granulometry was decisive in the quality of the organic matter. In particular, the clay soil fraction was closely related to the total N and the Recalcitrance index controlling, in part, the quality and stability of soil organic matter. In summary, the amount of organic matter accumulated during the abandonment was determined by the age of abandonment of the plots. The slope makes a difference among plots with the same abandonment age. This work was supported by the Madrid Autonomous Region through the CARESOIL Programme (Ref.P2013/MAE2739).

Selection of perennial plant for rehabilitation lime stone mining area

*Nalin Sittitoon*¹; *Jirathon Hongrathanakorn*²; *Wasana E-ka*²

¹ Institute of Medicine; ² Sila Sakol Pattana Co. Ltd, TH

This study was conducted in limestone mining area at Sila Sakol Pattana Co. Ltd, Pak Chong, Nakhon Ratchasima, Thailand. According to the previous plans for rehabilitation, the rehabilitation had been doing during the same period with the mining until the end. In 2014-2015, cover crop such as *Mimosa pudica* L., *Acacia auriculiformis* Cunn. and perennial plant including Siamese Neem Tree (*Azadirachta indica* var. *siamensis*), *Pithecellobium dulce*, Jamican cherry (*Muntingia calabura* L.) were planted with the cooperation of Silasakon Company and people in community. It can be seen that some of these plants are birds' food that increase the integrity of ecosystem. The aim of this study was to screen dominant tree species for rehabilitation in lime stone mining area focusing on perennial plants that endure the low quality soil and give colorful flowers. Eight species were selected (5 species in Family: CAESALPINIACEAE Golden shower (*Cassia fistula* L.), Pink shower (*Cassia bakeriana* Craib), *Cassia agnes* Brenan, *Delonix regia* (BoJ. ex Hook.) Raf, Orchid Tree (*Bauhinia purpurea* Linn.), 2 species in Family: FABACEAE (LEGUMINOSAE- CAESALPINIOIDEAE) were *Cassia grandis* L.f. and *Phyllocarpus septentrionalis* Donn. Sm. and 1 species in Family: LYTHRACEAE; *Lagerstroemia tomentosa* C. Presl). The soil in planting areas was taken from mining area to fill up the slope in form of steps. The width of each step is about 3 meters. This soil was improved by using "Hinfoon" a by-product from limestone milling factory in complementary with chemical fertilizer. Polymer gel was added into the bottom of the pit before planting for water absorption along the steps so that the plants will survive more. By the end of mining process, the whole area will be changed into reservoir for community. This area can be developed for tourism purpose in the future.

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Hildegard Feldmann
Ogarit Uhlmann
F&U confirm
Permoserstraße 15
04318 Leipzig
Germany
Phone: +49 341 235 2264
Email: aquaconsoil@fu-confirm.de





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The printing of this booklet is supported by the Auvergne-Rhône-Alpes Region

