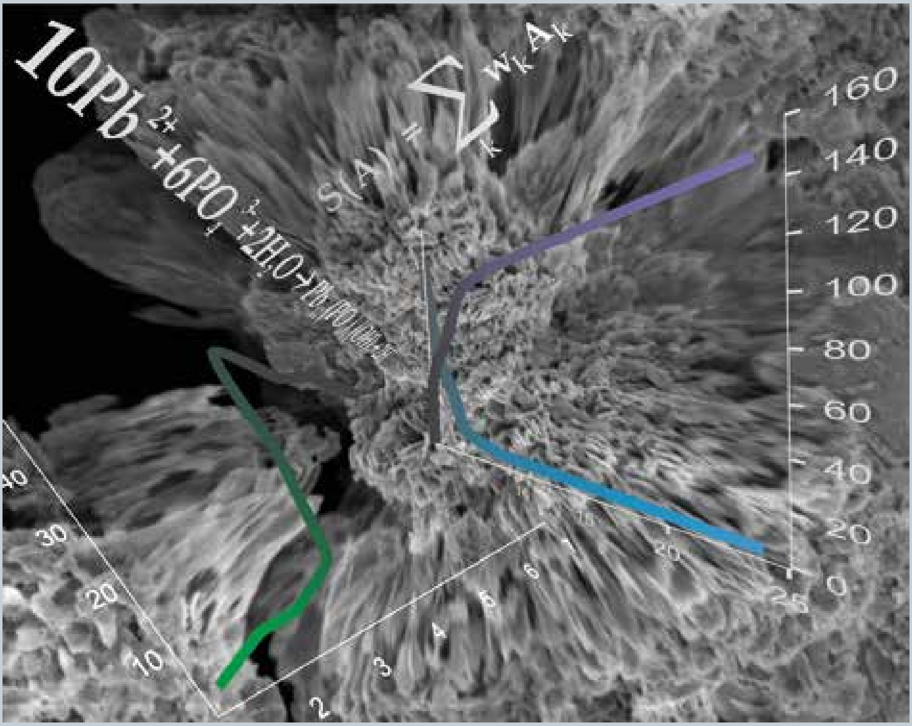
UNIVERSITY OF LATVIA
FACULTY OF GEOGRAPHY AND EARTH SCIENCES
DEPARTMENT OF ENVIRONMENTAL SCIENCE

Juris Burlakovs

CONTAMINATION REMEDIATION WITH SOIL AMENDMENTS BY IMMOBILIZATION OF HEAVY METALS

PIESĀRŅOTU GRUNŠU UN AUGŠŅU REKULTIVĀCIJA AR MODIFICĒTĀM PIEDEVĀM – SMAGO METĀLU IMOBILIZĀCIJA

Doctoral Thesis



Rīga, 2015

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DOCTORAL THESIS

Submitted for the degree of Doctor of Geography in Environmental Science
Subfield of Environmental Protection

Scientific supervisor:
Professor, *Dr. habil. chem.* Māris Kļaviņš

Rīga, 2015

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The thesis contains an introduction, 3 chapters, conclusions, a reference list and II annexes. Form of the thesis: dissertation in geography, field of environmental science, subfield of environmental protection.

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Professor, *Dr. habil. sc. ing.* **Gintaras Denafas**, Kaunas University of Technology, Lithuania.

The thesis will be defended at a public session of the Doctoral Committee of Environmental Science, University of Latvia, at the Faculty of Geography and Earth Sciences of the University of Latvia (10 Alberta Street, Riga, Latvia) on March 27, 2015 at 10:00.

The thesis is available at the Library of the University of Latvia (19 Rainis Blvd., Riga, Latvia).

The thesis was accepted for the commencement of the degree of Doctor of Geography, Environmental Science on March 27, 2015 by the Doctoral Committee of Environmental Science, University of Latvia.

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CONTENTS

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
AFCEE	Air Force Centre for Engineering and the Environment (USA)
AHP	Analytical Hierarchy Procedure
AMD	Acid mine drainage
BET	Brunauer-Emmett-Teller method for specific surface area measurements
BOD	Biological oxygen demand
CEC	Cation exchange capacity
CEPA	Canadian Environmental Protection Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act (USA)
CERCLIS	Comprehensive Environmental Response, Compensation and Liability Information System (USA)
CETESB	Companhia de Tecnologia de Saneamento Ambiental de Brasil
CLAIRE (CL:AIRE)	Contaminated Land: Applications in Real Environments (UK)
CLEA UK	Contaminated Land Exposure Assessment Model
CLM Act	Contaminated Land Management Act (Australia)
CLR	Contaminated Land Register
COD	Chemical oxygen demand
DC	Direct current
DDT	Dichlorodiphenyltrichloroethane
DECCW	Department of Environment, Climate Change and Water (Australia)
DEFRA	Department for Food, Environment and Rural Affairs
EMR	Environmental Management Register
EC	European Commission
EDTA	Ethylenediaminetetraacetic acid
EEA	European Environment Agency
EK	Electrokinetics
ELECTRE	ELimination Et Choix Traduisant la REalité (ELimination and Choice Expressing REality) method
EUGRIS	EU's web portal for information and services on topics related to soil and water
EURODEMO	European Coordination Action for Demonstration of Efficient Soil and Groundwater Remediation
EUSD	European Commission's Sustainable Development's web site
FPXRF	Field portable X-ray fluorescence
FRTR	Federal Remediation Technologies Roundtable (USA)
FTIR	Fourier transform infrared spectroscopy
HA	Humic acids
HAp	Hydroxyapatite
HRS	Hazard Ranking System (USA)
HS	Humic substances

ICP-MS	Inductively coupled plasma masspectrometry
LCA	Life cycle assessment
LEGMC	Latvian Environment, Geology and Meteorology Centre
LFM	Landfill mining
LNAPL	Light Non-Aqueous Phase Liquid
MAUT	Multi-Attribute Utility Model
MCDA	Multi-criteria decision analysis
MEPRD	Ministry of Environmental Protection and Regional Development (Latvia)
MSWI	Municipal solid waste incineration
NDP	National Development Plan (Latvia)
NEBA	Net environmental benefit analysis
NEPP	National Environmental Policy Plan (Latvia)
NICOLE	Network for Industrially Contaminated Lands in Europe
NPL	National Priority List (USA)
NRCT	National Register of Contaminated Territories (Latvia)
NMR	Nuclear magnetic resonance
NSW	New South Wales territory (Australia)
PAHs	Polycyclic aromatic hydrocarbons
PA/SI	Assessment/Site Inspection
PC	Portland cement
PLI	Pollution load index
PRB	Permeable reactive barriers
PROMETHEE	The Preference Ranking Organization METHod for Enrichment of Evaluations
PRP	Potentially responsible parties
RBCA	Risk-based corrective action (USA)
ROD	The Record of Decision (USA)
RPM	Rounds per minute
SARA	The Superfund Amendments and Reauthorization Act of 1986 (USA)
SEM	Scanning electronic microscopy
SITE	The Superfund Innovative Technology Evaluation (USA)
SP Act	Sustainable Planning Act (Australia)
S/S	Stabilization / solidification
SURF	Sustainable Remediation Forum (International)
SVOC	Semi-volatile organic compounds
TXRF	Total Reflection X-ray Fluorescence
US EPA	United States Environmental Protection Agency
VOC	Volatile organic compounds
XRD	X-Ray difractometry
XRF	X-Ray fluorescence spectrometry

DEFINITIONS

Aeration zone is located under the ground surface and above the water table, where the pores in soil and rock contain both air and water.

Bioavailability (of elements or substances) is the availability for uptake by plants, animals and humans of elements or substances.

Brownfields are abandoned, idled, or under-used industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination (Brownfield land, 2013).

Complex contamination in present thesis refers to multi-element and/or multi-substances contamination.

Contaminant means a substance causing contamination.

Contaminated site, polluted site, degraded site and ***brownfield***: very frequently are used as synonyms or similar terms, but they do not actually have the same meaning. Contaminated land or site – is a place where there is at least a suspicion that the contamination could be harmful to humans, water, buildings, or ecosystems (EUGRIS, 2013).

Contaminated site means an area of the land in which the soil or any groundwater lying beneath it, or the water or the underlying sediment, contains (a) a hazardous waste, or (b) another prescribed substance in quantities or concentrations exceeding prescribed risk based or numerical criteria or standards or conditions as defined in legislation (Environment Canada. CEPA, 1999).

Decision support system is a flexible indicative tool, which provides an analytical approach for the best available choice of remediation under specific circumstances.

Degraded site is a broad term defining areas and buildings that are abandoned and are not available for reuse without treatment by cleanup and/or demolition/excavation activities.

Gentle remediation includes various and in general plant-based approaches to remediate trace element contaminated soils at low cost and without significant negative effects for the environment. Although it comprises very innovative and efficient technologies, they are still not widely used as practical site solution due to several reasons of hindrance (GREENLAND project, 2014).

Groundwater is water below the land surface filling (saturating) pore spaces, fractures or other voids (Encyclopedia of Soil Science, 2008).

Hard remediation includes stabilization/solidification, electrokinetic, excavation and other heavy affecting environment technologies to remediate trace element contaminated soils at comparably high cost and with significant negative effects for the environment. As the opposite – read also about *gentle remediation* techniques.

Heavy metals: a weakly defined group of elements that exhibit metallic properties with density >5 g cm^{-3}. It mainly includes category of elements that contains transition metals, some of metalloids, actinides and lanthanides. As various definitions are given in literature, heavy metals are mostly classified by atomic weight, chemical properties and toxicity (Duffus, 2002). In the present thesis, this term is used for metals heavier than calcium as well as metalloids creating environmental problems most often. Cu, Pb, Zn, Ni, Cd, Cr are the most common metallic elements of concern, whereas As, Se and Sb are metalloids.

Metal speciation refers to aspects of the chemical and physical form of an element: oxidation state, stoichiometry, coordination (including the number and type of ligands), and physical state or association with other phases all contribute to define speciation. These properties govern the chemical behaviour of elements, whether in environmental settings or in human organs, and play a crucial role in determining toxicity (Reeder et al., 2006).

Polluted site is a broad term which includes areas of land or point sources of pollution (heaps, spills) that can have an adverse impact on the environment and humans.

Recultivation – a general term used for the making of bare areas (raw material soils) fertile again through bioengineering and re-fertilization (ENCYCLO, 2012). In this case the term refers to contaminated sites.

Remediation deals with the removal of pollution or contaminants from environmental media such as soil, groundwater, sediment, or surface water for the general protection of human health and the environment or from a brownfield site intended for redevelopment (Remediation, 2013).

Remediation technology is a soil and/or groundwater treatment technology which is used for site cleanup.

Saturated zone is the region in soil under the groundwater table.

Site cleanup is a complex procedure, which includes various stages: historical data analysis, preliminary research, decision-making, remediation and monitoring.

Soils are porous media created at the land surface through weathering processes mediated by biological, geological, and hydrological phenomena (Sposito, 2008). Another definition says: ***Soil*** is the loose material composed of weathered rock and other minerals and also partly decayed organic matter and humus that covers large parts of the land surface of the Earth (Wild, 2003). ***Soils*** differ from weathered rocks and their main composition is the result of combined influence from water and biological processes. Soils have a more or less layered structure, and each of the horizons has its own properties and role in elemental cycles. If we consider it from the point of view of chemistry, soils are a complex multi-component system, where interactions among them and the atmosphere, hydrosphere and biosphere take place. All these interactions greatly influence properties in space and time of distinct soils created in distinct geographic areas (Sposito, 2008; Kabata-Pendias and Pendias, 2010).

Threshold value is the level of concentration of an element or substance in soil or groundwater, above which the impact on the environment is adverse.

Toxicity (including chronic toxicity) is the degree to which a substance is able to damage an exposed organism. Toxicity can refer to the effect on a whole organism, such as an animal, bacterium or plant, as well as the effect on a substructure of the organism, such as a cell or an organ, such as the liver (effects are dose dependent) (Examples of harmful properties, 2013).

Ecotoxicity (with or without bioaccumulation): potential for biological, chemical or physical stressors to affect ecosystems. Stressors might occur in the natural environment at densities, concentrations or levels high enough to disrupt the natural biochemistry, physiology, behaviour and interactions of the living organisms that make up the ecosystem (Examples of harmful properties, 2013).

Vadose zone is the region in soil above the groundwater table.

ANNOTATION

Heavy metal contamination is the inheritance of modern society and a serious environmental problem. Brownfields, dump sites, former and active industrial and military areas often demand remedial solutions concerning this problem. The aim of the dissertation “Contamination remediation with soil amendments by immobilization of heavy metals” included the development and testing of applicable soil amendments for *hard* and *gentle* heavy metal remediation approaches and the elaboration of an indicative decision support model for choosing the best available solution. In addition, aspects of metal speciation and immobilization efficiency were studied through experimental work with innovative modified clay and humic substances as remedial soil amendments. The obtained results revealed broad perspectives for the use of local resources in *gentle* remediation by soil amendments for heavy metal contaminated territories and showed indicative guidelines on how to choose the right applicable method in different cases.

Key words: heavy metals, *gentle* remediation, stabilization/solidification, decision support tool, soil amendments, modified clay, Latvia.

ANOTĀCIJA

Piesārņojums ar smagajiem metāliem augsnē ir nopietna vides problēma. Bijušajās rūpnieciskajās, izgāztuvju, militārajās teritorijās atstātais vēsturiskais augsnes piesārņojums un tā rekultivācija ir jautājums, kura risināšanai iespējami dažādi varianti. Promocijas darbā “Piesārņotu grunšu un augšņu rekultivācija ar modificētām piedevām – smago metālu imobilizācija” tika veikti eksperimentāli pētījumi par inovatīvu modificētu piedevu – modificēta māla un humusvielu – izmantošanu efektīvai smago metālu piesārņojuma imobilizācijai. Papildus tika izvērtētas metālu atrašanās formas piesārņotajās un rekultivētajās augsnēs, kā arī inovatīvo augsnes sorbentu efektivitāte. Papildus izstrādāti ieteikumi pamatotai atbilstošo modificēto piedevu izvēlei kompleksa piesārņojuma gadījumos.

Pētījumu rezultāti liecina, ka modificētajām piedevām, kas iegūtas no lokālām izejvielām, ir labas perspektīvas, lai videi draudzīgi rekultivētu ar smagajiem metāliem piesārņotu substrātu; piedāvāts indikatīvais modelis piemērotu rekultivācijas tehnoloģiju izvēles pamatojuma izstrādes vajadzībām.

Atslēgvārdi: smagie metāli, *vieglā* rekultivācija, stabilizācija/sacietināšana, lēmumu pieņemšana, modificētas piedevas, modificēts māls, Latvija.

INTRODUCTION

Contamination of soils and the groundwater is the inheritance of modern society and a serious environmental problem. Brownfields, dump sites, former and active industrial and military areas often demand technical and economic evaluation of the environmental situation and the means to solve contamination problems. The 1960s came with the "Silent Spring" and "The Tragedy of the Commons" – a huge change in environmental philosophy – development that has to be based on environmental and industrial coexistence (Carson, 1965; Hardin, 1968).

Almost half a million sites with potential contamination have been reported in the US over the last decades. In the reports given under the supervision of the US EPA (Environmental Protection Agency), the term *contaminated site* refers to a specific spatial area which is defined as contaminated (Superfund, 2014). Superfund sites are tens of thousands of objects waiting for immediate remedial actions, which differ in contamination character, costs, risks and other factors. According to the European Commission, there are around 3-5 million potentially contaminated sites and 500,000 sites known as contaminated in Europe (Vanheusden, 2009). There is also a huge amount of contaminated areas, which are situated in other parts of the world, including developing countries. In Latvia, the assessment and evaluation of contaminated and potentially contaminated sites began already in the 1980s; nowadays the National Register of Contaminated Territories (NRCT) covers areas that are contaminated with various inorganic and organic pollutants. The NRCT sites fall into three categories: the first includes 244 contaminated sites (contamination exceeds the permissible 10 times or more); the second category (potentially contaminated) – 2,642 sites, and the third (removed from the first and second after remediation or detailed assessments) – 684 contaminated areas (NRCT, 2014). Although environmental problems related to historical pollution are relatively well known, these are very often subject of political debate, and public opinion catalyzed by the media. Since resources for treatment operations in both wealthy and developing countries are limited, the aims and scope of remedial actions should first be addressed through careful environmental research to achieve the best results. When remedial actions are required, a technology must be chosen that is most effective from different aspects.

Remediation technologies can be classified in two categories: *in-situ* and *ex-situ* (Reddy et al., 1999). *In-situ* technologies are used for the treatment of unexcavated soil or unextracted groundwater that remains relatively undisturbed after the cleanup. Technologies include biological, physical separation, chemical, physical-chemical, thermal, and containment techniques. The *ex-situ* approach such as excavation and *in-situ* such as containment technologies have so far predominantly been used in Latvia as the solution in case of heavy metal contamination. There exist different approaches for the treatment of contaminated soils, but simplified models are often far from the reality and a complex approach is required for complex contamination cases. The cycle of elements in heterogeneous media can be compared to the *system of determined chaos* (Stone, 1989; Smith, 1998, Siliņš, 1999), where the behaviour of the system is hard to predict. The need for and sustainability of the treatment should be evaluated and priorities should be set using a practical and universal scoreboard. Decision-makers can use this scoreboard as an indicative model.

Soils in Latvia predominantly have a high organic and clayey particle content; the speciation of toxic heavy metals is therefore important. Research on controlled batch experiments provides information on the properties of soil amendment material and behaviour of heavy metal contamination. The use of local resources such as limestone, clay and peat for immobilization of heavy metals in soils is a great challenge to ensure that remediation works are environmentally friendly.

Aim of the Thesis

The aim of the dissertation is to develop and test applicable soil amendments capable of immobilizing pollutants for *hard* and *gentle* remediation of heavy metal contamination and to elaborate an indicative decision support model for choosing the best available remedial solutions.

Tasks of the Thesis:

- To perform historical data analysis and classify heavy metal contaminated sites in Latvia regarding the source and intensity of contamination;
- To choose typical heavy metal contamination case study sites, perform field works, sampling and analysis, and describe the situation for potential application of soil amendments as remedial agents;
- To elaborate and test applicable local material-based soil amendments with an efficient qualitative and quantitative composition through batch experiments for the immobilization of heavy metals by *hard* and *gentle* remedial methods;
- To give a characterization of the physical and chemical properties for the tested soil amendments;
- To evaluate and compare the efficiency of innovative soil amendments and assess the influence on heavy metal speciation and bioavailability in contaminated soils;
- To propose recommendations for innovative use of fine fraction enriched with metallic compounds in landfill soils for complex use in dump site recultivation projects;
- To elaborate a flexible indicative decision support model for the selection of a feasible set of remedial actions in different environmental and complex heavy metal contamination cases.

Scientific novelty of the study

1) Heavy metal contaminated soils have been studied in case studies in Latvia and Estonia and *hard* and *gentle* remedial approaches recommended.
2) Clay sorbents based on hydroxyapatite and iron oxyhydroxides have been developed for economically effective *gentle* remediation of heavy metal contamination and tested in laboratory conditions.
3) Humic substances alone and in concert action with clay amendments have been tested for stabilization of soils contaminated with heavy metals.

4) The physical and chemical properties of innovative modified clay sorbents have been investigated.
5) Heavy metal speciation analysis has been performed for the fine fraction of the newly developed covering layer of a dump site as part of a full-scale landfill mining project in Estonia.
6) A decision support system has been created for the selection of a feasible set of *hard* and *gentle* remedial actions for complex heavy metal contaminated cases.

Major achievements

1) A comprehensive evaluation of contaminated sites in Latvia and identification of major problems related to remediation of complex heavy metal contamination.
2) Development of a scientific background for the selection guidelines of remedial techniques for fast and effective site cleanup.
3) Modification of clay and use of humic substances for the testing of immobilization processes for heavy metal contamination in batch conditions.
4) Soil amendment use as an experimental technology for future field studies.
5) Metal speciation analysis performed as a complex contamination full scale research activity.
6) Creation of a decision support system based on a full scale case study analysis and multi-criteria approach.

Approbation

The results of the doctoral thesis have been published in 13 scientific articles. The results of the research work have been presented in 16 reports at international conferences and in 10 reports at local conferences in Latvia.

In relation to the research field, the author of the thesis has supervised 3 bachelor research works and has advised the preparation of 3 master theses.

Scientific publications

1. **Burlakovs, J.**, Klavins, M., Osinska, L., Purmalis, O. (2013) The impact of humic substances as remediation agents to the speciation forms of metals in soil. *APCBEE Procedia*[1], 5, 192-196.
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[2] *Indexed in EBSCO Publishing database, CSA/ProQuest, VINITI – Russian Academy of Science.*

[3] *Indexed in EBSCO, CSA/ProQuest, VINITI, Chemical Abstracts.*

[4] *Indexed in Scopus, EBSCO Publishing database, CSA/ProQuest, VINITI – Russian Academy of Science.*

[5] *Indexed in Scopus, CrossRef databases, EBSCO.*

[6] *Indexed in Scopus, CrossRef databases, EBSCO.*

[7] *Indexed in AGRICOLA, Celdes, CAS, CNKI Scholar, CNPIEC, EBSCO Discovery Service, VINITI, Google Scholar, WorldCat.*

[8] *Indexed in Science Citation Index Expanded, Google Scholar.*

[9] *Indexed in Scopus, ISI Web of Science, Versita.*

[10] *Indexed in EBSCO Publishing database, CSA/ProQuest, VINITI – Russian Academy of Science.*

[11] *Indexed in ISI Web of Science, Scopus, CrossRef databases, EBSCO.*

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4. **Burlakovs, J.** (2013) Environmental pollution and remediation workshop (organizer and chairman). *13th International Multidisciplinary Scientific GeoConferences (SGEM): International Conference on Modern Management of Mine Producing, Geology and Environmental Protection*, Albena (Bulgaria), 16-22 June, 2013. *Best Workshop Award.*
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9. **Burlakovs, J.** (2012) Dumps in Latvia: Preliminary research and remediation. *12th International Multidisciplinary Scientific GeoConferences (SGEM): International Conference on Modern Management of Mine Producing, Geology and Environmental Protection*, Albena (Bulgaria), 17-23 June, 2012. *Best Presentation Award.*
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Author's contribution

The author has studied contaminated sites, performed groundwater monitoring, drilled more than 250 shallow groundwater wells and analyzed site contamination, flow direction and discharges. Ten contaminated sites as well as potential heavy metal contamination sites were considered as representative to be described in the thesis in more detail. The results of the doctoral study were tested in four remediation projects (national and international) and recommendations have been reported to state authorities. Laboratory investigations at the University of Latvia, Faculties of Geography and Earth Sciences, Physics and Mathematics, Biology as well as Linnaeus University, Sweden, have been performed to research innovative soil amendments for immobilization of heavy metals in batch tests. Laboratory works included modification of clays, batch leaching experiments, sorption kinetics and analytical measurements. An indicative model was created based on environmental management principles and the multi-criteria decision analysis theory.

1. LITERATURE REVIEW

1.1. Soil contamination with metals

Soils are a vitally important structural element of the biosphere and are formed because of biogeochemical processes. Some major and trace elements are particularly important for life on Earth. The major elements that make up, e.g., plant tissues are carbon, oxygen, phosphorous, sulphur, hydrogen, nitrogen, calcium, magnesium, potassium and sodium. Other elements are necessary for plant physiology, mainly copper, iron, manganese, zinc, boron and molybdenum but also others. Though present in cellular tissues at often very low concentration (minor or trace elements) from a few mg kg^{-1} to g kg^{-1}, a deficiency in these elements can inhibit plant growth and has high availability results in respect to toxicity (Coppenet and Juste, 1982). As all these elements are taken up from soil to plants, from plants further to animals and so forth, a good knowledge of the concentration and availability of biogenic and toxic elements is required. Other elements are also crucial for living organisms even though they are present at lower trace levels. Diseases arise in regions with deficiency of iodine, selenium and other elements. Molybdenum plays an important role in both plants and animals, e.g., in the nitrogen cycle, where it facilitates reduction of nitrogen dioxide to nitrogen. Vanadium has a similar function, but selenium can accumulate in plants and become toxic for livestock (Coppenet and Juste, 1982; Pansu and Gautheroy, 2006). A chemical balance in living organisms is a basic condition for their proper growth and development. Interactions of chemical elements are also of similar importance to deficiency and toxicity in the physiology of plants, as between chemical elements those may be both antagonistic and synergistic, and their imbalanced reactions may cause a real chemical stress in plants (Kabata-Pendias and Pendias, 2010). Organisms have adjusted during the course of evolution and life to the chemical composition of their environment and have developed their biochemistry in close connection to the composition of the background environment. These phenomena have been easily observed, mainly in microorganisms and plant populations that have evolved tolerance to high concentrations of trace elements either in natural geochemical provinces, or under man-induced conditions (Pendias and Mukherjee, 2007). Nickel-ferrous serpentine soils (averaging 10g of Ni per kg of soil) in New Caledonia are a good example, where nickel-resistant bacteria as well as higher plants are good hyperaccumulators of nickel, and the dry weight of nickel in leaf reaches 1 %. This is an interesting ecosystem with its own *nickel cycle* – trees are hyperaccumulating the nickel from deep soil up to the leaves and when those are shed, nickel leaches to the surrounding topsoil. Bacteria, fungi, protozoa – all are resistant to the nickel in this ecosystem (Lelie and Tibazarwa, 2001).

Trace elements play fundamental roles in the normal development and health of organisms. Functions of most of the essential trace elements in metabolic and growth processes have been relatively well recognized and their crucial role is attributed commonly to functions of metaloenzymes. Especially essential for the physiological functions are Cu, Zn, and Fe (Kleczkowski et al., 2004). However, heavy metals are toxic either as ions or in compounds, because they are soluble in water and may be readily absorbed into living organisms. After absorption, these metals can bind to vital cellular components such as structural proteins, enzymes, and nucleic acids, and interfere with their functioning. In humans, some of these metals, even in small amounts, can cause severe physiological and health effects (Wayne and Ming-Ho, 2003). Energy and mineral consumption by civilization is the main cause of pollution in the biosphere. Global release of trace elements as pollutants into the environment may be correlated with the world mineral and energy consumption (Kabata-Pendias and Pendias, 2010). According to Bowen (1979), if the rate of impact from mining exceeds the natural rate of element cycling by a factor of ten or more, those must be considered as potential contaminants. Trace metals that are most hazardous to the biosphere according to this conclusion are Ag, Au, Cd, Cr, Hg, Mn, Pb, Sb, Sn, Te, W, and Zn. This list does not correspond directly to the list of environmental concern mostly known from consultancy and legislation summaries. The best-known pollutants in soils are Pb, As, Cd, Cr, Cu, Zn, Hg, and Ni that are used in industry and fall into the category of the so-called heavy metals, which includes all metallic elements with a density higher than 5000 kg m^{-3}. Nevertheless, some of metallic elements with a lower density as well as metalloids are also of concern (Botkin and Keller, 2005).

Toxicity and hazards. Contamination with heavy metals is an important problem as bioaccumulation effects create direct and indirect hazards to the environment and human health. The quality of soil and groundwater is fundamentally important and different technologies are used in order to treat contamination from diffuse and point sources generated by industrial as well as natural sources. Heavy metals are toxic and hazardous for human health and the environment both when sources are natural processes such as volcanoes and erosion of rocks or anthropogenic such as industry, mining, diffuse air pollutant precipitation and others (Lado et al., 2008). Toxic heavy metal ions are non-biodegradable and tend to accumulate in living organisms, causing severe disorders and diseases (Lee et al., 2012; Yin et al., 2006; Yaday et al., 2013). Overexposure to heavy metals including lead promotes the development of many workplace illnesses. As an example, the US Department of Labor introduced a five-year strategic plan in order to diminish the impact of hazardous lead on employees by 15% (OSHA, 2013).

Metal speciation. The speciation or chemical form in which an element is present is important in case of trace element analysis. The oxidation state of various elements (e.g., Fe, Mn, and Cr) is dependent on pH and redox potential. Elements of another type (such as As, Hg, Pb, or Sn) can form metallo-organic complexes. Aspects of trace element speciation (for heavy metals and metalloids) are often ignored when analysis is done and decisions on leachate control from mining fields, landfills and contaminated sites are made. Sulphide precipitation and formation of metal complexes with organic substances is important, as well as mineral phases of mobility of contaminants. Mobility of inorganic contaminants is dependent on bonding, e.g., with organic substances. The soil predominantly consists of clay minerals, carbonates, hydrated iron and manganese oxides, and organic matter (Knödel et al., 2007).

In order to assess interactions in a full perspective, various methods of separation can be used as single-stage and sequential extraction (elution). Batch or column tests provide information on binding of substances and evaluate the leaching process. Extraction and speciation tests increase the value of assessment as it is closer to real conditions in soil in nature. In contrast to single-stage elution tests, more complex, sequential extraction tests can provide information on the distribution of elements in the sample, phase changes in the leachate, influence of pH and redox potential, and other factors through time. Various classifications are presented by Tessier et al. (1979), Lake et al. (1984), Ure and Davidson (1995) for fractions of trace elements according to their speciation in soils: water soluble, exchangeable, carbonate bound, easily reducible substrates, easily extractable organics, moderately reducible oxides, oxidizable oxides and sulphides, crystalline Fe-oxides, and residual minerals (Knödel et al., 2007).

Bioavailability is another aspect, which is important when toxicity of trace elements needs to be evaluated. In the field of medical geology, bioavailability research and risk assessment are important tools to investigate influence of chemical species to human and animal health. The bioaccumulation of trace elements is an important aspect in the food chain that must be well understood. Overall, bioaccumulation could be defined as *the process by which organisms absorb chemicals or elements directly from the environment* (Dissanayake and Chandrajith, 2009). The bioaccumulation concept is addressed specifically to quantitative data; concentration of heavy metals is compared among dissolved, taken up (adsorbed) by plants and other forms (Streit, 1992). The selective concentration of elements leads to overexposure, and bioavailability can be defined as *the extent to which a substance can be absorbed by a living organism and can cause an adverse physiological or toxicological response* (Guide for incorporating bioavailability…, 2000). For environmental risk assessments it means that trace elements are bioavailable if they are ready to be absorbed under specific conditions. A number of processes in the soil environment affect the mobility of metals such as dissolution and precipitation, sorption, ion exchange and oxidation-reduction reactions. In such an environment, mobility and the bioavailability of metals are reduced by conditions that promote precipitation or sorption (Dissanayake and Chandrajith, 2009). Metals with the highest bioavailability form weak outer complexes with inorganic materials such as iron and manganese oxides or clay and organic matter in soil, hence, metals which form inner sphere complexes are not desorbed so easily and hence are less bioavailable because they are incorporated into the structure of minerals. The remaining part – not adsorbed or involved in complexes – may become bioavailable. Risk assessment is a set of methods to evaluate the potential hazard that can affect humans and the environment, and it helps identify populations or areas that are under the soil, water or air contamination threats. Ecological risk assessment is much more complex than assessment of the impact on humans; however, the latter has much more ethical considerations and is much more difficult to test *in vivo* (Dissanayake and Chandrajith, 2009).

Soil and plant factors. Base rock, soil age and type as well as the dominating flora dictate the accumulation of heavy metals in the sorption complex of soils that are rich in organic material, but the solution released into the soil is weak because of high binding of metals to organic compounds. The soil's pH, colloidal and microbial processes, redox potential and aeration also play a significant role, e.g., liming of the soil with increasing of the Ca^{2+} content significantly decrease metal uptake by plant roots, but this is even more affected by soil colloids as those decrease the availability of free ions. The chelating of metals also stimulates the uptake mechanism – it is easier for divalent and trivalent cations. However, soil factors influence the process for various elements differently, e.g., for Zn it is the Zn-buffering mechanism, but for other metals such as Fe, Mn, Pb it is the pH of the soil and redox conditions. The two main ways of heavy metal uptake by plants can be classified as non-metabolic uptake by energy-independent and metabolic uptake by energy-dependent mechanisms. The first type is when the concentration of metals near the roots is high and elements passively diffuse into organic structures, whereas the second type is when ion passing to the cell is stimulated by proton motive force, which creates pH, and electro-potential that guarantees ion passing (Siedlecka et al., 2001).

The elemental composition of the soil in Latvia is very dependent on its mineralogical composition and organic matter content. Geochemical mapping of Latvia has been performed and results presented in a monograph (Gilucis, 2007). Sources of industrial and natural pollution should be analyzed and prevented (OSHA, 2013). Geochemical background elements in Latvian soils, according to Gilucis (2007), can be divided into three main groups: *pelitophilic* (Ga, Al, Fe, Co, Ni, V, Cr, Mg, K, Tl, La, Th, Ti, Sc and probably U), *phytophilic* (Pb, Ag, Sb, Cd, Hg, S, Bi and Se) and *carbonatic* (Mg, Ca, Sr, P and Ba). It means that these elements are mainly found in associations with clayey fractions of soil, plants and organic matter and carbonatic bedrock respectively. Elemental content in the soil is dependent on its granulometric (textural) content, the amount of organic matter, the intensity of agrochemical influence and other factors. Geochemical anomalies are mostly of a *shallow* kind, when elements (Pb, Cd, Sb, U, Bi, S, La, P, Hg, Se, Zn, As, Ba, Mo, Ag, Co, B, Ni, Cr; and partly Fe, Mn) have been accumulated on geochemical barriers from anthropogenic pollution sources. Only a small part of anomalies is the so-called *deep* ones and contains increased concentrations of Ca, Mg, Th, Ga, Sr, Al from the bedrock (Gilucis, 2007).

1.2. Legislation and remediation of contaminated sites

The remediation industry principles in developed countries were laid down in the late 1970s, when environmental legislation and programs were created to manage and sometimes fund cleanup actions. The industry and consultant teams, responsible parties and remediation stakeholders made large-scale investments in order to create pump-and-treat systems, perform soil excavation and disposal, incineration, and thermal treatment activities. A fast injection of funds developed remediation projects with a demand for a lot of energy resources and capital investments (Contaminants in the subsurface, 2005). The early years have shown, e.g., in US New Jersey's example, that the difference between the two proposed remedial projects could be as high as 2 percent of the annual greenhouse gas emissions for the entire state (Ellis et al., 2009). As any conventional industry, remediation activities also use a huge amount of energy, consume raw materials, and thus contribute to humankind's carbon footprint (Ellis et al., 2009). Over the years, the remediation ideas as well as the principles of sustainability have evolved and have been implemented in environmental legislation worldwide.

United States of America. In the United States of America, the Environmental Protection Agency (EPA) oversees site remediation, and finances are mainly collected from fines shared among companies linked to activities causing environmental contamination. Some of the cities in the US also offer tax and zoning incentives for realtors attracted to the development of hotspot areas. EPA carries out research and supports a set of voluntary pollution reduction programs. Funds are gained through the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), better known as the Superfund, active from 1980 since the Love Canal disaster case in Kentucky gained public attention. The second federal Act for corrective action provisions is the Resource Conservation and Recovery Act (RCRA) allowing authorities or entrepreneurs to perform cleanup and redevelopment of brownfields. It minimizes environmental risks to residents living close to these sites, but the EPA with its large staff of lawyers and other legal professionals ensures execution of projects under the scope of law (Superfund, 2014; SARA Overview, 2011).

The Superfund cleanup process starts with site discovery or notification to the EPA of possible release of hazardous substances reported by stakeholders, including citizens, State agencies and EPA Regional offices. New sites are added to the Comprehensive Environmental Response, Compensation and Liability Information System's (CERCLIS) computerized database. Later the EPA carefully evaluates all aspects, publicly announces the Record of Decision (ROD) about remedial actions that should be performed in sites of the National Priority List (NPL) created through the Remedial Investigation and Feasibility study (SARA Overview, 2011; National Priority List, 2012).

Superfund manages the federal Brownfield program and has created the Hazard Ranking System (HRS) (SARA Overview, 2011). The implementation of this program during early years *has been criticized as being ineffective due to R. Reagan administration's laissez-faire policies when 16 of the 799 Superfund sites were cleaned, but only 40 million USD of 700 million USD in recoverable funds from responsible parties were collected* (Opinion…, 1994).

The Superfund Amendments and Reauthorization Act of 1986 (SARA) transformed CERCLA and added 8.5 billion USD to perform Superfund actions (SARA Overview, 2011).

Later in 1994, B. Clinton's administration proposed a new Superfund reform bill (Cushman Jr., 1994) and most of the funding was collected from a tax on the petroleum and chemical industries – the *polluters pay* principle was applied. The CERCLA authorizes emergency remedial actions, which can be conducted at sites listed on the EPA NPL in the United States and the territories. Potentially responsible parties (PRP) are liable for contamination at a Superfund site: 1) the current owner or operator of the site; 2) the owner or operator of a site in time when disposal of a hazardous substance, pollutant or contaminant occurred; 3) the person who arranged the disposal of a contaminant and 4) the person who transported a hazardous substance, pollutant or contaminant to a site or selected that site.

Inclusion of a site in the NPL does not itself require PRPs to initiate cleanup action of the site, nor does it assign liability to any person. The NPL serves primarily as an information source, notifying the government and public that remedial actions are required. However, the Superfund trust fund lacks sufficient capacity to clean up even a small number of the sites included in the NPL, therefore the government will typically order PRPs to clean up the site themselves. The EPA conducts a Preliminary Assessment / Site Inspection (PA/SI) including reviews, interviews, visual inspections, limited field sampling, and the gathered information is used to determine the status of the site. A HRS is developed to calculate a site score (ranging from 0 to 100) based on the actual or potential release of hazardous substances from a site (Superfund, 2014, SARA Overview, 2011). The ROD according to the PA/SI proposes alternatives of actions. The Superfund Innovative Technology Evaluation (SITE) program supports remediation technology development programs that entail four related components: the Demonstration Program, the Emerging Technologies Program, the Monitoring and Measurement Technologies Program, and Technology Transfer activities (Superfund, 2014). On 29 November 2010, the total of 1,280 sites were listed on the NPL; additional 347 have been delisted, and 62 new sites have been proposed (National Priority List, 2012). Around 70 % of Superfund cleanup activities have historically been paid by PRPs. Cleanup costs are not borne by the responsible party when that party either cannot be found or is unable to pay for the cleanup. Hereby fees and taxes were intended to provide cleanup (Superfund Program: Updated Appropriation and Expenditure Data, 2004).

In 2006, remediation experts created the Sustainable Remediation Forum (SURF) to establish a framework that incorporates sustainable concepts throughout the remedial action process, while continuing to provide long-term protection of human health and the environment and achieving public and regulatory acceptance. Although environmental remediation activities represent only a fraction of the US economy (approximately 5 billion USD in 2006) (Farkas and Frangione, 2009) of the 16.16 trillion USD of US gross domestic product (The World Fact Book, 2012), the remediation stakeholders keep the concept *think global, act local*. The SURF is mainly working on sustainability concepts and technology transfer (Ellis et al., 2009).

The concept adopted by the Minnesota Pollution Control Agency, *Green Remediation: Incorporating Sustainable Environmental Practices into Remediation of Contaminated Sites,* describes remediation methods and approaches that consider all environmental effects of cleanup actions and incorporate strategies to maximize the net environmental benefit (Green Remediation, 2008b). The concept provides 18 pollution prevention and sustainability options organized into the following three scenarios: cleanup remedy selection, existing and new business operations, development and renovation. The format is a decision tree that sequentially takes the user through a series of steps in planning remediation. The toolkit also gives suggestions for streamlining the regulatory process to expedite remedial decisions (Toolkit for Greener Practices, 2011).

The California Department of Toxic Substances Control developed the *Green Remediation Initiative* to promote the use of green technologies in site remediation work. The focus of the initiative is to evaluate and promote green remediation technologies in the cleanup of active and closed military facilities, formerly used defensive sites, military ammunition storage sites (California's Green Remediation Initiative, 2011).

The Illinois' EPA has created a matrix to guide site owners and consultants to find out sustainable practices for site assessment, planning, design and cleanup. The matrix counts individual actions, followed by a qualitative ranking of their level of difficulty and feasibility (subcategorized by cost, schedule, and technical complexity). The benefits of each action to the environmental quality of air, water, land, and energy are also identified (Illinois' Greener Cleanups Matrix, 2008).

Canada. The Canadian Environmental Protection Act (CEPA) was implemented on 31 March 2000 by the federal government. The Act declares pollution prevention as the cornerstone of national efforts to reduce releases of toxic substances in the environment. The CEPA recognizes the contribution of pollution prevention as well as management and control of toxic substances and hazardous waste flows as the means to reduce threats to Canada's ecosystems and biological diversity. The provinces set most standards for remedial performances individually, but the Canadian Council of Ministers of the Environment provides guidance at a federal level in the form of Canadian Environmental Quality Guidelines, Canada-Wide Standards and Canada-Wide Standard for Petroleum Hydrocarbons in Soil (Environment Canada. Environmental Registry, 1999).

In 1998, the Ministry of Environment of the Province of Quebec (now called the Ministry of Sustainable Development, Environment, and Parks) introduced the sustainable development concept in the guideline document entitled *Soil Protection and Contaminated Sites Rehabilitation Policy* with its four principles forming the basis of the policy: prevention, rehabilitation-reclamation principle, polluter pays and fairness principles. Most of the remedial actions in Quebec are conducted primarily to comply with generic criteria. As a result, 67 % of the soil remediation work completed in Quebec to date falls into the category of *excavation and off-site landfilling*, while another 29 % fits into *excavation and ex-situ treatment* (Environment Canada. Environmental Registry, 1999; Ellis and Hadley, 1999).

Australia. One of the four national research priorities of Australia presented by the prime minister in 2002 reveals a commitment to the areas of research in environmental technology and management for the future of Australia. The first priority is "An Environmentally Sustainable Australia", which focuses on new, cost-effective, and safe ways to detect, assess, and remediate contaminated urban, rural, or industrial sites, thus enabling the sustainable use of the land (Australian Government, 2013).

The New South Wales (NSW) territory (around the capital) has a Department of Environment, Climate Change and Water (DECCW), which uses its powers under the Contaminated Land Management Act 1997 (CLM Act) to deal with site contamination that is significant enough. The CLM Act sets out the role of the DECCW and the rights and responsibilities of parties it might direct to manage significantly contaminated land (CLM Act, 1997). Local councils work with other sites under the planning and development framework, including State Environmental Planning Policy No. 55 – Remediation of Land and Managing Land Contamination – Planning Guidelines.

In Queensland the management of *contaminated land* refers to sites contaminated with hazardous substances (arsenic, DDT or oil etc.) which may pose a risk to human health and/or the environment. The Sustainable Planning Act (SP Act, 2009) is administered by the Department of Local Government, Planning, Sport and Recreation and it provides a process to appropriately investigate the land (through a contaminated site investigation) using the process stipulated in the Environmental Protection and Biodiversity Conservation Act of 1994 for contaminated land management. Under this Act, the department maintains two public registers that contain land use planning information – the Environmental Management Register (EMR) and the Contaminated Land Register (CLR).

South America. The State of São Paulo (Brazil) is often considered in South America as a reference in terms of environmental regulations. Since 1999, São Paulo has implemented a remediation approach promoting risk-based corrective actions. The São Paulo agency *Companhia de Tecnologia de Saneamento Ambiental de Brasil* (CETESB) accepts a risk-based corrective action (RBCA) methodology based on the US EPA protocols for conducting risk assessments at service stations. However, the agency has experienced a wide variability in the risk assessments received, which has led to the development of a standard spreadsheet that is used to calculate risk at service stations. This spreadsheet is used for industrial sites as well and was released to the public in 2009. Although there is currently no official framework or protocol in Brazil applicable to evaluating and measuring sustainable practices and impacts in remediation, conditions are favourable for the promotion and implementation of sustainable activities. An example of this is *Petrobras*, the largest oil company in South America and the largest corporation in Brazil, involved in remediation of contaminated sites. *Petrobras* governs a set of ten social and environmental principles and is a United Nations Global Compact signatory listed on the Dow Jones sustainability index. The company is recognized as one of the most sustainable and influential Brazilian companies (Ellis et al., 2009).

China. Economic growth in Asia/China has been impressive over the past 15 years with strongly positive impacts on reducing poverty. However, the increased pollution resulting from such economic growth has degraded natural resource systems and is threatening public health, thus undermining economic productivity. A policy guideline on sustainable energy was released by China's government on 5 June 2008, but site remediation acts are still absent. Rather than a call to action, the policy guideline is primarily the government's show of agreement regarding sustainability concepts. In Taiwan, the soil and groundwater pollution remediation act was promulgated in 2000, but associated efforts remain in preliminary stages. It appears that sustainability principles will not play a significant role in remediation technology selection in China and Taiwan until a significant number of sites move into the remediation phase (Ellis et al., 2009).

Japan. The Soil Contamination Countermeasures Law of 2003 influences most remediation activities in Japan, but the Environment Agency has initiated discussions regarding sustainability in remediation. According to the Secretary General of the Geo-Environmental Protection Centre, Japanese law has been reviewed in early 2009.

Republic of South Africa. The Ministry of Water and Environmental Affairs on 20 March, 2012, published the public comment under the National Environmental Management: Waste Act, 2008 (Act No. 59 of 2008) the Draft National Norms and Standards for the Remediation of Contaminated Land and Soil Quality, which requires the Minister to set standards which could be a cornerstone to define thresholds for the remediation of contaminated land. The requirements set out in the draft norms and standards apply to any person who undertakes any remediation activity within South Africa. The purpose of the norms and standards is to provide a national approach to the remediation of contaminated land and limit uncertainties on appropriate criteria and methods of contaminated land assessment. The norms were finally accepted and published on June 10, 2013 (National Norms and Standards for the Remediation of Contaminated Land and Soil Quality, 2013).

Russia. The main laws in Russia include the aspect of environmental protection and are in general of a federal kind. Remediation of contaminated sites is a relatively new topic; the law mostly focusses on prevention and saving natural resources of the country – mineral and biological (On Environmental Protection in RF, 2002; On the Sanitary-Epidemiological Welfare of the Population in RF, 1999; On RF Strategy of Environmental Protection and Sustainable Development: the Order, 2002).

State requirements are determined by standards and regulations that apply to the territory of the Russian Federation (RF) and set the maximum permissible concentration (MPC) of chemicals in the soil for different land use (On the Sanitary-Epidemiological Welfare of the Population in RF, 1999). There are several health requirements governing pollution of soils such as sanitary protection of soils, sanitary and epidemiological requirements for the quality of the soil and guidelines for hygienic evaluation of soil quality in residential areas. A single-level indicator of soil contamination is expressed as pollutant content in micrograms or milligrams per 1 kg of soil. No specific legislative documents on contaminated soils are in place yet, but contaminated soils are to be treated as hazardous waste depending on the contamination level and must fulfil the requirements defined in the legislation for waste management. Remediation works should be applied if contaminated by the following activities: mining and pipeline input and use areas, elimination of existing structures, storage and disposal of industrial, municipal and other waste, elimination of the consequences of land contamination (if recovery requires the removal of topsoil), conducting military exercises outside the areas designated for this purpose, performing any type of works related to the disturbance of soil cover. Contamination is owned by the State, but if the land is purchased and is planned for use by a private stakeholder, remediation should be performed at the new owner's own expense (On Environmental Protection in RF, 2002; On the Sanitary-Epidemiological Welfare of the Population in RF, 1999).

European Union. The European Environment Agency (EEA) estimates that soil contamination requiring cleanup is present at around 250,000 sites and more than 80,000 sites have been cleaned up during the last 30 years in the EU countries. The most common harmful contaminants are heavy metals (37 %) and mineral oils (33 %). The EU Directive 2004/35/EC establishes a comprehensive liability regime for damage to the environment according to the *polluter pays* principle and it leaves significant discretion for implementation to the Member States. Potentially polluting entities are not required by the EU to carry insurance or establish other financial security mechanisms to protect them against the cost of potential cleanup. A considerable share of remediation expenditure, about 35% on average, comes from public budgets in the EU countries, because legally responsible polluters no longer exist, cannot be identified, or are insolvent. The remedial activities of industrial sites receive funding through EU structural funds; the total budget for this purpose was EUR 2.25 billion for 2005-2013 (Soils Policy…, 2009).

The EU Waste Framework Directive (2006/12/EC), the EU Water Framework Directive (2000/60/EC) and the EU Groundwater Directive (2002/118/EC) are important legislative tools for environmental protection. A number of other governmental and non-governmental resources exist in Europe to support work on the remediation of contaminated lands such as The European Commission's Joint Research Centre (JRC) Land Management and Natural Hazards Unit that undertakes prevention and remediation of soil contamination and EUGRIS which is the EU's web portal for information and services on topics related to soil and water. The EU adopted the Environmental Technology Action Plan in 2004 to encourage the development and broader use of environmental technologies, including environmental remediation technologies. The Network for Industrially Contaminated Lands in Europe (NICOLE) is a leading independent forum on contaminated land management in Europe. The European Coordination Action for

Demonstration of Efficient Soil and Groundwater Remediation (EURODEMO) promoted sustainable, cost-effective soil and groundwater remediation technologies, exchanged experience and developed common protocols. Its efforts were important drivers in achieving the priority goals of the European Sustainable Development Strategy, which had set overall objectives and specific actions for seven key priority challenges until 2010. According to the European Commission's Sustainable Development website (EUSD, 2013), the overall aim of the strategy was *to identify and develop actions to enable the European Union to achieve a continuous, long-term improvement of the quality of life through the creation of sustainable communities*. In 2008, a workshop among many organizations took place about sustainable groundwater and soil remediation technologies (EUGRIS, 2008).

United Kingdom. The generic guidance commonly used in the UK is the Soil Guideline Values published by the Department for Food, Environment and Rural Affairs (DEFRA) and the Environment Agency. Screening of values on contamination is derived from the Contaminated Land Exposure Assessment Model (CLEA UK). *Contaminated Land: Applications in Real Environments* (CLAIRE) describes itself as an independent, not-for-profit organization established to stimulate the regeneration of contaminated land in the United Kingdom by promoting practice of sustainable remediation technologies. It is currently leading the Sustainable Remediation Forum—United Kingdom (SURF UK). The working mission statement of the group is *to develop a framework in order to embed balanced decision making in the selection of the remediation strategy to address land contamination as an integral part of sustainable development* (*Contaminated Land: Applications in Real Environments*, 2013).

Latvia. The Law "On Pollution" (came into force on 1 July 2001) defines the procedures in the area of contamination (*On Pollution*, 2001). The purpose of the Law (Section 2) is to prevent or reduce harm caused to human health, property or the environment due to pollution and to eliminate the consequences of the harm caused. A local government in co-operation with the relevant Regional Environmental Board of the State Environmental Service has an obligation to ascertain and initially assess polluted and potentially polluted sites in a relevant administrative territory (Section 33). The Latvian Environment, Geology and Meteorology Centre (LEGMC, under the auspices of the Ministry of Environmental Protection and Regional Development, MEPRD) has an obligation to maintain all collected and processed information about contaminated sites. Methods and procedures for ascertaining polluted and potentially polluted sites, as well as the procedures for financing, conditions for data collection and utilization are regulated by the Cabinet of Ministers Regulations No. 483 adopted on November 20, 2001 "Inventory and Registration of Contaminated and Potentially Contaminated Areas" (Regulation of the Cabinet of Ministers No. 483). Contamination of soil and groundwater is defined by the Instructions of the Cabinet of Ministers and are largely derived from the EU legislation.

The National Development Plan (NDP) of Latvia 2007-2013 included provisions for performing the clean environment policy and one of the tasks was to promote the remediation of historically contaminated sites (*Latvian National Development…*, 2007-2013). This document was followed by the NDP 2014-2020, which was approved in 2012 and is in force from 2014 (LETA, 2012) as an integral part of the "Latvia 2030" programme. This document is a continuation of the former environmental policy and speaks about sustainable growth with an environment that is not endangered. Relevant decisions have to be taken in the following areas:

- Environmental legislation and environmental improvement of the institutional framework,
- Reduction of environmental pollution,
- Individual ecosystem protection and preservation,
- Environmental data acquisition and processing system development for decision-making on environmental protection and sustainable development,
- Information for the public and its involvement in decision-making on environmental issues.

The National Environmental Policy Plan 2004-2008 has partly lost its actuality; however, Environmental Policy Strategy 2009-2015 defines the environmental policy and the general objectives for the rehabilitation (revitalization) of historically contaminated sites:

- To prevent or reduce contamination and its harmful effects on human health, property, the environment and biodiversity resulting from military and economic activities;
- To achieve improvements of the soil, groundwater and surface water quality in contaminated areas;
- To prevent contamination from entering surface and ground waters;
- To restore and improve the quality of contaminated sites;
- To consider environmental contamination aspects in territorial planning;
- To determine the real value of the land and the corresponding real estate tax according to the degree of contamination (NEPP, 2004-2008). These aspects were included in the Environmental Policy Strategy of Latvia 2009-2015.

1.3. Remediation technologies for heavy metal contaminated soil

1.3.1. Criteria and classification of remediation technologies

Contaminated areas and hazardous sites in the USA and West European countries became generally recognized in the 1970s, but a decade later industrial nations started to improve the decision-making process for the evaluation and the treatment of contaminated land (Roehl and Gregolec, 2005). Soil and groundwater are environmental subjects primarily influenced by industrial development with its output of waste and inadequate dumping. As a result there is a huge number of contaminated sites that are disseminated in post-industrialized countries (Prokop et al., 2000; Critto et al., 2006). In the EU, the number of such sites varies from 300 000 to 1.5 million (due to the uncertainty of the common definition for contaminated sites, different approaches to acceptable risk levels, and exposure parameters) (CLARINET, 2002). Heavy metal contaminated sites in the US that need major remediation programs constitute 77 % of the Superfund sites (Superfund, 2014), 72 % of the Department of Defense (DOD) sites and 55 % of the Department of Energy (DOE) sites. The USEPA estimates that over 50 million cubic meters of soil at current NPL sites are contaminated with metals (Superfund Program, 2004).

The motivation is to develop site remediation projects in order to eliminate or at least reduce contamination presence in the soil and groundwater. The aim of activities is to transform unusable property into one that is available for use and thus to conserve land resources, to improve the environmental condition at the contaminated site, as well as to reduce the risk to humans and the environment. Remediation means actions taken to clean up, mitigate, correct, abate, minimize, eliminate, control and contain or prevent a release of a contaminant into the environment in order to protect human health and the environment, including actions to study or assess any actual or suspected release (9VAC20-160-10, Definitions, 1997). The above definition shows that it is a broader term than cleanup and includes the management of a contaminant at a site to prevent, minimize, or mitigate damage to human health or the environment (Prokop et al., 2000). Soil and groundwater remediation technologies are developed to eliminate historically and currently contaminated sites as contamination causes loss of land as a resource (Directive 2008/1/EC). A variety of methods are proposed for soil and groundwater remediation ranging from biological to advanced and complicated engineering techniques; those may be specific to the site and dependent on the contaminant or contaminant class. Considering the concept of sustainable development, remediation technologies have to correspond to the principle of low energy and resource use, low waste production, minimized footprint, and have an innovative character (Schrenk et al., 2007). The decision on the technology choice should have the following goals:

a) Short-term and/or long-term effectiveness;
b) Effectiveness of contaminant reduction at the site;
c) Reduction of contaminant toxicity;
d) Cost effectiveness of remediation.

Regarding the contamination level and the geological and hydrological character of the site, the criteria should be improved to include factors of social, health and environmental significance. The analysis of the advantages and disadvantages of each technology set additional criteria for the choice of remediation technologies. Technologies are divided into subgroups, for example, technologies for heavy metals, inorganic salts, non-halogenated volatiles and semi-volatiles, fuel hydrocarbons, explosives and others. Radioactive substances comprise a separate group that originates mainly from the nuclear research, production, accidental spills, fuel-cycle facilities and other sources. Heavy metals involve a group of metals and some metalloids as environmental pollutants (V, Cr, Fe, Co, Ni, Cu, Zn, As, Ag, Cd, Sn, Sb, Hg, Tl, and Pb) based on the ecological and toxicological significance considering the unified pollutant classification (Duffus, 2002; Nieboer and Richardson, 1980; Martin and Coughtrey, 1982). In the anthropogenic environment, heavy metals comprise an important group of soil, sediment, and groundwater contaminants because they cannot be destroyed but under local natural conditions, heavy metals transform into various chemical species. Therefore, the remediation of metal-contaminated soil consists primarily of manipulating (i.e., exploiting, increasing, decreasing, or maintaining) the mobility of metal contaminant(s) to produce a treated soil that has an acceptable total or leachable metal content (McLean and Bledsoe, 1992; Mulligan et al., 2001). There are reported factors that influence metal mobility in soil-waste systems: the type and quantity of soil, the concentration of the metal of interest, the concentration and type of competing ions and complexes forming ligands, both organic and inorganic, pH, and redox status.

The potential mobility of heavy metals changes through natural processes of weathering, human manipulation and changes of the soil condition.

Remediation technologies can be divided into two categories: *in-situ* and *ex-situ* (Reddy et al., 1999). An *in-situ* technology means that a contaminated substance in the soil or groundwater is treated on site with contamination determined. *In-situ* technologies are used for the treatment of unexcavated soil or unextracted groundwater that remains relatively undisturbed after the cleanup process. This approach demands detailed information of physical, chemical and biochemical characteristics of the matrix and pollution, geological, hydrogeological and other conditions. In this case, the safety level for the personnel involved in the process of treatment is higher; it is more economical and has a lower impact on the site. In the off-site treatment process, the contaminated soil and/or groundwater is removed from the excavated site (*ex-situ* approach). It demands the transportation of the contaminated soil and/or groundwater to the treatment facilities. *Ex-situ* technologies are applied to excavated soil and/or extracted groundwater and can be performed both on and off site.

The following *in-situ* and *ex-situ* remediation technologies are used for the reduction of the heavy metal contamination level:

a) *In-situ* and *ex-situ* technologies – bioremediation, stabilization/solidification and separation/concentration;
b) *In-situ* technologies – soil flushing, electrokinetics, barriers / treatment walls, chemical treatment, soil amendments and phytoremediation;
c) *Ex-situ* technologies – soil washing.

Remediation technologies based on their scope of application include vadose and saturated zone technologies. The vadose zone includes the geological profile from the surface to the upper surface of the principal water-bearing formation. Some treatment methods can be only used for vadose zone treatment, but not for the treatment of contaminated groundwater. The most common practice to remediate the vadose zone of contamination is excavation and transportation to landfills. The contaminated soil can be treated or untreated before the disposal. This is the best approach for smaller-sized contaminated sites; however, when it has to be applied to larger sites, the cost of excavation, transportation and treatment rises (Reddy et al., 1999; Roehl and Gregolec, 2004; Mulligan et al., 2001).

The technologies that are based on the processes used include biological, physical separation, chemical, physical-chemical, thermal, and containment techniques. In bioremediation technologies, microbiological metabolism is used to transform or degrade soil or groundwater contaminants into harmless substances. The latter can be carbon dioxide, water, fatty acids and some others. Physical and chemical treatment technologies are based on the physical and/or chemical properties of the contaminants as well as on the contaminated media to chemically convert, separate, or contain the contamination.

1.3.2. Biological technologies

Biological technologies for remediation take advantage of the pathways developed by microorganisms to protect themselves from oil products and metals. Common protection mechanisms include oxidation/reduction, sorption and methylation. At present biotechnologies that incorporate these mechanisms are in an advanced stage of development for the remediation of organic compounds, but experience is limited for inorganic contaminants. Biological treatment technologies will be experimentally tested in some brownfield areas in the nearest future. Such processes as bioleaching, biosorption, biovolatilization, biological oxidation and reduction may provide *in-situ* treatments without the use of environmentally aggressive chemicals (Lombi et al., 1998, FRTR, 2007). High requirements for strong reagents result in the formation of toxic sludge and secondary environmental pollution, thus leading to problems with contaminated groundwater, hazardous effluents from mine tailings and an increased amount of industrial wastewater. Biotechnologies can provide solutions for groundwater as well as soil treatment. Microorganisms have evolved various measures to respond to heavy metal transport across the cell membrane, biosorption to cell walls and entrapment in extracellular capsules, precipitation, complexation and oxidation – reduction reactions (Veglio et al., 1997). Microorganisms have proven capability to uptake heavy metals from aqueous solutions when the metal concentrations in the effluent range from less than 1 to about 20 mg L^{-1} (Brierley, 1990). Extensive research of biological methods for metal removal was therefore promoted. However, field techniques for the extraction of oil products and heavy metals by microbiological means are rather limited; the main technologies include bioleaching and oxidation/reduction reactions. Microorganisms are also known to oxidize and reduce heavy metals, e.g. Hg and Cd can be oxidized, As and Fe can be reduced by microorganisms, but Cr (VI) can be reduced to Cr (III), so that it is less mobile and toxic. Bacteria such as *Bacillus subtilis* and sulphate reducing bacteria in the presence of sulphur can perform such reactions. Soluble and membrane-associated enzymes were found to mediate the process of Cr^{6+} reduction under anaerobic conditions. Unlike the Cr^{6+} reductases isolated from aerobes, the Cr^{6+} reducing activities of anaerobes are associated with their electron transfer systems ubiquitously catalyzing the electron shuttle along the respiratory chains (Wang and Shen, 1995). The cytochrome families are involved in the enzymatic anaerobic Cr^{6+} reduction. It means that such type of bioremediation has a good potential, which would only require the amendment of nutrients and the adjustment of physical conditions to promote the reaction (Turick et al., 1996; Cheung and Gu, 2007). The research of heavy metal bioremediation by a multi-metal resistant endophytic bacteria L14 (EB L14) isolated from the cadmium hyperaccumulator *Solanum nigrum* L. was characterized for its potential application in metal treatment by Hanjun et al. (2010). Investigations pinpointed the practical bioremediation potential of EB L14; multi-metal resistance and its hormesis were observed, good adaptation abilities for practical *in-situ* bioremediation of heavy metals as well as a significantly high uptake of Cd (II), Pb (II) and Cu (II) within 24 h incubation was achieved, but no significant effect on Cr removal was observed. Efficiencies were promoted by inhibiting the activities of ATPase. Bioremediation was practiced in vivo so results proved that no secondary pollution appears during testing (Hanjun et al., 2010).

Bioremediation (neither any other remediation technology) does not provide degradation or elimination of inorganic contaminants but during the treatment process the valence state of inorganic contaminants can be changed thus promoting adsorption and immobilization of soil particles, precipitation, uptake, accumulation as well as concentration of heavy metals in the biomaterial. Stabilization of soils in terms of heavy metal immobilization is researched a lot but is still most often experimental and lacks improvement in large field scales (FRTR, 2007).

Heavy metal ions can be included in the cellular structure and afterwards biosorbed onto the binding sites present in the cellular structure. This method of uptake is independent of the metabolic cycle and is called *biosorption* or *passive uptake*. Heavy metals can also come into the cell across the membrane through the metabolic cycle. This mode is referred to as *active uptake*. The metal uptake by both passive and active modes can be named as *bioaccumulation*. Most of the studies dealing with growing cells describe the biphasic uptake of metals: rapid biosorption is followed by slower metabolic processes (Garnham et al., 1992; Donmez and Aksu, 1999). The research of the use for bioremediation of marine microalgae growing cultures has shown that intracellular heavy metal levels such as for Cd are often higher than the biosorbed ones (Perez-Rama et al., 2002). Newly developed bacterial strains have the ability to bi-phase transfer of heavy metals in cells.

Genetic engineering is developing new approaches in order to improve the bio-impact of newly modified bacterial strains for the use in bioremediation. Pilot scale testing has been done, e.g., in Northern Sweden, where the use of acidophilic bacteria strain consortia has shown high metal uptake and stability against environmentally tough semi-Arctic conditions (Dopson, 2012). Mesophilic iron and sulphur-oxidizing acidophiles are readily found in acid mine drainage sites as well as bioleaching operations; however, relatively little is known about their activities at suboptimal temperatures and in cold environments. Sub-ambient incubation temperatures allow temporal isolation of redox reactions, and pH changes associated with single and dual substrate oxidation, precipitation and chemical reactions are also relatively slow. The temperature variety was large for the oxidation of solid-phase and soluble substrates by *Acidithiobacillus* strain SS3, and the strain was also tolerant to processes of oxidation of elemental sulphur (S^0), tetrathionate ($S_4O_6^{2-}$) and ferrous iron (Fe^{2+}) (Kupka et al., 2007; Kupka et al., 2009). Psychrotrophic *Acidithiobacillus* strain SS3 is an example of biological tool to simulate biogeochemical reactions and control iron and sulphur oxidation rates at low temperatures, a mission that is impossible to accomplish with a strictly chemical reaction sequence (Kupka et al., 2009; Dopson et al., 2007). The soil in mining areas can therefore achieve a higher pH and the accessory trace elements become less bioavailable and leachable from tailings. However, there can be no universal process to suit all kinds of metal bioremedial actions, and these technologies need to stand the test of time.

Phytoremediation is a relatively new approach to remove contaminants from the environment. Plants remove, destroy or sequester hazardous substances; however, even plants that are relatively tolerant to various environmental contaminants often have a relatively low biomass in the presence of a contaminant (Glick, 2003). Table 1.1 summarises the main advantages and disadvantages relevant to the phytoremediation technology in general.

The most considerable limitation for the use of phytoremediation is a relatively narrow range of heavy metal concentrations within which the method can be applied (potential of plant toxicity). Problems also arise because of weather aspects, toxic by-product utilization as hazardous waste and climatic conditions – the further to north, the less choice of plant species tolerant to climate and toxicity and shorter biomass production

Table 1.1

Advantages and disadvantages of phytoremediation
(modified by author after Belz, 1998)

Advantages	Disadvantages
Aesthetically pleasing and energy efficient	Can take many growing seasons to clean up a site, can clean up soil or groundwater only near the surface *in-situ* 1-2 m deep; 3-5 m deep treatment possible only with a special design
Works with metals and slightly hydrophobic compounds	
Can stimulate bioremediation in the soil closely associated with the plant root in a symbiotic manner	Tree roots grow in the capillary fringe, but do not extend deep in to the aquifer
Relatively inexpensive – phytoremediation can cost as little as 18-180 USD per m^3 whereas metal washing can cost 3 times more (Wantanabe, 1997).	Plants that absorb toxic materials may contaminate the food chain
Even if the plants are contaminated and unusable, the resulting ash is approximately 20-30 t per 5000 t soil (Schnoor, 1997).	Volatilization of compounds can transform a groundwater pollution problem to an air pollution problem
Having ground cover on property reduces exposure risk to the community (i.e., lead).	Returning the water to the earth after aquaculture must be permitted
Planting vegetation on a site also reduces erosion by wind and water	Less efficient for hydrophobic contaminants, which bind tightly to the soil
Can leave usable topsoil intact	

period. For soils polluted with heavy metals the most common are phytoextraction and phytostabilization. Phytoextraction is a biological method where specific species of plants uptake and accumulate contaminants from the soil as hyperaccumulators, but often limitations appear due to sparse production of biomass and problems with mechanical harvesting. Depending on the local climate and chemistry of pollutants being removed, the most commonly used species for heavy-metal extraction are *Brassica* and *Helianthus*. Laboratory testing, performance, streamline tests, harvesting, various amendments, seedbed preparations and plant protection during field tests, fertilization, irrigation, crop disposal and monitoring is described by A. Sas-Nowosielska and colleagues (2007).

Phytoextraction is very dependent on plant and soil factors, such as soil suitability for plant growth, depth of the contamination, depth of the plant root system, level of contamination, and urgency in cleaning up. Furthermore, there is a need for a full understanding of the physiology, biochemistry, uptake and other factors of the plants employed (Gonzaga et al., 2006). The climatic conditions and bioavailability of metals must be taken into consideration when using phytoremediation. The plants will have to be isolated from wildlife and agricultural lands. Once contaminated, the plants will have to be disposed of in an appropriate fashion. Some techniques include drying, incineration, gasification, pyrolysis, acid extractions, anaerobic digestion, extract of the oil, chlorophyll, fibres from the plants or disposal (Bolenz et al., 1990; Sas-Nowosielska et al., 2005).

Phytoremediation is most applicable to shallow soils with low levels of contamination (2.5-100 mg kg^{-1}). In comparison with other remediation technologies, phytoremediation is a permanent technology. More research is needed to enhance the extraction of the metals by the plants through genetic breeding and to correlate bioavailability with metal uptake. Crop plants that grow fast may be viable for phytoremediation (Mulligan et al., 2001). In spite of the slow process of phytoremediation that is limited by specific metal hyperaccumulator species and some other factors, phytoremediation mitigates environmental problems without the need to excavate the contaminated soil. Sarma (2011) has reported that more than 750 terrestrial and aquatic plants have potential value for phytoremediation that can be used to reduce heavy metal concentration in contaminated land and groundwater, e.g., as Ni, Cu, Cd, Cr, Hg, As, Ag, Se, Zn. Results of A. Sas-Nowosielska with colleagues (2005) indicate the potential for using some species of plants to treat Hg contaminated soil through stabilization rather than extraction. However, in Latvia phytoremediation has not been done in contaminated industrial sites, but this approach should be used in further decontamination works, where the concentration of metals is not so high. This approach is especially attractive because the price is much lower compared to other technologies (see Tables 1.2, 1.3).

The efficiency of phytoextraction can be improved by the use of amendments, such as chelating agents (EDTA), but the impact of the resulting possible organic-metallic compounds should be carefully assessed. Phytoextraction is mainly used for lead, but other metals such as Zn and Cd can also be significantly uptaken. Laboratory testing results must be carefully transferred to field scale as is the case for all remediation technologies.

Table 1.2

Cost Advantage of Phytoextraction for Metals

(after Schnoor, 1997; Electrokinetics Technology Overview Report, 1997 recalculated according to Measuring Worth, 2014)

Type of treatment	Costs, USD per m^3	Time required, months	Additional factors/ expenses	Safety issues
Fixation	135-300	6-9	Transport/excavation Long-term monitoring	Leaching
Landfilling	150-600	6-9	Long-term monitoring	Leaching
Soil extraction	350-750	8-12	5 000 m^3 minimum Chemical recycling	Residue disposal
Phytoextraction	25-60	15-40	Time/land commitment	Residue disposal
Electrokinetics	300-500	12-36	Time/land commitment	Residue disposal

The use of certain plant species to immobilize contaminants in the soil and groundwater through accumulation and absorption by roots, adsorption onto roots' epidermis, or precipitation within the root zone is called phytostabilization (Sas-Nowosielska et al., 2005). It does not remove contaminants from the soil, but reduces danger to human health and the environment as plants are used to prevent erosion of the soil, reduce water percolation and prevent direct contact with the soil-immobilized contaminants by controlling the soil's pH, gases, and redox conditions (Vangronsveld et al., 1995). Phytochemostabilization can be achieved if an appropriate plant cover is constructed in combination with soil amendments. The approach is suitable for areas heavily polluted with bivalent heavy metals, where commercially available species for revegetation cannot survive. It is possible to introduce plant cover with soil amendments thus stopping mechanical deterioration of the soil and the leaching of metals; concerted action of phyto- and chemostabilization may yield positive results. Hazard reduction is the measure of the method's efficiency (Sas-Nowosielski et al., 2005).

Table 1.3

Cost advantage of phytoremediation of soils using fine-rooted grasses compared to other techniques

(according to Schnoor, 1997; Cauwenberghe, 1997 – recalculated according to Measuring Worth, 2014)

Type of treatment	Range of costs, USD per ton
Phytoremediation	15-55
In-situ bioremediation	75-225
Indirect thermal	30-330
Soil washing	180-450
Solidification/Stabilization	120-300
Solvent extraction	360-500
Incineration	480-660
Soil venting	300-2,250
Electrokinetics	120-150

Phytostabilization is advised to be performed by using phosphate amendments, but not in cases when the contaminants are arsenic or other metalloids. Continuous monitoring is necessary in order to evaluate the impact of precipitation, freeze-thaw processes and the fate of heavy metals in remediated areas.

Contaminated sites usually have a mixture of inorganic and organic pollutants that require complex remediation. Phytoremediation itself can be considered as a technology for the remediation of soils contaminated with both organic and inorganic contaminants, and innovative studies have shown that phytoremediation is a good solution at selected sites with mixed contaminants (Wang et al., 2013). It is not an easy task to remediate mixed contamination as the effectiveness of phytoremediation can be limited because of toxicity, growth inhibition and low contaminant bioavailability. A combined electrokinetic/phytoremediation technology is an innovative green and sustainable technology for the remediation of contaminated sites. This technology compiles advantages of both technologies in order to try to overcome the limitations of each one. It has been tested at the laboratory scale with soils contaminated with heavy metals, but not for mixed contamination, and has great perspectives for further studies (Cameselle et al., 2013).

1.3.3. Physical treatment technologies

Physical treatment involves phase transfer of metal contaminants from the contaminated media by exploiting differences in certain physical characteristics between metal bearing and native soil particles considering their size, density, magnetism, and hydrophobic surface properties. Physical separation is basically a technique of metal-bearing particle concentration applied in the mining and mineral processing industry, whereas in soil remediation it indicates separation of metal-containing particles from the soil (Dermont et al., 2008). The use of physical separation technologies is exactly dependent on soil sorption capacity, chemical forms of heavy metals in soil, and the concentration level. Separation technologies are therefore mostly applied in industrial areas with high heavy metal concentration in anthropogenic soils.

Ex-situ technologies include soil excavation followed by separation based on the physical properties of the particles. These systems are useful in two situations:

a) When the pollutant is present in the form of discrete particles in soil;
b) When the pollutant is concentrated in specific particle-size fractions, as is common for trace elements in the fine fraction of soil (Lombi et al., 1998; FRTR, 2007).

Soil washing refers to *ex-situ* techniques that employ physical and/or chemical procedures to extract heavy metal contaminants from the soil. Important soil parameters for physical separation are size, density, magnetism, and surface properties (for separation by physical washing). Chemical extraction means solubilization of metal contaminants from the soil with the extraction of liquids such as acids or chelating agents. Soil washing can differ in terminology from author to author, but the main idea is that heavy metal contaminants are washed out with the fraction of particles and thus the volume of contaminated soil is significantly diminished. In the US and in Europe, soil remediation processes based on mineral processing technologies are often referred to by the broad term of *soil washing* (FRTR, 2007; CLARINET, 2002), although the term *physical separation* is more accurate (Griffits, 1995; USEPA, 1995). The term *soil washing* is also used for describing processes that involve chemical extraction (Mulligan et al., 2001; Abumaizar and Smith, 1999). Federal Remediation Technologies Roundtable (FRTR) distinguishes *soil washing* from *chemical extraction*: soil washing generally uses water or water with wash-improving additives and differs from chemical extraction, which uses an extracting chemical. Confusion resulting from these misnomers often contributes to the propagation of misconceptions about the soil washing technology (Dermont et al., 2008).

Soil washing is a combination of physical separation and aqueous-based separation unit operations to reduce contaminant concentrations to site-specific remedial goals. Physical separation is done by different techniques such as gravitational, magnetic, froth flotation, electrostatic and attrition scrubbing. Although soil washing is sometimes used as a stand-alone treatment technology, it is more often combined with other technologies to complete site remediation. Heavy metals can be removed from soils using various chemical compounds added to the soil. Inorganic acids, such as sulphuric and hydrochloric acids with pH less than 2, organic acids including acetic and citric acids (pH not less than 4), chelators such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetate and various combinations of the above are used. The cleaned soil is then returned to the original site. Soils with less than 10-20 % of clay and organic content (i.e., sandy soils) are most efficiently remediated with these extractants. Both organic matter and heavy metals are removed (Mulligan et al., 2001).

The selection of the separation technology strongly depends on the site and soil type – technogenic soils are mostly located in urban or industrial areas (e.g., shooting ranges, smelting sites, brownfields etc.). These soils are typically composed of hazardous waste, landfill material, construction waste and heavy metal contaminated soil masses. On the other hand, physical separation is not appropriate for treating *natural* soils affected by a diffuse contamination because: (1) metals are added to particles in a sorbed form; (2) target concentration is low; (3) silt and clay percentage is typically high. Physical separation is often associated with chemical procedures to enhance metal removal from silty and clayey particles with contamination sorbed on them (Dermont et al., 2008).

Physical separation presents the following advantages: (1) this technology can treat organic as well as metal contaminants in the same treatment system; (2) volume of the soil for additional treatment is reduced; (3) the processed soil can be cheaply returned in site; (4) metals can be sent for recycling; (5) treatment systems are mobile; and (6) the technologies are very well established in the mineral processing industry and the operational costs are usually low. The disadvantages are that: (1) a large equipment and space are required; (2) small volumes of soil are not feasible to wash (>1000 m^3 for treatment on site); (3) the problem of wastewater treatment arises (Technical and Regulatory Guidelines for Soil Washing, 1997).

Treatment costs vary widely for soil washing as the most important factor influencing costs is the amount of fines in soil. If the treatment goals can be achieved using physical treatment only, the costs may approach 75 USD per ton. Costs in the range of 150-300 USD per ton can be expected when treatment involves both kinds of separation. European markets have prices of 40-180 USD per ton (recalculated using Measuring Worth, 2014) (Technical and Regulatory Guidelines for Soil Washing, 1997).

Soil washing systems can be combined with chemical extraction technologies depending on matrix characteristics, metal speciation and type of metal to be treated. Chemical leaching can be followed by wet screening or may involve a simultaneous process of both methods. Attrition scrubbing can be improved with acids, surfactants or chelating agents and then followed by a wet screening/hydrocycloning stage to separate the fine fines from the clean fraction. Crushing and grinding procedures for soil particles can be a pre-treatment option for enhancing the efficiency of chemical treatment. Ultrasound and cavitation can be done for promoting chemical treatment as well (Mason, 2007).

Soil washing is frequently used in Europe, but not very intensively in the US and Canada. It has been performed successfully in Europe due to regulatory actions taken to restrict landfilling. In Europe it is mostly performed in fixed areas and facilities, but in the US and Canada mobile systems are used more often (Dermont et al., 2008).

Electrokinetic technology (EK) (Fig.1.1) can be applied in wide areas where there are no economic activities now, e.g. former industrial and military firing-grounds. This technology is relatively expensive and is applicable to water soluble contaminants at sites with homogeneous soils that are fine-grained and exhibit both high permeability and high moisture contents. The technology is most efficient when the salinity and cation exchange capacity are low (Emerging…, 1997).

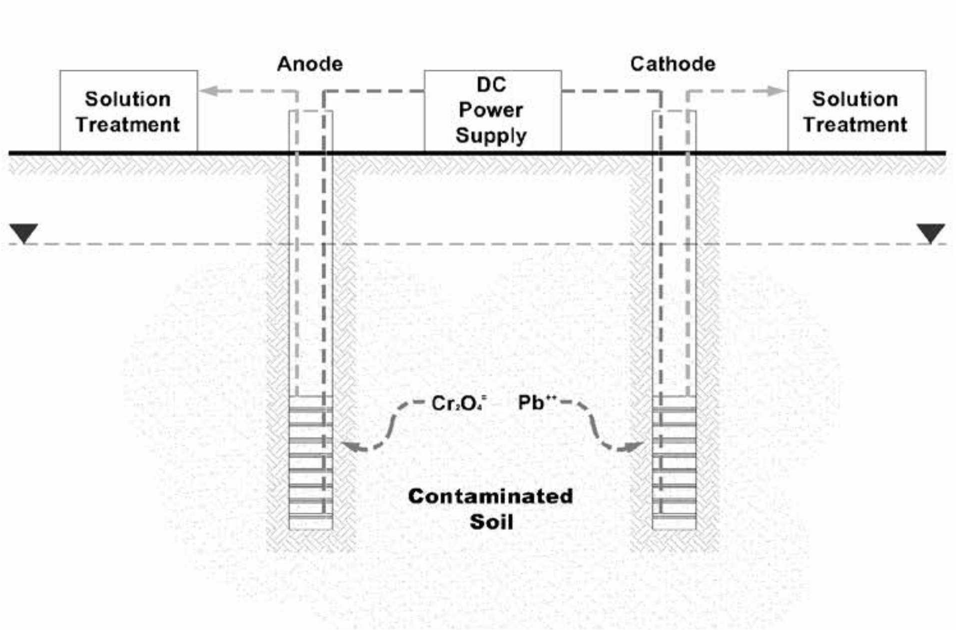

Figure 1.1. Electrokinetic technology for remediation of heavy metal contamination (author's work out, according to Emerging…, 1997)

The EK technology has the following advantages: 1) provides treatment of soils not accessible for excavation; 2) effective in both saturated and unsaturated zones; 3) applicable in soils of low hydraulic conductivity, particularly with a high clay content; 4) can treat both organic and inorganic contaminants. Applicability limitations of the EK technology include following aspects: 1) contaminant solubility and the desorption of contaminants from the soil matrix may limit the success of the technology; 2) process may not be efficient when the target ion concentration is low and the non-target ion concentration (background) is high; 3) technology requires the presence of a conducting pore fluid to mobilize contaminants; 4) heterogeneous soil or anomalies found at sites, such as submerged foundations, rubble, large quantities of iron or iron oxides, and large rocks or gravels may reduce removal efficiencies (Emerging…, 1997).

EK remediation is based on the application of a direct current electric potential to the contaminated soil by one or more series of electrodes adjusted as anodes and cathodes. The electric potential among anodes and cathodes promotes reactions and transport processes in soil resulting in mobilization and transport of contaminants towards electrodes, which can thus be used for extraction of contaminants. The main EK mechanisms are called *electro-migration* and *electro-osmosis*. The first creates the movement of ionic species towards the electrode of opposite charge in the electric field. An electro-osmotic flow of water with contaminants moves in porous soil. The combining effects of the electric field and the electric charge result in an electro-osmotic flow towards the cathode (Cameselle and Reddy, 2012). During the electrolysis of water at the electrodes ionic products

(H^+ and OH^-) are generated and then transported towards these electrodes. The acidic front (H^+) is transported from the anode towards the cathode, but the alkaline (OH^-) – from the cathode towards the anode (Acar and Alshawabkeh, 1993). This causes pH changes inside the treated matrix: a low pH close to the anode, and a high pH close to cathode. Some reports suggest that the pH in soil has a significant influence on contaminant retention and the electro-osmotic flow (Gomez et al., 2009; Ko et al., 2000).

The EK remediation works significantly change the properties of the soil such as pH, induce electrolysis of water, sorption processes, promote acid base reactions and create the ionic flow together with the water. This type of remediation was initially used for heavy metal extraction from contaminated soils; however, organic contamination can also be destroyed with the help of EK. Nowadays the EK technology is used in a combined way with other technologies, e.g., phytoremediation, use of chelating agents, bioremediation, chemical reduction/oxidation, permeable reactive barriers, but only pilot research has been done so far (Reddy and Cameselle, 2009).

The coupled EK-phytoremediation technology has showed highly valuable results for the treatment of heavy metal contaminated soils. Before field applications, it is necessary to test and select hyperaccumulator plants as well as to evaluate the impact onto the soil and biota in it. Geochemical evaluation of the results is necessary to increase the efficiency of the coupled technology. It is thought that biological availability increases and the toxicity of heavy metals is lower when the electric current is applied during phytoremediation. The electro-osmotic flow also takes target contaminants closer to the roots of the plants from the deeper horizons (Cameselle et al., 2013).

In a study by K.R. Reddy and colleagues (2006), soil remediation was improved at a manufactured gas plant area by the use of surfactants, co-solvents and cyclodextrin for polycyclic aromatic hydrocarbons (PAHs), but no significant removal of heavy metals was observed in this study in a mixed contamination case. The partially solubilized PAHs migrated from anode towards the cathode due to the electro-osmotic flow, but heavy metals are mostly present as precipitates due to the high pH and high acid buffering capacity of the soil. In another study, the utility of humic acid as a surfactant for use in the EK remediation for soil containing copper (II)-oxinate ($Cu(OX)_2$) was examined, in which its amount removed from the clayey soils in the presence of HA was three times higher than that in the absence of HA (Sawada et al., 2003). EK remediation costs are dependent on specific chemical and hydraulic properties of soils. Pilot-scale field studies have shown that the energy consumption for extracting heavy metals from soils may reach 500 kW h m^{-3} or more with electrode spacing of 1.0-1.5 m. Consumption can be decreased if depolarization techniques are used since no low conductivity zone would be formed around the cathode compartment, as the total power consumed is directly proportional to the time required for total ionic migration. It would be approximately 2.5 cm per day. Prices of field soil treatment with EK vary from 80 to 270 USD per m^3. Factors that have a significant effect on the unit price are initial and target contaminant and non-target ion concentrations, conductivity of pore water, soil characteristics and moisture content, quantity of waste, depth of contamination, residual waste handling and processing, site preparation requirements, electricity and labour rates (Emerging…, 1997). One of demonstration studies of lead extraction at a US Army firing range in Louisiana was conducted by the Department of Defence's Small Business Innovative Research Program and Electrokinetics, Inc. EPA, where pilot-scale studies have proven the diminishment of lead concentration to less than 300 mg kg^{-1} in 30 weeks of EK processing from original as high as 4500 mg kg^{-1} of lead (Mining Waste Treatment Technology Selection, 2013).

EK remediation is competing with excavation, soil washing, phytoremediation and stabilization/solidification. Digging and treatment off-site is difficult in the saturated zone of the soil; soil washing is possible only if environmental impacts are diminished. Phytoremediation is applicable for degradation of organic contaminants, uptake of metal and radionuclides, but if concentrations are high, this technology is not appropriate. Legislative aspects in some countries, e.g., the UK also do not allow for its official use as a remediation technology because of the low speed of process. Comparison of technologies in the US NAWS Point Mugu site case study has shown that excavation followed by S/S and soil washing is more effective than EK, but the latter can be improved by developing some technological aspects (In Situ Environmental Remediation for Heavy Metal Contaminated Sites, 2001). The costs of the use of other technologies is 2-4 times lower, so the application of EK should be chosen in specific conditions and the choice should be made taking into consideration many indicative aspects, not only the costs.

Landfill mining. Landfill mining (LFM) is the excavation and treatment of waste from an active or closed landfill. LFM involves the excavation, screening and separation of material from older (generally unlined) landfills into various components including soil, recyclable materials, hazardous material and residues. Material recovery projects have been carried out throughout the world during the last 50 years for following purposes: 1) conservation of landfill space; 2) reduction in landfill area; 3) expanding landfill lifetime; 4) elimination of potential sources of contamination; 5) mitigation of an existing contamination source; 6) energy recovery; 7) recycling of recovered materials; 8) reduction in management system costs; 9) site redevelopment. It was for the first time introduced in Israel in 1953 (Shual and Hillel, 1953; Savage et al., 1993), later in Europe and the USA (Hogland and Cossu, 1996), with pilot studies in England, Italy, Sweden and Germany (Hogland et al., 1995, 1996; Cossu et al., 1995).

Contamination from dump sites and landfills is linked with the groundwater and basins of the key river and lake systems, from which it is further directed towards the seas. A large portion of pollutants comes from landfills and dumps sites, whether those are constructed in a better or in a very inappropriate way. Former dump sites of mixed waste can especially be composed of hazardous waste as well as all other types of waste. In former times, especially in Eastern bloc countries, various types of municipal, residential and construction waste as well as hazardous substances and materials were often dumped in these sites. Since 2002, the actual prices of minerals have doubled; the global need for scarce minerals will rise due to continued industrialization of the developing world, with the global demand for minerals expected to double in the next 25 years (Scarcity of Minerals, 2010). Today the humanity consumes mineral commodities very rapidly as a result of: 1) technological advances; 2) new applications; 3) rapidly rising living standards globally increase demands; 4) world population increase (Stenis and Hogland, 2011).

The idea of landfill mining has been well-known to experts of environmental engineering for two decades already. Although the potential for resource recovery from landfills appears significant, facilitating the realization of such a new perspective on landfill mining also involves a number of challenges. For any emerging strategy, the issue of uncertainty is often an overall factor prohibiting implementation since it makes it difficult for companies to foresee the outcome of such initiatives. In order for landfill mining to be feasible for individual companies, economic benefits must simply outweigh the costs. So far, this type of project has mainly been initiated, funded and operated by local authorities, i.e., owners of landfills, aiming to solve a specific issue of relevance for their region such as the lack of landfill space (Dickinson, 1995; Zee van der et al., 2004). Several pilot studies have been performed in Sweden thus providing the experience needed to further share the performance specifics and experience with other countries. Usually landfills are capped and monitored in Sweden as well as in other countries, but the capping in many cases can be insufficient, thus the landfill needs to be exhumed such as the one in Ringstorp, since the value of the land commonly exceeds the value of the content in a landfill (Zee van der et al., 2004). Case studies in Landskrona and Strängnas were led by individual leaders who initiated the idea that the landfill could be extracted and the deposited waste recycled. Anyway, even in Sweden there were a lot of tensions and problems with the implementation of projects larger than pilot scale. These projects should be run with the engagement of authorities and public relation experts, demonstrating that landfills in the form of *mines* can serve for wider policy concerns (Johansson et al., 2012). For example, landfill mining can create jobs (Jones et al., 2012), reduce carbon emissions (Frandegaard et al., 2012), prevent future leakage, postpone metal scarcity and increase autonomy of governments. The latest initiative is in progress in Katrineholm, where the project is run simultaneously by private investments and municipal stakeholders, the extraction of valuables by separation is done by modern robotic technologies avoiding health risks for the labour force involved in project. Legislation and funding should be taken into account when planning for remedial activities, including landfill mining activities. Emissions and residuals during the works must be utilized under strong control.

Feasibility studies of the LFM are in progress in the context of developing economic processes and global reduction of raw resources: quality and risk assessment, detailed LFM and post-LFM monitoring planning, costs of the LFM itself, market situation, cement industry needs, incineration capacities and many other factors.

Figure 1.2. Kudjape landfill and surrounding area at Saaremaa Island, Estonia. LFM project, February and August 2013 (author's photos)

The approbation of the implemented LFM project in Estonia took place in May and September 2013 among authorities, entrepreneurs and researchers. Decisions concerning future LFM applications must allow some flexibility in order to avoid too high costs and stagnation of the process.

1.3.4. Chemical treatment technologies

Chemical treatment includes reduction of the bioavailability/mobility of heavy metals as well as other contaminants upon chemical reactions with specific reagents.

Chemical extraction uses an extracting fluid, e.g., acids/bases, surfactants, chelating agents, salts or redox agents to wash out metals to the solution. In hydrometallurgy chemical extraction agents-fluids are extensively used for recovery of the metals from ores, concentrates, and recycled or residual materials (Gupta et al., 1990). Solubility improvement can be done by leaching solutions in which metal contaminants are dissolved or by conversion to soluble metal salts by valence change. Typical extracting agents are acids, salts, chloride solutions, chelation agents, surfactants, reducing or oxidizing (redox) agents.

Acids work as dissolution agents to extract metals. High-concentration chloride salt solutions at low pH conditions combine acid leaching action and formation of metallic-chlorine complexes. Chelators are complex forming agents, but surfactants desorb metals from the surface of soil particles. The redox manipulation provides valence change and metals precipitate. Choosing the right reagent depends on the metal type, concentration, fractionation/speciation as well as soil characteristics. Hydrochloric acid as the dissolution agent and EDTA as the complex forming agent are well known as chemical extractors (Dermont et al., 2008).

Technologies for heavy metal remediation are based on precipitation, oxidation-reduction, and organic-metal complex forming reactions that are well known and a widely studied technique in chemistry, for example, chemical technology, environmental, analytical, and radio-analytical chemistry. The use of chemical processes has a drawback related to the possible side effects on the environment that has to be taken into consideration in the choice of chemical reagents in the treatment process (Lombi et al., 1998; Smith et al., 1995). Dissolved heavy metals in groundwater can be precipitated out of the solution in the form of various insoluble compounds. The most common heavy metal precipitates are hydroxides, sulphides, carbonates, phosphates, oxalates, and some others. The solubility product constant (K_{sp}) of the insoluble compound characterizes the precipitation reaction. Using, for example, phosphate containing precipitating substances, U, Pu, and heavy metals (Cu, Cd, Pb, and Zn) are transformed into a low-solubility phosphate mineral phase in which they are not bioavailable. Effectiveness is provided due to the extremely low K_{sp} value, for example, the solubility product constant of U-phosphate (autunite) is $K_{sp}=10^{-49}$, and of Pb-apatite (pyromorphite) – $K_{sp}=10^{-80}$ (Conca et al., 2000). The lower the solubility product constant, the more insoluble the precipitated compound is. Precipitation of an insoluble substance causes two other processes: co-precipitation and sorption that occur simultaneously with the formation of precipitates. Thereby heavy metals that in aqueous media are in minor and micro concentrations are also concentrated in a solid phase. Precipitation, co-precipitation and sorption are spontaneous processes with the tendency of disorder (entropy) decreasing, i.e., contaminants can be found in the solid phase.

Chemical treatment by reductive as well as oxidative mechanisms may be used to detoxify or decrease the mobility of metal contaminants (Evanko and Dzombak, 1997). This method is commonly used for wastewater treatment. Oxidation reactions which detoxify, precipitate or solubilise metals involve the addition of potassium permanganate, hydrogen peroxide and hypochlorite or oxygen, ozone, chlorine. Neutralization reactions are performed to adjust the pH of acidic or basic soils. Reduction reactions are induced through the addition of alkali metals such as sodium, sulphur dioxide, sulphite salts and ferrous sulphate. Sometimes chemical treatment is used to *pre-treat* the soil for solidification or other treatments. For example, chemical reduction of Cr(VI) is performed during solidification/stabilization (S/S). Oxidation is less commonly used with S/S. These reactions are, however, not specific and there is a risk of converting other metals into more toxic or mobile forms. Arsenic is most applicable for chemical oxidation since As(V) is less toxic than As(III). Co-precipitation of high concentrations of As(V) and Fe(III) forms $FeAsO_4$ while low concentrations of As(V) co-precipitate with FeOOH with high concentrations of Fe (III) to form arsenic ferric hydride, a product that is resistant to acid and neutral leaching (Robins, 1992). Mercury, lead, selenium and silver are also applicable for reduction. These chemical treatments can be performed *in-situ* by injection into the groundwater, but have the potential to cause further contamination (Mulligan et al., 2001).

Chemical treatment has several advantages over physical separation techniques, e.g., the sorbed metal forms can be treated, certain metal compounds can be dissolved, fine-grained soils may be treated as well, but extracted metals can be treated or recycled further. Minuses in large-scale applications are encountering the cost of chemical substances, changed soil properties causing impossibility of its further use, the presence of toxic chemicals in the final soil or a great amount of the residual sludge. The wide application of chemical substances in the treatment can impact the environment in a very negative way and cause environmental problems. For instance, the soil treated by EDTA is bad for agriculture as the chelating agent stays in the soil, whereas wastewater treatment may produce large amounts of toxic sludge (Dermont et al., 2008).

Soil flushing is *in-situ* extraction of contaminants from the soil via an appropriate washing solution (Fig. 1.3). Water or an aqueous solution is injected into or sprayed onto the area of contamination, and the contaminated eluate is collected and pumped to the surface for removal, recirculation or on-site treatment and reinjection (Jankaite and Vasarevicius, 2005). Soil flushing is accomplished by passing the extraction fluid through soils via injection or infiltration. Contaminants are moved by solution of the flushing agent and impacted with such mechanisms as solubilisation, emulsification or chemical reaction. The solution with the contaminants should be recovered to prevent uncontrolled transport of pollutants. It is advisable to add nutrients and distribute the flushing solution on the soil to promote pollutant bioremediation.

Nevertheless, the treatment is required to allow the reuse of the fluid for continued flushing or release to wastewater treatment facilities; the recovered solution of the flushing agent must be reused in the flushing process to the maximum extent. The separation of surfactants from the recovered flushing fluids is a large problem factor in the cost of soil flushing. These processes result in high amounts of spent carbon and ion

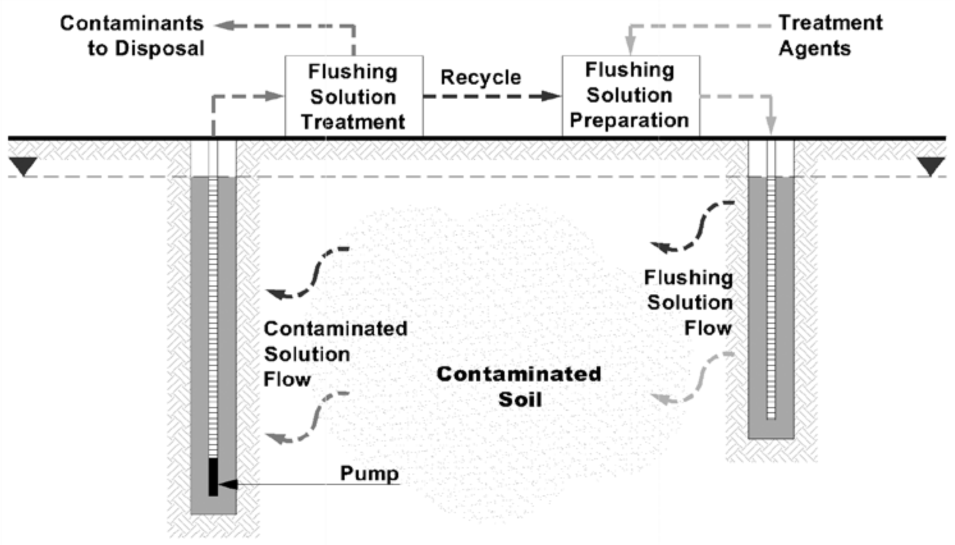

Figure 1.3. Soil flushing technology (author's work out, according to FRTR, 2007)

exchange resin, which must be appropriately treated before disposal. Air emissions of volatile contaminants are to be collected and treated in an appropriate way and should meet applicable regulatory standards. Residual flushing additives in the soil may contain problem substances and should be assessed accurately before industrial use (FRTR, 2007).

Soil flushing is performed by pushing the extraction fluid through soils under the ground using an injection or free infiltration process. The extracted groundwater with the contaminants should be pumped out and recycled. Co-solvents can be introduced in the vadose or saturated zone; fluids degrading the organic contaminants or react with inorganic substances through the involvement of chelating agents. The recovered fluids, solvents and chelators, ion exchange resins and carbon filters should be treated in a correct way before disposal. Air emissions – if such are created – must be also collected in special recuperation systems to meet the applicable regulatory standards. Flushing agents can remain in the soil and groundwater and even react with other substances thus creating even more hazardous substances. The duration of soil flushing is generally short to medium term; the target contaminant groups for soil flushing are VOCs, SVOCs, fuels, pesticides, remains from explosives, heavy metals, and radioactive substances. The price of soil flushing varies and depends mostly on the size and complexity of the site and the depth of contamination, and can vary from 50 to 120 USD per m^3. The addition of various compatible or incompatible surfactants can improve soil properties or impact it negatively. The technology offers good potential for the recovery of metals and can transport organic and inorganic contaminants from coarse-grained soils. The most incompatible factors are low permeability and heterogeneous soils, which makes the process ineffective. Surfactants can clog the systems, reactions can be unpredictable and if groundwater modelling is done incorrectly or inaccurately, the soil flushing solution will be lost and the leachate can create hazards for the environment. Separation and treatment can drive the economics of the process if the recyclables are of high value (FRTR, 2007).

1.3.5. Containment

Physical barriers prevent contamination migration within the groundwater flow. These containment technologies include either surface capping or subsurface barriers (vertical and horizontal) that limit the infiltration of uncontaminated surface water or reduce lateral or vertical migration of contaminated groundwater (Smith et al., 1995). These technologies are used when subsurface contamination precludes excavation and removal of the soil.

Reactive walls offer a passive approach for groundwater remediation. In general, a permeable wall containing an appropriate reactive material is placed across the path of a contaminant plume. As contaminated water passes through the wall, contaminants are either removed or degraded. When designing the wall, not only must an appropriate reactive medium be chosen, but also wall dimensions must be designed to assure the entire contaminant plume to be intercepted and enough residence time applied for remediation to take place. Reactive walls are often economically advantageous because no mechanical equipment is required, eliminating substantial capital, operating, and maintenance costs (Reddy et al., 1999).

Permeable reactive barriers (PRB) containing a reactive substance are being evaluated for reducing the mobilization of metals in the groundwater at contaminated sites (Fig. 1.4).

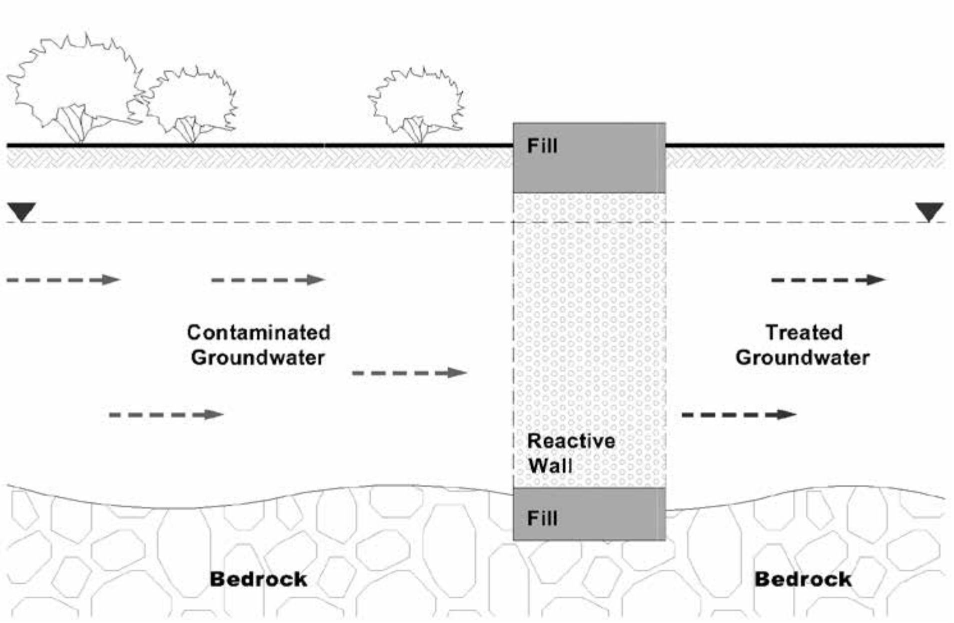

Figure 1.4. Permeable reactive barriers – various materials have been studied and include zeolite, hydroxyapatite, elemental iron, limestone and others, e.g., elemental iron can be used for chromium reduction and limestone for lead precipitation (author's work out, after Evanko, Dzombak, 1997)

Large mining activities worldwide create contamination from the so-called acid mine drainage (AMD) originated from the biochemical oxidation of pyritic minerals in both abandoned and active mines. An exposure to atmospheric oxygen and water leads to acidic heavy metal and sulphate-rich drainage process, and in the event of improper care after the abandonment of the mines landfill leachate and accidental spills can degrade the soils and groundwater. PRB is a growing technology for AMD-contaminated groundwater remediation and it helps mitigate such aspects as acidity, heavy metals and sulphate contamination. Nevertheless, not only success is reported – failures can also happen (e.g., improper hydraulic and/or geological characterization): problems at field scales are reported as a sequence of events from limited capture of the plume, diversion and partial or total by-pass of the groundwater around the PRB and loss of hydraulic control. The significant influence of the climatic conditions and hydrologic conditions of the aquifer, in particular following heavy and sustained rainfalls, create complex problems with the PRB use. Limited sulphate reduction is a second drawback often reported when field remediation is applied. The problem with sulphates is probably due to poor degradability of organic matter and too short contamination residence time at the PRB. Case study in Aznalcóllar, Spain, reported successful neutralization of the pH and removal of heavy metals from the groundwater (Al, Zn and Cu removals >96 %, >95 % and >98 %, respectively), but problems with sulphate reduction and aquifer modelling appeared thereby leading to incomplete remedial action (Gibert et al., 2011). PRBs are mostly used for groundwater treatment, but groundwater and soil contamination is tightly connected and sometimes cannot be taken separately in order to find solutions for environmental problems.

Soil amendments. Contaminated soils can be ameliorated using amendments such as zeolites, lime, phosphate, and organic matter. The addition of lime reduces bioavailability of heavy metals; whereas zeolites can be used as molecular sieves for water treatment. Adsorption is considered as an effective method for heavy metal ion removal from the aqueous solution due to its cost-effectiveness and high efficiency (Lee et al., 2012; Wang et al., 2011). Zeolite (clay) is a class of alkaline porous alumo-silicate, with a negative charge (Mohamed, 2001), neutralized by introducing exchanged cations in the structure sites (Breck, 1974; Mondales et al., 1995). Zeolites are being developed because they diminishing the solubility and thus the biological availability of metals: salts and complexes, also oxides and metal-carbonate precipitates are formed (Chlopecka and Adriano, 1996; Querol et al., 2006). Natural zeolites are not as good as synthetic, but clay minerals can in many cases be used as good sorbents for heavy metal removal; wastewater can be treated much cheaper with a good efficiency (Vengris, 2001). Research nowadays concentrates on zeolites as effective treatment agents because of lower costs; sorbents such as natural and modified clay can be used for groundwater and wastewater treatment from arsenic, tungsten, uranium, selenium, lead and many other elements with toxic properties (Bhattacharrya and Sen Gupta, 2008).

The importance of layer silicate clays in remediation is commonly illustrated by the cation exchange capacity (CEC); permanent negative charged sites in clay minerals keep off the leaching of elements from soils, but still keep them available as nutrients to plants. Smectites are clays which are mostly of small particle size, but vermiculite and zeolite are coarser and have high negative charge (Dixon, 1998). Zeolite particles are strongly charged and the size of tunnels limits and controls the selectivity of different ion passages through them (Ming and Mumpton, 1987). M. F. de Boodt (1991) has examined applications of heat-treated clay use together with $Al(OH)_3$ coatings for removal of both anionic and cationic contaminants from the wastewater. Remediation of Hg contaminated Wabigoon-English-Winnipeg River system by the use of uncontaminated masses of clay and silt was proposed by Parks and Hamilton (1987). Microbial methylating activity can be inhibited; also clay minerals are capable of sorbing and desorbing cations and anions as well as uncharged metal species and participate in exchange reactions. Binding capacities and energies vary greatly depending of the type of clay – the capacity is greatly the function of specific surface area. Anions and cations are loosely held by surface charge, but stronger by binding sites with ligands. Bonds among ions can be ionic to covalent; van der Waals forces and other dipole effects play a significant role in the sorption of uncharged species. Sorption is a relatively rapid process; nevertheless, it takes a while for species to invade inter-lamellar structures (Jackson, 1998).

Stabilization/solidification technology (Fig. 1.5) is based on the treatment of contaminated soils with materials such as cements and siliceous pozzolans. The technology can be employed *in-situ* or to excavated material. As a result, the mobility of the contaminant is reduced by both physical and chemical processes. Typically, the stabilization processes also involve some form of physical solidification (Shi and Fernandez-Jimenez, 2006). Solidification of the polluted substrate with cement restricts its contact with the groundwater and air. Cement and siliceous pozzolans react with metals and cause the formation of hydroxides, carbonates and silicates of very low solubility. This treatment is not efficient for heavy metals that form soluble hydroxides or anionic species. It should be emphasized that the mixing process and the heat generated by cement hydration reaction can increase the vaporization of organic pollutants (Lombi et al., 1998). S/S technologies have been used for decades as the final treatment step prior to the disposal of both radioactive and chemically hazardous wastes. The stabilization refers to an alteration of waste contaminants to a more chemically stable form, thereby resulting in the formation of more environmentally acceptable forms. Successful results of the S/S process could be achieved considering the type of solidified hazardous substances, their properties and the selected inorganic or organic binders. The possible binders used in the S/S technology include fluid fly ash, classic fly ash and cement. Cement, however, is the most common and most often used binder (Kafka and Puncocharova, 2002; Malviya and Chaudhary, 2006; Kafka and Vosicky, 1999).

The environmental impact is assessed by leaching tests that are based on extraction to define the possibility of the solidified mass to release contaminants into the environment (Kosson et al., 2002). The compressive strength characterizes the geotechnical stability of solidified mass and good stability ensures its safe disposal (Gailius et al., 2010). Natural soils are often complex assemblages of soil fractions, components and possibly contaminants, and S/S treatment introduces new components, which react through complex chemical interactions to produce more stable forms with less mobile components. However, the long-term effectiveness and chemical durability of S/S treated materials are still not well known (Bone et al., 2004).

Stabilized material is affected by the interactions and controlling factors (John et al., 2011). Ensuring the best available technologies for stabilization is to use additives for

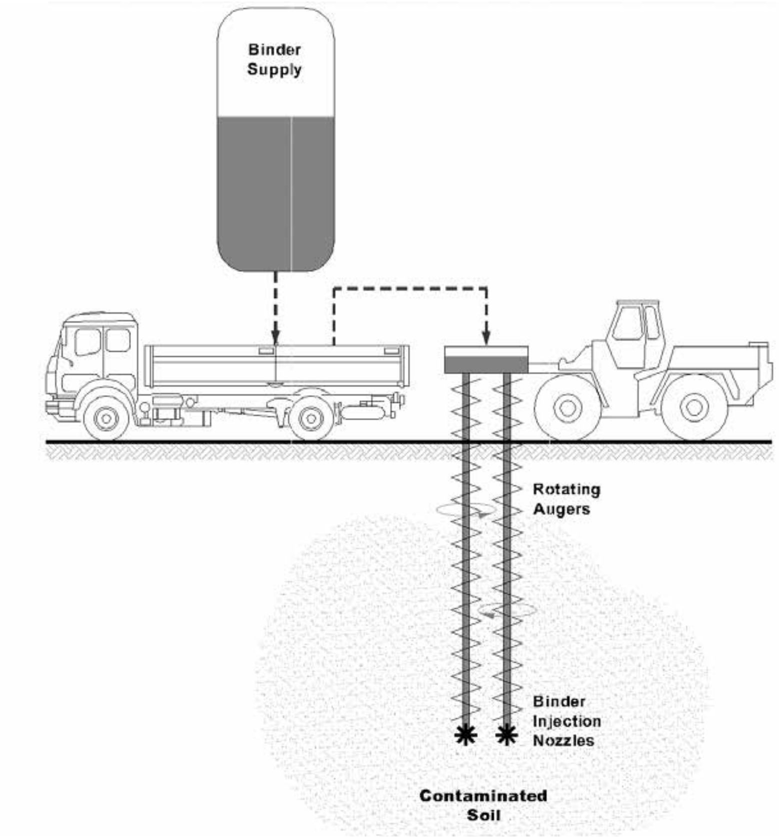

Figure 1.5. Stabilization/solidification technology for remediation using binders, usually Portland cement (author's work out)

increasing mechanical strength of the contaminated stabilized soil. One of the approaches is to use MSWI bottom and fly ash for increasing the geotechnical stability of the soil, thereby extending the lifetime of immobilized solidified soil. Batch tests should be followed by pilot and field scale studies, and environmental risks should be evaluated and monitored during the real-time remediation process.

Municipal solid waste (MSW) management is an increasing problem, and incineration of MSW offers an advantage as the volume reduction of waste can reach up to 90 %, but the incineration also produces by-products (bottom and fly ashes) in the amount of about 33 wt. % of the incinerated waste (Qiao et al., 2008). Ashes must be processed before landfilling or reused to avoid leaching of heavy metal ions and resulting consequent pollution (Reijnders, 2005). Since MSWI ash contains a high amount of various heavy metals and salts, serious environmental problems will occur if the waste is not treated properly before the final disposal. Some approaches for MSWI ash disposal have been proposed, mainly for recycling into construction materials (Mangialardi, 2003). Cement-based treatment is amended with fly ash stabilization, not only due to economic factors but also because it is easy to apply. Fly ash is defined as hazardous waste, and double benefits can be achieved if S/S is used. Alba et al. (2002) evaluated the stability/solidification relationship between fly ash and Portland cement; and the achieved carbonation effect as a way to stabilize the final disposal was good. Some studies (Polettini et al., 2001; Aubert et al., 2006) pinpoint that up to 20 % of fly ash in a mass content of cement is strong enough to maintain necessary thresholds for the S/S technology, although this depends on the nature and the technology involved in fly ash production. The reuse of fly ashes as aggregate for concrete is also feasible. Collivignarelli and Sorlini (2002) described the improvement of concrete with a compressive strength higher than 15 MPa when replacing bottom ash aggregate by fly ash.

The thermal processes include contaminant properties such as volatility, burning, decomposing, destructing and some others using heat. Some classifications add vitrification to a S/S sub-category because of the similar result at the end of the vitrification process. However, the process is different in comparison with the classical S/S technique.

Vitrification involves the insertion of electrodes into the soil which must be able to lead a current, and then to solidify, as it cools. *In-situ* vitrification employs electrical power to heat and melts contaminated soil. Organic contaminants are destroyed through pyrolysis, while volatile metals may evolve in off-gases, necessitating off-gas treatment. Vitrification is applicable for soils contaminated with heavy metals, organic contaminants with high sorption coefficients, and radioactive materials as well. However, effectiveness is reduced in soils with high organic matter, high moisture content or soils containing large metallic objects (e.g., pipes or drums). As an alternative, *in-situ* soil heating decontaminates soils through vaporization, steam distillation and stripping, and may be performed through power line frequency heating or radiofrequency heating (Reddy et al., 1999). During the vitrification process, toxic gases can also be produced. Full-scale application exists for As, Pb and Cr contaminated soils. Mixed wastes can also be treated using vitrification. High clay and moisture contents and debris can affect the efficiency of the process that can be applied in shallow depths for large volumes of soil (Mulligan et al., 2001).

Vitrification is most applicable to sites containing low-volatility metals with high glass solubilities and is appropriate for treatment of soils with contamination of

Table 1.4

Approximate vapour pressure and glass solubility limits for metals

(after (a) CRC, 1991; (b) Smith et al., 1995)

Element	Temperature at which metal vapor pressure is equal to1mm Hg, °C (a)	Maximum allowed oxide content for sample silicate glass, % (b)
As	372	5
Cd	394	1
Cr	1840	2
Cu	1628	5
Hg	126	~0
Pb	973	30
Zn	487	20

lead, chromium, arsenic, zinc, cadmium and copper wastes (Table 1.4). Vitrification characteristics can be adjusted by amending the necessary technological amount of silica in order to improve glass type melting. If the content of volatiles is high, the technology is less appropriate, e.g., mercury's high volatility and low glass solubility makes it unsuitable for vitrification. Remediation by vitrification *ex-situ* is not feasible if the moisture content is higher than 25 % (Evanko and Dzombak, 1997). SITE programme demonstrations have been completed for treatment of cesium-contaminated tank wastes from the Oak Ridge Reservation (PNNL, 1997).

The first full-scale application of *in-situ* vitrification was performed at the Parsons Chemical/ETM Enterprises Superfund site in Grand Ledge, Michigan under the EPA SITE programme. The process was used for the treatment of soils and sediments contaminated with pesticides, metals (As, Cr, Hg, Pb) and dioxins, and required the use of eight cycles of melts over a time frame of 10 to 20 days. An air emission control system was also established to treat volatilized contaminants such as mercury. The soil contaminated with Hg mixed in other metal/organic wastes could also be remediated by vitrification, because the exhaust of gases was organized to avoid toxic mercury air emissions (Contaminants and Remedial Options at Selected Metal-Contaminated Sites, 1995).

1.3.6. Short summary of remediation technologies

Metals have a different speciation forms in soil: remediation activities at contaminated sites with heavy metals are therefore focused on the solid-phase sources or repositories of metals. Excavation and treatment by the chosen *ex-situ* method can be followed by disposal at an appropriate hazardous waste storage site. S/S through addition of chemical reagents is one of the most often used *ex-situ* technologies, e.g., contaminated sediments from 100-year old port aquatic areas can be transported to specially prepared lagoons and stabilized.

In-situ remediation technologies provide significant cost savings over *ex-situ* techniques (excavation, pump-and-treat of groundwater). *In-situ* S/S technologies are effective for shallow (up to 3-4 m below surface) wastes and are rarely implemented at greater depths. Vitrification of waste is not cheap, but it is an effective solution if the concentrations of metals do not exceed glass solubility.

Soil flushing or EK techniques *in-situ* have been proven as successful in limited cases, but phytoremediation technologies are appropriate for remediation in sites with a lower level of contamination. Treatment (permeable) walls are effective, low-cost, passive remediation technologies for the treatment of metals in groundwater; although not directly meant for soil remediation, however, they enable treatment of the groundwater contaminated from contact with metal-bearing solids.

Soil washing and/or flushing techniques are often used in concerted action with soil additives for the improvement of metal extraction. The application of *in-situ* S/S is being aided by the development of wide-diameter auger drilling devices that are equipped with chemical reagent delivery systems and are supported by construction industries in large projects.

Phytoremediation in combination with soil amendment applications, EK and bioremediation are of great interest to scientists – additional research in this direction is therefore highly recommended. Plants from different climatic and biogeographical zones are under research for metal extraction in contaminated sites where soil is improved with soil amendments and bioremediation techniques.

1.4. Decision support tools for remediation planning

Sustainable remediation is a new domain of activities among stakeholders, including site owners, regulatory entities, the public, and industry service providers that are financially and vocationally accountable for the cleanup of contaminated sites. Sustainable remediation is broadly described as a remedy or combination of green technologies whose net benefit on human health and the environment is maximized through the judicious use of limited resources. Resource use should be evaluated and sustainable remediation plans should include a disciplined evaluation of the potential net environmental benefit among various remediation alternatives. Conventionally, the selection of a remediation technology is based on factors such as the effectiveness of the remedy, ability of implementation, cost considerations (capital and operating), and time constraints. Protection of the public via interception of contaminants, reduction of source(s), and mitigation of exposure pathways are prerequisites of remedy selection. Traditional evaluation of critical components for remediation should be done from the environmental, economical and social points of view. The qualitative approach is most often applied during screening of different remedial options. The remaining tools outlined herein are quantitative; some of the metrics are carbon dioxide emissions, energy consumption, and occupational risk. Methodologies of sustainability analysis are described in Ellis et al., 2009, Fiorenza et al., 2009 as well as elsewhere.

Weight indicators (e.g., carbon dioxide emissions, energy consumption, and resource service for land and/or groundwater) and estimates of professional work groups are crucial to consider the sustainability of various remediation technologies.

1.4.1. Life cycle assessment

Life-cycle assessment (LCA) is a standardized method to determine the environmental and human health impacts of products or services (ISO 14040, 2006). LCA analyses the cycle of products and carbon footprint, and calculates sustainability. It helps remediation professionals to recognize how the selection of technology can benefit the economy, the environment, and the society. The environmental footprint of remedial activities should not be larger than the work performed at a site (e.g., materials and energy consumed, emissions). External impacts are not included in decision-making for a site, but the costs of these external impacts ultimately become a burden to the society. Cleanup activities may exert indirect impacts on humans and the environment, which may or may not be directly associated with site activities. LCA can provide the information on specific environmental impacts and burdens that occur due to on-site and off-site activities. For remediation, this relates primarily to consuming resources and energy on site, but also adds any environmental impacts outside of contaminated property. For example, one could consider not only the transportation emission impacts, but also the fuel production impacts and the regional health and global impacts from emissions. In general, LCA can be used within remediation in several ways: (1) to provide benchmarking for existing systems, (2) to identify retrospectively opportunities to decrease impacts in future cleanups, (3) to identify retrospectively where specific improvements would be most advantageous, and (4) to compare different remediation options during the technology selection process. LCA is based on ISO 14044 guidelines: compiling an inventory of energy and material inputs and environmental releases, evaluating the environmental impacts and interpreting the results for better decisions.

1.4.2. Net environmental benefit analysis

Net environmental benefit analysis (NEBA) approach is used to study the impact of remedial actions on resources (Efroymson et al., 2004). It is defined as a risk-benefit analysis applied to environmental management options and it quantifies and compares ecosystem service impacts that occur as a result of an action. The benefits of each alternative are analyzed from the economic perspective (e.g., biodiversity, recreation potential). Habitat analysis is used to quantify ecological services and is reported in Favara et al. (2008).

The aesthetic value and cost of biodiversity can be quantified using contingent valuation, e.g., from recreational (swimming, bird-watching etc.) or commercial (e.g., fishing) aspects. These services are quantified using economic models, such as revealed preference (e.g., travel cost, any random utility) or benefit transfer. NEBA approaches are used by several state environmental regulatory agencies – the Texas Commission on Environmental Quality, the State of Florida Department of Environmental Protection, and regulated also by Washington State Model Toxics Control Act (Efroymson et al., 2004).

1.4.3. Cost-benefit analysis

The Environment Agency of the United Kingdom has developed guidance on how to assess the costs and benefits of soil and groundwater remediation after the threshold criterion of health protection has been achieved. In comparison with the US where numeric goals of treatment are most important, this approach is applied for the analysis of economic gains from remediation. The costs and benefits of sustainability factors (i.e., environmental, economic, and social) are defined as *private* – they impact the site owner and the society. The apportionment of costs and benefits between different stakeholders is also a factor to be considered in the final decision. One of the great advantages of conducting a cost-benefit analysis is to understand the benefits being achieved (e.g., improvement in aquifer quality) and weigh the benefit against the cost (e.g., equipment cost, carbon dioxide emissions) in a common unit of measure (OECD, 2006; Ellis and Hadley, 2009).

1.4.4. Quantitative assessment tools

The remediation community has been developing new tools to assess the impact of applied technologies to the environment, society, and economics. Some of the organizations that have developed these tools are the Air Force Centre for Engineering and the Environment (AFCEE), DuPont, the Dutch Research Programme for *in-situ* Bioremediation, the Danish National Railway Agency, the British Electric National Grid, and the Swedish Riksdag. In the UK, the cost-benefit analysis approach was used to incorporate sustainability principles into the remedial decision-making process at a service station site (Ellis and Hadley, 2009).

Remediation selection and optimization assessments using sustainability metrics have proliferated recently across the US and elsewhere. Assessments are beneficial if threshold criteria are met – human health and the environment are protected. Sustainability is never the sole criteria for remedy selection or optimization (FRTR, 2007).

1.4.5. Multi-criteria decision analysis (MCDA)

Multi-criteria analysis is in literature also called multi-objective decision support system (MODSS), multi-objective decision making and multi-criteria decision aid tool. It is a method that can assist decision-makers in making a choice among alternative policies, strategies and projects in situations where multiple objectives exist. The difference from the methods described above, e.g., cost-benefit and NEBA analysis, is that MCDA incorporates costs and benefits which cannot be valued in financial terms. The CBA described in Chapter 1.4.3. may be considered as a special case of MCDA in which options are evaluated in monetary terms (Asafu-Adjaye, 2007).

The MCDA analyses decision problems and tries to identify the best option from the decision-maker's point of view. For (almost) all MCDA methods the criteria need to be weighed, and the most important need is a decision matrix and criteria weights (for all MCDA methods). This information is fed into an algorithm (sequence of calculations), which provides a result.

Several sub-methods can be applied, such as weight determination via the Analytical Hierarchy Procedure (AHP), which offers an indirect approach where various criteria are compared pairwise and the degree of dominance evaluated one over another.

The option is to use the Multi-Attribute Utility Model (MAUT) in order to transform the raw performance values to a dimensionless scale. The algorithm divides each performance by the sum of all performances with respect to the corresponding criterion and does the normalization. Several approaches can be performed, where the main idea is to define criteria with outranking properties, e.g., if A is at least as good as B, then A outranks the B etc. (Triantaphyllou, 2000; Geldermann and Rentz, 2007).

Concordance methods such as ELECTRE (ELimination and Choice Expressing REality) (Roy, 1990) use the pairwise comparison where concordance and disconcordance indices are summed up. The concordance index is composed of weighted sum of criteria based on the best alternatives from the first choice over the second. The discordance index, on the contrary, is given by the largest score differences among the criteria where the first alternative's choice is lower than that of the second one (Asafu-Adjaye, 2007).

Scoring the alternatives by different models, the acceptance of criteria and weights of indicators are identified through workshops held for stakeholders. The information gathered from the target groups through surveys is used as it is not expected that individual experts and stakeholders have sufficient knowledge to enable scoring and ranging of preferences. The expert group is combined of specialists from the social, economic and scientific fields, the alternatives scored in a variety of measures using, e.g., money units, tons per ha, aesthetic value preservation and many more (quantitative and qualitative parameters in nominal, ordinal, interval, ration and even linguistic terms can be defined). Ranking should be done equally to avoid individual judgment preference, so the effectiveness of the MCDA brings together various points of view for solving common questions. In spite of many advantages of the MCDA, there are also negative aspects. One is that there exists a wide range of evaluation methods and not so much guidance has been defined as to which of them is better. The second aspect is that a subjective approach in judgments cannot be avoided, what can lead to poor reflection of various preferences in a good balance among societal, environmental and economic problems (Asafu-Adjaye, 2007).

2. MATERIALS AND METHODS

2.1. Field works

2.1.1. Selection of research sites

Sites contaminated with heavy metals, oil products and other possibly toxic substances and hazardous materials can be found in current as well as abandoned industrial territories, illegal dump sites, harbours, agricultural and residential areas with historical contamination, road sides and elsewhere. In Latvia, the assessment and evaluation of contaminated and potentially contaminated sites began in the 1990s. The National Register of Contaminated Territories (NRCT) covers the territories that are contaminated with various materials, inorganic and organic hazardous and non-hazardous substances. In the NRCT the sites are divided into three groups: the first includes 244 contaminated sites (contamination exceeds the acceptable legislative norms 10 times or more); the second – 2,642 sites (potentially contaminated according to unproven data), and the third – 684 areas (NRCT, 2014). The latter comprises the territories excluded from the lists of the first and second categories after the risk assessment and/or remediation activities. Contamination with heavy metals and oil products predominates. Ten sites selected for case study analysis in the thesis are shown in Fig. 2.1.

Figure 2.1. Schematic map of case study sites in Latvia and Estonia: 1) BLB Baltijas Termināls; 2) Vega Stividors; 3) Former agricultural machinery factory “Selmash”; 4) Former wooden industry brownfield at Katlakalna Street; 5) Former military warehouse area “Jaunais Mežaparks”; 6) Former military area “Freja” in Daugavgrīva; 7) Deglava dump site; 8) Kleisti dump site; 9) Liquid toxic waste dump site near Jelgava; 10) Kudjape landfill (Saaremaa, Estonia)

The selection of the research areas was mainly determined by the necessity to include typical areas of environmental concern – point contaminated sites with heavy metals of historical origin. Results from field research as well as experimental studies were used in order to prepare an indicative model as the decision support tool for choosing the applicable technologies for remediation.

2.1.2. Drilling and soil sampling

Field studies are crucial to investigate the environmental quality and level of pollution at contaminated sites to obtain information about the *status quo* of the situation, make decisions about feasibility and risks of different scenarios and plan steps for further actions of site clean-up. Soil as well as groundwater sampling should be done after a careful analysis of historical documentation from the previous environmental quality research or assessments. Preliminary studies are vital in order to describe the situation in general and plan effective and progressive remedial actions if such are necessary, including the historical data and pollution distribution analysis. Afterwards detailed sampling and testing should be organized for the soil and groundwater, and an analysis of the potential pollution transfer to potential receptors should be carried out. Drilling sites are chosen and sampling works were carried out by manual and/or motorized drilling methods. Technological capabilities are of great importance for planning research and the ensuing remedial works (Standard guide for soil testing…, 2006; Theocharopoulos et al., 2001).

The author has chosen the auger drilling method for sampling in different depths and installation of groundwater wells. Sampling was carried out from layers of various depths to obtain information on soil composition. The upper layers of the sampled soil was mainly 0.0-2 m in depth (for the estimation of soil composition at the upper layer), other intervals were chosen to have information about soil environmental quality in deeper layers. Study sub- areas have been chosen based on the geological and geochemical mapping principles, taking into account historical information about events in each separate object. The ensuing detailed soil sampling gave a full-scale description of the environmental situation at sites and supported laboratory analysis with representative samples (Carter and Gregorich, 2006; Standard guide for soil testing…, 2006; Theocharopoulos et al., 2001).

Groundwater sampling is an essential part of environmental research as contaminants leach from the soil further to the groundwater and pose threats to the environment and public health. Groundwater pollution mostly correlates with soil pollution and the analysis must be done simultaneously. Research methods of groundwater composition help to determine the distribution and spatial spread of contamination in order to apply the best remediation and risk prevention strategies (On pollution, 2001).

In order to show the overall methodology of the field work procedures, several case studies are given further. Every case is slightly different; however, the idea of representative sampling from the field remains the same throughout the study. Sampling and the ensuing analysis with the interpretation of results has been used as tools to predict the behaviour of contamination movement in space and time if the groundwater flow rate and other geological and hydrogeological factors were known. Standard operations ISO 10381 as well as sampling procedures described in Carter and Gregorich, 2006, Weber-Shirk et al., 2006 were used for sampling, preservation, transport, storage and pre-treatment of soil samples in all cases mentioned further.

Description of case study sites (shown on Fig. 2.1)

1) *BLB Baltijas Termināls (NRCT N°01964/611)* and 2) *Vega Stividors (NRCT N°01964/629)* – research on the potential remediation technology choice decision support was carried out in two main stages using the pre-study data (Burlakovs and Klavins, 2012). The first stage included the analysis of former research data and preliminary sampling with analysis. The second was a more detailed stage carried out after gaining results from the first stage and included sampling and testing for laboratory analysis for perspective S/S technology use. Area was divided in three sub-areas, field works included drilling works with a *Fraste Terra-in* drilling machine using the auger drilling method: 7 boreholes up to 5 m of depth were drilled. The sampling of soil was done from the upper part that covers an interval of 0.3-1.0 m in depth (for the estimation of soil composition at the upper layer), second interval in the depth of 1.0-2.5 m, third interval 2.5-5.00 m. Intervals and areas for sampling here and further were chosen by slightly modified method described in (Carter and Gregorich, 2006; Standard guide for soil testing…, 2006) as Theocharopoulos et al. (2001) argued that it is impossible to apply identical methods in each distinct case due to specific circumstances in field objects. Legislation of Latvia prescribes the use of standard methods for analysis and defines target concentrations under the Regulation No 804 (25.10.2005) issued by the Cabinet of Ministers of Latvia. Pre-treatment of samples as mentioned in these standards should be done by *aqua regis*, complete sample mineralization is described in detail in (FAO, 2006; Gilucis, 2007; Pansu and Gautheyrou, 2006). In some cases total content was determined by the use of concentrated nitric acid as described in the study done by V. Rudovica (2012), where author affirms that both methodologies can be comparable.

The pilot study area was chosen based on the research results of the first stage. More detailed soil sampling from the upper part during the pilot study covered 1.82 ha (Fig. 3.3). Samples for the leaching and compression testing were chosen in order to validate possible application of the S/S remedial method in the laboratory studies.

3) *Former agricultural machinery factory "Selmash" (NRCT N°01924/4125, 3rd category)* (Fig. 2.2). Research was performed while the site was in the first category of NRCT list, the sampling of soil was done for two layers of technogenic topsoil up to the depth of 0.5 m and 1.0-2.5 m for 3 sectors (mixed in 2 joint samples). Soil samples from 10 drilling sites from four intervals up to 5.0 m were taken (Table 3.1.) and 16 groundwater monitoring wells were installed. All soil samples were analyzed for heavy metals regarding Regulation N° 804 (25.10.2005) of the Cabinet of Ministers of Latvia "Requirements for Quality Normative of Top and Bottom Soils". Soil samples for S/S technology testing were taken similarly as in case studies N° 1 and N° 2.

Two cycles of the research were carried out there in 2001 and 2008-2009, respectively. A subsequent remediation of solvent (not described in frame of this thesis) and heavy metal contamination in two periods – 2002-2004 and 2009 was performed. Careful quantitative and qualitative comparison of soil and groundwater data before and after the remediation cycles was performed by the author.

4) *Former wooden industry brownfield at 22 Katlakalna Str. (not listed in NRCT).* Similar to previously described studies, the sampling of soil was done from the upper

Figure 2.2. Former agricultural machinery factory "Selmash": areas contaminated with heavy metals and solvents (two cycles of remediation were carried out in 2002-2004 and 2009); arrows indicate groundwater flow direction (as the base maps – Latvia Geospatial Information Agency ortophoto maps)

part of the soil cover to estimate the soil composition at the study site. In total 50 soil samples were taken, mixed and combined in joint soil sample thus representing the soil composition in the study area upper soil cover. 13 samples were taken from the depth of 3-6 m, and all were analyzed to determine the concentration of heavy metals and arsenic (Cu, Ni, Pb, Zn, Cd, Cr, Hg and As). Soil samples for S/S testing were taken as well.

5) *Former military warehouse area "Jaunais Mežaparks" (not listed in NRCT).* To estimate the soil quality in the research area, samples of soil were taken from the upper part of the soil up to the depth of 0.40 m. A hand probe was used for this purpose. The sampling territory of 30 ha was split into 7 sub-areas 4-5 ha each. One joint sample was taken from 0.4-1.0 m depth: 7 drilling points in 7 sub-areas were selected, and 7 samples

were mixed in this joint sample in order to have the data about the average heavy metal content in the deeper interval just under the organic soil for the whole area. 175 shallower and 7 deeper samples were taken from each of these sub-areas and mixed accordingly in 7 and 1 joint samples for heavy metal laboratory analysis (Burlakovs and Gorbunovs, 2012). The areal research using the joint samples was chosen as the former military warehouse area was demolished, dismantled and potentially contaminated soil settled and smoothed by tractors.

6) *Former military area "Freja" in Daugavgrīva (NRCT N°01924/665).* Today there is a wood logistics facility where raw timber cargos are reloaded. Sampling was done from several drilling sites as well as the average value was calculated from the upper part of the soil where asphalt layer is absent. The sampling for groundwater quality evaluation in "Freja" is carried out for monitoring purposes every year in the framework of the Rīga Freeport monitoring program. Additional research by the author on heavy metal content in soil and groundwater was carried out in this area, soil samples were tested for S/S testing.

7) *Liquid toxic waste dump site near Jelgava (NRCT N°09004/2259).* Field works were carried out similarly to the former agricultural machinery factory "Selmash", albeit on a larger scale, as this object is included in the national priority program for historical contaminated site remediation (National Programme on Historical Contamination, 2008).

8) *Deglava dump site (NRCT N°01944/675).* The research approach including geophysical methods, field sampling of soil, waste and groundwater, gas emission calculations and parameters for testing was chosen similar to the research on Kleisti dump site described below.

9) *Kleisti dump site (NRCT N°01924/673)* study included geological, environmental and geophysical research packages, which made information about the spatial location of contaminated groundwater and soil available (Fig. 2.3).

The very low frequency (5 and 30 kHz) electromagnetic (VLF-EM) method for geophysical research was performed as it is considered as one of the best methods used in research on contamination spatial distribution. The data was collected and interpreted in order to plan drilling and sampling sites for the evaluation of contamination in soil and groundwater (Burlakovs et al., 2013e). The drilling work was carried out with "Fraste Terrain" and "Iveco" drilling machines. The sites were chosen taking into account groundwater and leachate provisional flow in the dump site, as well as to reach representative samples of the soil under and around the waste body. The auger drilling method has been chosen, and 6 boreholes 1-12 m of depth were drilled, including three boreholes done through the waste. Temporary monitoring wells were installed in sites around and on the dump hill sites for groundwater sampling. Surface waters, sediments from ditches were sampled in closest area around the dump site to determine indicative parameters.

10) *Kudjape landfill.* Landfill mining was carried out in Kudjape municipality, where 'former' dump site was situated on Saaremaa Island in Estonia (N 58:16, E 22:32), 2 km south-east from Kuressaare town. Scientific research of waste and fine fraction of it was performed as the dump site was covered with shredded and sorted fine material from the site itself.

The total area of the landfill was 5.6 ha, and the main excavation area covered 4.2 ha (Fig. 2.4). Mainly municipal waste had been intensively dumped there from the early

Figure 2.3. Kleisti dump site: location of drilling points; arrows indicate leachate and groundwater flow direction (as the base maps – Latvia Geospatial Information Agency ortophoto maps)

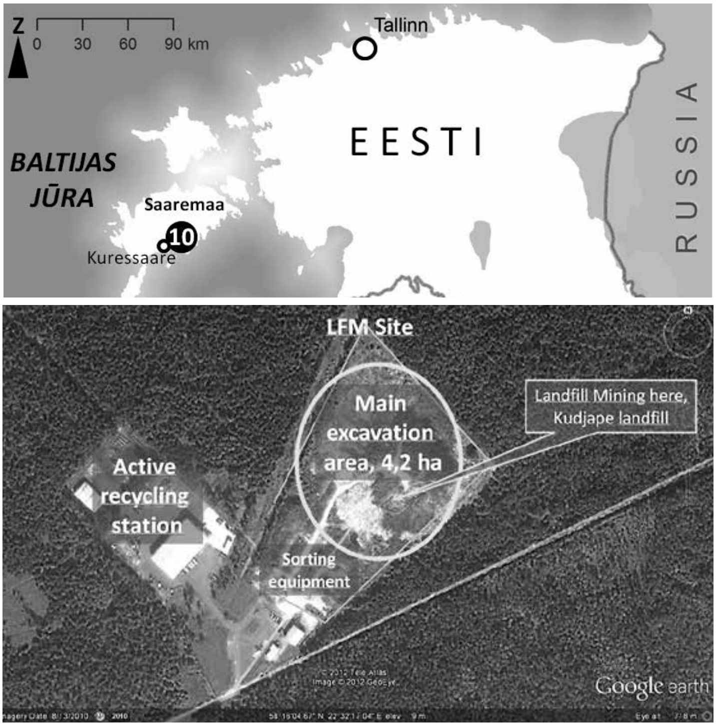

Figure 2.4. Kudjape landfill and waste recycling station (base map Google Earth)

1970s up to 2009 when it was closed. The waste was dumped on a flat area, 4 m above the sea level, and the landfill reached a height of up to 12 m. The waste was compacted by a compactor during the last years of operation. Detailed description about waste sampling is available in Chapter 2.1.4.

The key information gained from the research of contaminated sites allows evaluating the potential hazards of pollution transfer with the groundwater to the recipients. The importance of this information is crucial from the environmental point of view for the preparation of decisions for site clean-up. The next sub-chapter provides an overview of how the main route of potential pollutant transfer can be predicted by the use of a simple groundwater flow direction determination method.

2.1.3. Groundwater flow direction determination

Groundwater flow determination is important to predict the flow of potential contaminants in space and time. Therefore it is important to consider geology, hydrogeology and geomorphology of the analyzed site. Regional hydrogeological models can rarely be used, as the geological structure of Quaternary layers and anthropogenic (technogenic) sediments have a complex unpredictable structure and texture properties.

The direction of the groundwater flow is determined by the surface hydraulic gradient of the groundwater flow. Measuring the surface of unconfined aquifer on the site and permeability data can tell us the properties of groundwater flow such as direction and rate (Thangarajan, 2007; Cardona et al., 2008).

The groundwater surface was determined by levelling the water well heads, whereas groundwater depth measurements were done – using a "Solinst" level meter instrument. All the measurements were done in as short a time as possible to avoid groundwater surface fluctuations dictated by river and lake level change in time. The measured surfaces were calculated in the absolute or relative height system and using the mathematical kriging method for drawing groundwater izolines in "Surfer 12". The levelling and groundwater level measurement data was put into the "Surfer 12" program and kriging performance was used as the basic tool. Base maps are in the GIS "ArcView" environment, but "Surfer 12" based interpolator tools such as inverse distance weighting (IDW), natural neighbour, spline or kriging can be used for surface trends interpolation (Fig. 2.5) (Berkowitz, 2005).

Kriging minimizes error and gives the best linear unbiased prediction of the intermediate value (Dagdelen and Turner, 1996). Surface static modelling with known data about groundwater levels in wells at the given date is possible by using "Surfer 12" software as it is shown in Fig. 2.5. The kriging technique and "Surfer 12" modelling was used for case studies N°1-9.

2.1.4. Sampling of waste

The excavation process in the Kudjape landfill. Four test-holes in the field were excavated, but waste was extracted from a vertical waste wall. A layer of weathered waste was removed to create a so-called *fresh cut*. The topsoil of 0.3 to 0.5 m was removed and the wall was divided into four equally large sections, removing each section as an

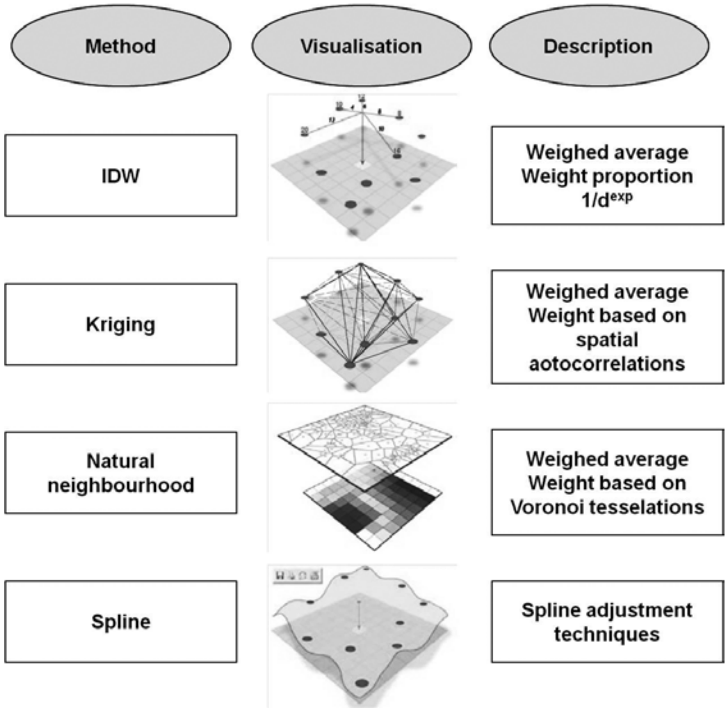

Figure 2.5. Interpolation methods for groundwater surface hydraulic gradient determination (author's work out, after Berkowitz, 2005)

individual bucket, and the depth of 4.5-4.9 m was achieved by the excavator, which allows for approximately one meter as the depth of each individual bucket (Fig. 2.6).

The bucket of waste was emptied into the trommel sieve with a 40 mm mesh; undersize and oversize fractions were collected separately. The material was piled on the ground and marked; specific large items, tyres and fishing nets were excluded as they might damage the equipment. Four sampling holes (H1 to H4) were excavated, and waste was obtained from four layers (B1 to B4), with 16 samples in total.

Sorting of the waste from the excavated field samples was carried out at a recycling station with a 40 mm rotary screen (180 mm diameter, 3600 mm length), conveyor belts, and 15 m long double-sided sorting belt. The sorted material was scaled and mass balances calculated.

Separation of fractions. First, manual sorting of large items was carried out on the belt in the recycling centre; the coarse fraction was separated proportionally from the fine fraction by sieving, and the fine fraction was homogenized from each individual hole and bucket thus creating 16 samples that were prepared for an analysis of trace elements, leaching and metal speciation studies (Fig. 2.7). The fine fraction in the landfill was planned for further used as the covering material of the mined landfill (Fig. 1.2).

Field testing vs. laboratory testing. Elements can be determined by several conventional analytical techniques including spectroscopic techniques – atomic absorption spectroscopy

Figure 2.6. Sampling site H1 at Kudjape landfill with layers B1 to B4 as indicated

Figure 2.7. Hand-picked fine fraction was stored separately in plastic bags

(AAS) and inductively coupled plasma – mass-spectroscopy (ICP-MS), which were also used in the laboratory part of this study. Among different techniques, field portable X-ray fluorescence analyzers (FPXRF) are considered effective tools in many environmental, geochemical and material study cases (Carr and Zhang, 2008; Markey et al., 2008, West et al., 2011). An Olympus DELTA DS-2000 Handheld XRF Analyzer with a 4W X-ray tube and optimized beam settings for environmental purposes was used for elemental express analysis in the fine fraction during field investigations directly after the excavation and separation of the fine fraction. The analyzer was calibrated before field work sessions and measurements were done in triplicates for homogenized samples. A CalCheck Standardization test cup 316 of stainless steel was used. ICP-MS and AAS was done to verify the results of analytical testing after the preparation of samples for analysis by wet digestion (Mäkinen et al., 2005). Leaching tests and speciation tests were applied in order to evaluate the environmental quality of the fine fraction as the dump site covering material and possible material for the recycling of rare metals.

2.2. Stabilization/solidification techniques

2.2.1. Application of Portland cement and municipal solid waste incineration bottom ash

Stabilization/solidification with Portland cement (PC). PC clinker is manufactured by burning at high temperature a raw meal consisting mainly of limestone and clay (Gineys, 2010). When cement is mixed with the water a paste is produced that surrounds all the individual pieces of aggregate to make a plastic mixture. A chemical reaction called hydration takes place between water and cement and then concrete normally changes from the plastic to the solid state in about 2 hours and thereafter concrete continues to gain strength as it cures.

Contaminated site N° 01964/611 has a total area of 20 ha, of which 1.82 ha was chosen as the source area for pilot scale sampling for stabilization/solidification technology efficiency testing. For comparison several samples from "Selmash", "Jaunais Mežaparks, "Freja" and 22 Katlakalna Street (*n*=5 for each site) were taken and tested similarly as for pilot testing area in BLB Baltijas Termināls / Vega Stividors areas.

The content of various heavy metals is high and representative for the whole site, therefore a sample of 20 kg was taken in each site, sieved and homogenized. Five times 100 g of the soil sample was taken; mixed with a suspension of 5 wt % Portland cement, 10 wt %, 13 wt % and 20 wt %, whereas the last sample was left as the control one without cement. After the hardening of samples (~24 h), the cemented material was prepared for leaching and stability testing. The leaching test (Standard: BS EN 12457-2:2002) was used in order to study the leaching behaviour of the solidified mass in the environment (see results in Chapter 3.1.1). Later geotechnical testing for compressive strength parameters was carried out (Chapter 2.2.2).

After a careful analysis of the pilot study results, additional research was performed for the whole industrial area combined from sites N° 01964/611 and N° 01964/629

(Annex I). The Portland cement grade PC500-D20 (CEM II/A-S 42.5N) was taken for the formation of the concrete-mixed contaminated (stabilized) soil. Portland cement clinker is manufactured by burning at high temperatures of a raw material consisting mainly of limestone and clay (Gineys et al., 2010). Soil samples without a binder were used for batch testing as *zero samples*, whereas cemented samples were made as small cubes with the size of 1 cm of the edge length. The setting time of a cementitious mixture is referred to as the period when water is introduced into the mixture system at the onset of hardening. The final setting time is defined as that at which the 5 mm cap ring left no noticeable mark when placed on the surface of the mortar mixture (Yin et al., 2006). Leaching tests were performed for heavy metal contaminated samples with and without Portland cement binder additive (see results in Chapter 3.1.1).

Municipal solid waste incineration (MSWI) bottom ash and Portland cement experiment. MSWI bottom ash with known elemental content was used, and samples of soil with known properties were spiked with copper (II) sulphate (ReagentPlus, >98 %) solution of known concentration 300 mg kg^{-1}. Then the spiked soil was homogenized and mixed with MSWI bottom ash bound with ordinary Portland cement (PC) (class 500) with the mixing ratio 50:35:15 (50 % of spiked soil with copper sulphate, 35 % of MSWI bottom ash, ordinary PC 15 %). Additional samples were used without the MSWI as control. The municipal solid waste (MSW) samples were taken from mechanical waste pre-treatment centres in Latvia after mechanical shredding, screening and separation of metal (Arina and Orupe, 2012). The ash content was determined according to the standard LVS EN 15403:2011 (Solid recovered fuels – Determination of ash content, 2011) (equipment – furnace “СНОЛ”). The ‘CLR-7K’ XRF fluorescence spectrometer was used for analysing the different elements in the ash. The content of elements in the ash was determined according to the LVS EN 15411:2012 (Solid recovered fuels – Methods, 2012) for the determination of the content of trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Tl, V and Zn). Leaching experiments were performed with 24 h of agitation as described in one of studies in (Burlakovs et al., 2013b).

Soils with different texture experiment. Samples from different soil profiles of different textures (Burlakovs et al., 2012a) were spiked with a known amount of copper sulphate, whereas others of the same original texture were not. All samples were bound with Portland cement and left for 10 days of stabilization and solidification procedure in special moulds having normal pressure and temperature +20°C. After 10 days of solidification, the samples were taken out of the moulds, crushed and sieved through a 2 mm sieve and carefully mixed for a homogenous spread of contamination in each sample. The procedures were followed by leaching tests with various time periods of 1, 4 and 24 h as described in the next sub-chapter.

2.2.2. Compression and leaching tests

Stabilized/solidified waste can be assessed under the BS EN 12457-2 standard for the effectiveness of the treatment. This criterion is chosen because the S/S technology is widely used for treatment, and the two main parameters are measured for determination of the effectiveness of remediation – UCS and leachability limits. The regulatory limit for copper leaching at a disposal site in the United Kingdom (Sollars and Perry, 1989) is given for comparison (see results in Chapters 3.1.2 and 3.1.3).

Experiments for the testing of geotechnical parameters were carried out, with three different cubes (10×10×10 cm) and cylinders (diameter 10 cm, height 5 cm) (Fig. 2.8) and geotechnical tests performed.

Figure 2.8. Solidified soil samples used for compressive strength and freeze thaw resistance studies

When Portland cement is mixed in the water, a chemical reaction called hydration takes place and concrete normally changes from a plastic to a solid state in about 2 h. Thereafter the concrete continues to gain strength as it cures. The industry has adopted the 28-day strength as a reference point, and specifications often refer to compression tests of cylinders of concrete which are crushed 28 days after they are made (Properties of concrete, 2013), the same principle was also used during the present research. Samples were bound with Portland cement (PC500-D20) with the mixing ratio 20:1 (5 %), 10:1 (10 %) and 5:1 (20 %) (Fig. 2.12) and geotechnical tests were performed. Compressive strength and freeze thaw resistance parameters were tested using PSY-125 compression testing equipment and a CT-700 freezing camera. 40 cycles of freezing and thawing were completed and after the compression a test was performed to these cubes until the samples were crashed.

Solidified material testing. The leaching test BS EN 12457-2 was used in order to study the behaviour of the solidified mass in the environment. During the batch leaching test vessels were filled with distilled water until a liquid-to-solid-ratio 10:1 (referred to the dry cube mass or not stabilized soil sample). Under continuous agitation at a rate of 100 RPM, the batch leaching test was done for samples with an agitation time period of 1, 4 and 24 h. The pH_{H2O} level was measured for all samples before and after the period. After this time the liquid was let to settle down for about 10 minutes. For the determination of inorganic compounds, the liquid was filtered through a 0.45 µm filter. Afterwards the content of leached metals was determined using atom absorption spectrometry with *Perkin Elmer GBC 932 Plus* (AAS).

2.3. Soil amendment experiments

2.3.1. Modification of clay

Modification of clay with iron oxyhydroxides. For $Fe(OH)_3$ preparation, 250 mL of 0.25 M and 0.5 M $FeCl_3 \cdot 6H_2O$ were mixed with 250 mL of 3 M NaOH for three hours. Washing and decanting were repeated three times and 100 g of Devonian clay was mixed in $Fe(OH)_3$ dispersion. Mixing, filtration and washing with deionized water (DI) was repeated, the drying for 12 h was done at room temperature, and in the end, the drying was done in a Gallenkamp Plus II oven for 4 h at a temperature of 60°C. Further on, the modified clays were used as soil amendment for spiked soils contaminated with lead, and leaching tests were applied in a slightly modified way as recommended in a number of studies (e.g., Lee and Tiwari, 2012).

Modification of clay with Ca and Na salts was carried out in two ways: 1) 5 g of clay was added in 500 mL of 0.5 M $CaCl_{2;}$ 2) 5 g of sorbent was added in 500 mL of 0.5 M NaCl and stirred for 24 h, then decanted 3 times and washed with DI water. Modified clays were dried in Gallenkamp Plus II at a temperature of 45°C for 8 h. Further on, modified clays were added to a solution spiked with lead, and kinetic sorption experimental series were applied (see sub-chapter 2.4.3 on kinetic experiments).

Modification of clay with protonation. 5 g of sorbent was added in 500 mL of 0.5 M HNO_3 and stirred for 24 h, then decanted 3 times and washed with DI water.

Modification of clay with hydroxyapatite. 8 g of clay was mixed with 30 ml of distilled water and 10 ml of 0.5 M $CaCl_2$, and was then let swelling for 12 h. Four different concentrations were calculated in order to get accurate equimolar proportions of Ca/P when KH_2PO_4 is added to get 1.6, 1.3, 1.0 and 0.5 proportions. The proportion of 1.6 corresponds more to hydroxyapatite, 0.5 to monetite. The pH for reactions was determined in all cases at 9.0 with the use of NH_4OH, after 12 h decanting and washing with D/I water was done until neutral conditions were achieved. Ethanol for the final removal of unnecessary salts was used and substance was dried in Gallenkamp Plus II oven at a temperature of 105 °C. Further on, modified clays were used as amendment to soils spiked with lead and leaching experiments were applied.

Soil amendment addition to spiked soil. Sets of amendment testing for each of three soil samples were done by adding 10 % of different amendments: unmodified – 1) Quaternary Satini quarry clay, 2) Zeiļu Lake clay, 3) Borovichi varved clay; modified – 4-7) Quaternary Lielauce clay modified in 4 different Ca/P equimolar proportions, 8;9) modified with 5 % FeOOH and 10 % FeOOH respectively, 10;11) unmodified Devonian red and grey-blue clay, 12;13) Devonian modified with Ca and Na salts respectively. 14) One test for spiked soil with no amendment was performed for control (more detailed in Chapters 3.2.1 and 3.2.2) (Burlakovs et al., 2013d).

Amendments were tested for soils spiked with lead and leaching tests applied. Soil samples were amended with amendments described in Chapter 2.3.1. Samples were spiked with lead nitrate or copper pentahydrate in order to apply known contamination.

2.3.2. Leaching tests for multi-contaminant system

During the batch leaching test, vessels were filled with distilled water until a liquid-to-solid-ratio 10:1 (refers to the dry sample). Leaching test preparation procedures are the same as described in Chapter 2.2.2.

The testing of efficiency for multi-contaminant immobilization in sandy soil (sand content 89 %) was performed by spiking of soil samples with mix of selected metals (Cu, Pb, Cd and Cr). The spiking was done with the following concentration of metals: 150 mg kg^{-1} of Pb, 150 mg kg^{-1} of Cu, 50 mg kg^{-1} of Cr and 50 mg kg^{-1} of Cd. Various clay additives were used as soil amendments adding them at a rate of 10% of dry weight. Leaching tests were performed by stirring the samples for 24 h, but measurements of element concentration were done by AAS with Perkin Elmer GBC 932 Plus.

2.3.3. Speciation of metals and sequential extraction

Sequential extraction means the isolation of different chemical species for analysis. Tessier et al. (1979) has developed the approach for speciation of trace elements and heavy metals in sediments and soils and distinguished the following groups: exchangeable, acid soluble (bound to carbonates), reducible (bound to Fe-Mn oxides), oxidising (bound to organic matter or sulphides), and residual. Mostly, the emphasis is placed on the choice of extraction chemicals and their selectivity in each solution. For example, ammonium acetate is usually used to liberate exchangeable metals, but sodium acetate or acetic acid is good at acidic pH values for the selective dissolution for carbonates (Reeder et al., 2006). Table 2.1. shows extractants that were used during the full speciation analysis.

Table 2.1

Determination of metal speciation (Tessier et al., 1979)

Metal speciation	Extraction procedure
Free exchange forms	1 M $MgCl_2$ (pH 7, 2 h, 25°C)
Bound with carbonates forms	1 M CH_3COONa (pH 5, 12 h, 25°C)
Bound with Fe/Mn oxides forms	0.1 M NH_2OH+0.01 M HNO_3 (pH 2, 12 h, 25°C)
Bound with organics and sulphides forms	30 % H_2O_2+0.01 M HNO_3 (pH 2, 3 h, 80°C)
Residual forms	HNO_3 (2 h, 100°C)

Soil samples were prepared, dried and extractants added for the isolation of different fractions. Table 2.2 describes the pH values and chemicals that were added as the solution in order to extract metals of different speciation to be later analyzed by AAS using Perkin Elmer GBC 932 Plus.

2.3.4. Sorption kinetics and calculations

Kinetic experiments for sorption ability testing of soil amendments were performed with 50, 100 and 300 mg L^{-1} lead solution with the pH adjusted at 5-5.1. Modified clays as sorbents to add were dried in Gallenkamp Plus II at a temperature of 45°C for 8 h (Fig. 2.9).

Figure 2.9. Modification of Devonian clay; modification with Na and Ca salts for sorption kinetics tests

Operating in batch mode at a room temperature, 0.025 g of every type of modified clay sorbent was added to each flask for kinetic experiments. The solution pH was maintained at 5.0 throughout these experiments. The experiments were carried out in 50 mL capped Erlenmeyer flasks containing 50 mL Pb (II) solution and 0.025 g raw and modified clays by shaking (130 rpm) (Grant OLS200) at 22°C for various time periods of 5, 10, 15, 30, 60, 120, 180, 240, 300, 360, 480 and 1440 minutes. After adjusting the pH, no further adjustment was performed and the final pH was documented after the experiments. After achieving equilibrium, solutions were separated by filtration through cellulose acetate membrane and analyzed for residual lead content by AAS with Perkin Elmer GBC 932 Plus **(**Gupta et al., 2010; Bhatnagar et al., 2012**).**

The concentration of contaminants, pH, temperature and time regimes were varied in sets of kinetic experiments, multi-contaminant solutions (e.g., Pb 270 mg L^{-1}, Zn 350 mg L^{-1}, Ni 100 mg L^{-1} and Cu 150 mg L^{-1}). Adjusted pH of 1.5, 2.0, 2.5, 3.0, 4.0, 4.5, 5.0, 5.5 and 6.0 as well as temperatures of 10°C and 40°C were applied to build sorption curves and construct isotherms (Burlakovs et al., 2013c, d).

2.4. Analytical techniques

2.4.1. Preparation of soil samples for analytical procedures

After soil sampling in the field, the samples were marked with careful identification notes and carried to the laboratory. In general, it is desirable to get most of the sample to less than 2 mm in diameter with the least amount of grinding, therefore air-dried soil samples were sieved through a 2 mm sieve and fractions finer than 0.05 mm were determined by pipette analysis (Van Reeuwijk, 1995). All contact with metal surfaces was avoided during the crushing and sieving procedures unless it had been clearly demonstrated that the metal was not a source of contamination. Cross-contamination between samples was avoided, as it is crucial for trace element analysis. The bulk soil sample was thoroughly homogenized by quadrupling, mixing with a stirring rod and taking the subsample from the homogenized mass. As much of the sample was loosened and mixed together, no segregation of the sample by aggregate size was apparent after mixing as it is consulted in detail in Hoskins and Ross, 2009. The percentage of sand, silt and clay was calculated from fine earth (<2 mm fraction). Soil pH_{KCl} was measured with a glass electrode in 1 M KCl (1:2.5 mass-to-volume ratio) in triplicates.

For the determination of the base cationic saturation, in each of the samples, the 0.1 M $BaCl_2$ was used, samples were batch treated, filtrated and analyzed by atomic absorption spectrometry by PerkinElmer Instrument AAnalyst 200. Another fast way of determination of the CEC is sorption on methylene blue. It gives comparably good results for the analysis of clays (Hang and Brindley, 1970), and was therefore used for the analysis of the surface of clay and modified clay samples. A calculated volume of 2.5 mmol L^{-1} methylene blue was added to 0.3 g of clay, the obtained suspensions were shaken for 24 h (Biosan Multi Shaker, PSU-20, 200rpm), then centrifuged (laboratory centrifuge Biosan LMC-300, 2500 rpm, 30 min). The changes in methylene blue concentration after sorption were detected with a Jenway 6300 spectrometer (l=1 cm, λ=664 nm) (Sarcevica and Actins, 2009).

Acid treatment to release the elements of interest from the sample matrix and transfer them to a liquid matrix for subsequent analysis was used by wet digestion in a beaker. Dissolution is a simple process of dissolving a substance in a suitable liquid (HNO_3) at a relatively low temperature, with or without a chemical reaction. The decomposition of matrix in most of experiments was done by adding nitric acid and hydrogen peroxide followed by heating after 24 h and repeating the addition of acid (Sample Preparation…, 2003).

The chemical analysis is concentrated on several main areas: qualitative testing, quantitative determinations and structural analysis by procedures requiring laborious and time-consuming calculations. Sometimes solution of the sample in a solvent suited to the spectrometric investigation is required – in case of atomic absorption spectroscopy, X-Ray fluorescence and inductively coupled plasma mass spectrometry (Kealey and Haines, 2005).

The results must be reliable (credible), that is, they must accurately (both precisely and truly) reflect the real content (amount) of analytes in a sample that is representative of the material object under research (Namiesnik and Szefer, 2008). The most important limiting factor is that it is not possible to make an analytical determination of chemical elements in the ppb level. The equipment for use in sample analysis is limited by its technical availability, the detection limit, sample characteristics, operator skills and other considerations (Arruda, 2007).

The advantages of this method are: multi-element, non-destructive, requires minimal sample preparation, high accuracy and sensitivity, can analyze different types of samples, rapid qualitative detection.

2.4.2. Powder X-Ray difractometry (PXRD)

The methods using optical microscopy are not suitable enough for the identification of mineralogical clays with small particles, which have a more or less unknown chemical composition compared to petrographical samples. XRD is one of the most efficient methods as coherent scattering of the incidental radiation makes it possible to identify parameters of the crystal lattice as well as geometrical distribution of atoms in a crystallic mesh. Detailed quantitative studies of clays and associated phases, oxides, hydroxides and more make it possible to explain unmatched results. Crystal is defined as a solid made up of atoms assembled in a three-dimensional periodic model and have determined lengths a, b, c, and angles α, β, γ between the planes define the mesh parameters of the basic unit. If monochromatic X-ray beams of defined wavelength strike a crystalline plane, atoms of the crystal reflect those. Signal is turned in a particular direction if the rays reflected by the different planes are in phase. Background noise appears due to incoherent reflectance and double reflectance of beams, but it can also be smoothed electronically with suitable software. The use of XRD is highly dependent on the nature of the components, and the degree of precision desired (Pansu and Gautheyrou, 2006). X-ray powder diffraction (PXRD) analyses for dry, finely ground clay samples were performed on a Bruker D8 Advance diffractometer (generator 40 kV, 40 mA) with 0.6 mm divergence slits, 0.2 mm detector slit, Copper K_α radiation (λ=0.15418 nm), 2θ interval from 3 to 60°, scan speed 0.5 s/step, step 0.02°, detector – LynxEye (1D-position sensitive) at the University of Latvia, Faculty of Chemistry.

2.4.3. Fourier transfer infrared spectroscopy (FTIR)

The technique of interferometry uses the mathematical technique of Fourier transformation – the interferogram, which is a time-domain representation, may be converted into a frequency-domain spectrum. In FTIR the source supplies a range of frequencies and a polychromatic source is used.. The radiation is split into two beams – those are combined and result as a function of the optical path difference, that is, an interferogram. The basic mathematics for analysing such complex patterns was devised by J. B. Fourier and is referred to as Fourier transforms (FT). The initial detector signal gives an intensity signal as a function of time, and is converted, using a Fourier transform algorithm into the relation between intensity and frequency, which is the normal form in which a spectrum is viewed (Kealey and Haines, 2005). The FTIR gives an interferogram, and it is used to detect in thesis the properties of substances. Samples for FTIR analysis are prepared by creating powder followed by homogenization after which it is possible to start analysis. FTIR spectra were obtained on an Perkin Elmer Spectrum BX II at the Faculty of Geography and Earth Sciences, University of Latvia. The infrared spectra (FTIR) were recorded from powder type sample containing 2 mg of the freeze-dried modified clay with 250 mg of dry KBr, spectrophotometer was covering a wavenumber range of 400–4000 cm^{-1} at 16 nms^{-1}.

2.4.4. Brunauer-Emmett-Teller (BET) surface area measurements

It explains the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material (Brunauer et al., 1938). Adsorption of gases on a surface is the base of this method and is presented by relationship between the surface excess (mole adsorbed per unit mass or surface area) and pressure at a given temperature. For the representation of mole per unit area, BET surface area is used and is the basis for a standard protocol where nitrogen at 77 K is the recommended adsorbate (Sing et al., 1985). An important parameter required in the BET theory is the molecular projection area which has a wide range, even for simple gases such as nitrogen (Gregg and Sing, 1985). Projection areas for nitrogen have been reported in the range 0.14−0.277 nm^2/molecule (Chung and Dash, 1977). BET measurements for the thesis were done in order to compare sorption capacities of modified clays. It provided a specific surface area evaluation for clay by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The result is given in m^2/g. The Micromeritics instrument Gemini2360 in Poland at J.S.Hamilton International was used for BET surface measurement. Samples were evacuated at 40°C over night. Nitrogen was introduced in eleven pressure steps (p/p0=0.05-0.3) at a temperature of 77.35 K (boiling temperature of nitrogen).

2.4.5. Scanning electron microscopy (SEM)

Electron microscopes are based on the interaction of electrons with matter. The energy of an electron accelerated by a voltage V is equal to $\mathbf{E = m v^2/2 = e V}$ (with m, v, e = mass, speed and charge of the electron, respectively). The nature of minerals is determined from their colour, opacity and refractive index and observable modifications in polarized light (e.g., pleochroism). Certain minerals have a more or less clear birefringence. The resolution is about 20–100 Å depending on the element observed. The intensity of the beam and scanning conditions are chosen to have the best resolution and optimal signal-to-noise ratio for a given power. 30 keV applied energy prevents very fine details from being observed, but it may be good to reduce the charge by using energy below 5 keV. (Pansu and Gautheyrou, 2006).

All samples should be of an appropriate size to fit in the specimen chamber and are mounted rigidly on a specimen holder – specimen stub. Conventional imaging in the SEM requires specimens to be electrically conductive in order to prevent the formation of electrostatical charge at the surface. Scanning electron microscopy (SEM) is used for investigation (evaluation) of topography of the surfaces and has a good depth of focus. The accelerating voltage was 5-10 Kv.

In order to confirm immobilization and characterize differences between the carriers, samples were studied using a scanning electron microscope (S-4800; Hitachi, Japan) operating at 5-10 kV. Preparations for scanning electron microscopy were covered by a thin layer of gold and palladium powder using an ion coater (JB-3; Eiko, Japan). Instrument is located at the Faculty of Biology, University of Latvia.

2.4.6. X-Ray fluorescence spectrometry (XRF)

X-ray fluorescence spectrometry identifies elements by measurement of characteristic X-ray emission wavelength or energy. It gives quantization of elements by measuring emitted characteristic lines of intensity and then considering this intensity to elemental concentration. An excited atom transfers an electron from an outer level in the atom to fill the vacancy in the inner circle. Each unique atom has a limited number of electrons for transfer and since a plethora of atoms are involved in the excitation; all available de-excitation routes are taken into account. The basic function of the spectrometer is to separate the polychromatic beam to various intensities of each individual characteristic line to be measured. The resolution of lines should be sufficient and thus four factors are important: resolution, response, background level and range. The improvement of resolution can invariably cause the lowering of absolute peak intensities. The XRF is particularly applicable to the qualitative and quantitative analysis for elements of low concentration in a wide range of samples; it also allows fulfilling the analysis of elements at higher concentrations in limited quantities of materials (X-Ray Characterization..., 1999). Total Reflection X-ray Fluorescence (TXRF) utilizes extremely low-angle X-ray excitation of a polished sample surface and a Röntec PicoTAX instrument in laboratory conditions for the detection of elements in some samples from BLB Baltijas Termināls was used.

The field portable X-ray fluorescence apparatus (FPXRF) is used in field applications and was applied during the doctoral research for landfill waste fine fraction analysis in Saaremaa, Estonia. A DELTA Olympus Handheld XRF Analyzer (Fig. 2.10) was calibrated before field work sessions and measurements done in triplicates for homogenized samples. CalCheck Standardization test cup 316 of stainless steel was used.

Figure 2.10. Portable DELTA Olympus Handheld XRF Analyzer in action (photo by F. Kaczala)

2.4.7. Atomic absorption spectrometry (AAS)

The energy levels of atoms are determined by quantum numbers of each element. Excited atoms absorb the energy in distinct wavelength (or frequency). The degree of absorbance will depend on the concentration, in the same way as with other spectrometric techniques. This technique is known as atomic absorption spectroscopy or spectrometry (AAS). The prepared samples are in solutions and are volatilized by a flame or furnace.

The source of the flame is a cathode lamp. There can be lamps for the detection of each element as well as multi-element lamps. Air-acetylene gives a flame temperature of about 2400 K, while air-propane is cooler (~1900 K), and nitrous oxide-acetylene hotter (~2900 K). The spectrometer should be calibrated by using standard solutions of the element necessary for measurement, prepared in the same way as the sample solution. Usually, acidic aqueous solutions are used; multi-element standard stock solutions are useful and permit more rapid determination of several elements of interest (Kealey and Haines, 2005).

The detection limits for AAS and ICP-MS are given in Table 2.2. These are formal numbers as many other reasons for errors occur during homogenization and preparation of samples for analysis, matrix effects and interfering properties of elements.

Table 2.2

Detection limits of AAS, ICP-MS and FPXRF instruments for key elements studied in thesis (Perkin Elmer, 2013; Delta Olympus, 2013) *

Element	Detection limit of applied analythical method		
	AAS, μg l^{-1}	ICP-MS, μg l^{-1}	FPXRF, μg kg^{-1}
As	150	0.0006	2000
Cd	0.8	0.00009	7000
Co	9	0.0009	75000
Cr	3	0.0002	8000
Cu	1.5	0.0002	6000
Hg	300	0.016	3000
Mn	1.5	0.00007	100000
Ni	6	0.0004	15000
Pb	15	0.00004	3000
V	60	0.0005	10000
Zn	1.5	0.0003	4000

** Detection limit for AAS and ICP-MS is given for wet digested sample analysis in liquid form, but for FPXRF detection limits for soil samples are given*

AAS is easy to use, widely available, well-documented, low-cost, well-researched on distorting factors, requires a relatively small sample measurement time, it is relatively sensitive and can identify elements at mg g^{-1} level. However, samples must be liquid and the analyte concentration must be relatively high. For the determination of lead by atomic absorption spectrometry (AAS), the liquid was filtered through a 0.45 μm filter (Simplepure, NY, Syringe filter). The analysis of trace elements (Pb, Cu, Zn, Ni, Cr and more) was carried out using appropriate wavelengths by a Perkin Elmer AAnalyst 200 instrument at the Faculty of Geography and Earth Sciences, University of Latvia. The concentration of Pb in the leached eluates was determined by the use of AAS instrument Perkin Elmer GBC 932 Plus with deuterium background correction and a spectral slit width of 0.5 nm for Pb and wavelength 283.31 nm at the Department of Biology and Environmental Sciences, Linnæus University.

2.4.8. Inductively coupled plasma masspectrometry (ICP-MS)

The plasma is the co-existence of positive ions, electrons and neutral species of an inert gas in a confined space. The most common gases are argon and helium which are used as inductively coupled plasma (ICP), direct-current plasma (DCP), microwave-induced plasma (MIP) and glow discharge. The ICP is formed in a plasma torch and initially sparked by Tesla coil. A spark as a flow of electrons ionizes the gas. High velocity gas forms a bullet shape and the temperature reaches 7-10 kK. Mass spectrometry (MS) measures the molecular weight of elements or compounds. MS has a high resolution and separates ions. Circa 70 % of the elements in the Mendeleev's Periodic Table have stable (nonradioactive) isotopes and MS has the ability to measure isotope ratios for tracer studies, and quantitative analysis (Dean, 2005).

ICP-MS is a high sensitivity, multi-element method; it performs fast measurements, takes little time and can thus provide a large number of sample analysis, requires a small sample volume of 1 ml for analysis and allows the determination of the elements from Li to U. The detection limits given in Table 2.2. were measured in a Class-100 Clean Room using Reaction mode with the most appropriate cell gas and conditions for that element in deionized water, except Hg, As and Cd that were performed under multi-element conditions in Standard mode.

During the determination of inorganic compounds for the present thesis, leached metals in eluates and trace elements in the fine fraction of the landfill soil samples were determined by ICP-MS (Perkin Elmer ELAN DRC-e) at the Faculty of Chemistry, University of Latvia.

2.4.9. Ionometry

The strength of the interaction between organic ligands and metals is usually expressed in terms of a stability constant of formed complexes. The knowledge of stability constants enables the behaviour of a metal ion with one or more ligands to be modelled as a function of pH and reactant concentration (Byrne et al., 2011). Consort Cu^{2+} ion selective electrode manufactured by *pHoenix Electrode Co.* was used in order to detect the amount of free copper ions, which can be related to biologically available forms (Electrochemistry Dictionary and Encyclopaedia, 2014). Electrode was connected to Hanna pH 213 microprocessor, samples in solution were measured while stirring with Biosan Magnetic stirrer MSH 300. The main element in this method is the membrane of the electrode, as it provides ion exchange with the solution. Ion exchange occurs due to the potential difference in electric field. In order to correctly determine the amount of free ions of copper in the solution, electrode is conditioned: electrode is filled with 10 % KNO_3 solution, then 2 mL of 5 M $NaNO_3$ and 1 mL of $Cu(NO_3)_2 \cdot 3H_2O$ (with Cu^{2+} concentration 1000 mg L^{-1}) are added to 100 ml of deionized water and potential difference determined. Afterwards 10 ml of $Cu(NO_3)_2 \cdot 3H_2O$ (with Cu^{2+} concentration 1000 mg L^{-1}) are added and again determination of potential difference performed. The producer of the electrode defines accurately the difference of these two aforementioned measurements as 27 ± 2 mV. Conditioning result in performance of the author was satisfactory – 27.9 mV.

The four different calibration $Cu(NO_3)_2 \cdot 3H_2O$ solutions (Cu^{2+} concentrations 1000; 100; 10; 1; 0.1 mg L^{-1}) were prepared and 2 mL of 5 M $NaNO_3$ solution was added to 100 mL of each.

Potentiometry results using the calibration data are recalculated to the concentration of metal ions in the solution as well as the ability of metals to bind with humic acids and zeolites according to formulas {1} and {2}:

$$\mathbf{Cu + HS = CuHS} \qquad \{1\},$$

where the Cu is the amount of Cu^{2+} moles in the solution and HS – the amount of moles of humic acid in the solution, and

$$\mathbf{Ko} = \frac{\mathbf{CuHS}}{[\mathbf{Cu}]\cdot(\mathbf{HS-CuHS})} \qquad \{2\},$$

where Cu – concentration of hydrated Cu^{2+} in the solution; Ko – stability constant of complex forming; CuHS – the amount of moles, which are included in complexes (Bresnahan et al., 1978).

2.5. Statistical analysis and data treatment

Statistical analysis was performed using the extended MS Excel data analysis program QI Macros and partly with the SPSS Software (QI Macros, 2013; SPSS, 2013). For every data set the range of statistical parameters such as standard deviation, mean, mode, median etc. were calculated, hence Pearson correlation was applied with the following ranges of correlation: $r < 0.5$ – slight, $0.5 < r < 0.8$ – medium, $r > 0.8$ – strong. For the comparison of data matrixes Student's tests were performed (t-Test: Two Sample Assuming Equal Variance; t-Test: Two Sample Assuming Unequal Variances) and other tests if applicable. Data set treatment was performed as described in (Havlicek and Crain, 1988).

"Surfer 12" software was used for groundwater surface modelling described in detail in Chapter 2.1.3., whereas MAUT, PROMETEE, ELECTRA and MCDA techniques were used in the MS Excel environment for a multi-criteria analysis provided for indicative model preparation described in the next sub-chapter.

2.6. Indicative model creation and appraisal of options

The MCDA analysis in the present thesis was considered as an important tool able to algorithmically combine different approaches mentioned in Chapters 1.4.1-1.4.4. Decision-makers can apply various arguments and develop their own indicators for every single case. As indicators and their weighting is individually subjective, more objectivity in decision-making can be reached by inviting a number of experts from different fields. Through discussions and fact analysis, indicators can be chosen and weighted and entered into the software developed for the MCDA mathematical analysis part. Thereby deficiencies of each single decision evaluation model can be avoided, and the data gained from other methods (NEBA, LCA, qualitative tools, cost-benefit analysis) can be entered into the MCDA matrix as indicators with different values. Different decision scenarios can be played through and results discussed among experts from various fields.

An indicative model for decision support was created on the methodological basis described by Triantaphyllou (2000), Geldermann and Rentz (2007), Figueira et al. (2005), Asafu-Adjaye (2007) and Böttle (2011) using MS Excel environment. In the thesis, several remedial options (alternatives) from the list of soil remediation technologies and a set of parameters defined such as the environmental benefit, construction expenses (including geological complexity and costs of materials), social aspects (aesthetics and public response) were chosen in order to perform multi-criteria choice analysis. Three options have been combined from technological alternatives (excavation, phytoremediation, soil amendments, stabilization/solidification) for the remediation. Alternatives have been provided for each segment of the case study research area, which were defined during the environmental research project carried out in BLB Baltijas Terminals and Vega Stividors areas (case studies No. 1 and No. 2). The Excel model allows modifying data for each option to see the result of the MCDA matrix calculation. Evaluation criteria were chosen from the economic (construction costs), social (impact on industrial activities in this case) and environmental (preference list in ordinal scale) areas. The criteria is weighted; the user can modify the weights of criteria in the model. The input of data for project expenses and preferences is done by the user and it can be modified. Other calculations are done by the MCDA model and the result is given as the MAUT, the PROMETHEE (The Preference Ranking Organization METHod for Enrichment of Evaluations) and the ELECTRE calculated results through the MCDA calculations. Thus the results are provided by three different methods including outperforming actions and scaling.

The MAUT approach defines the weights for parameters in order to fit the best for the judgement. The algorithm normalizes the performances by dividing each performance by the sum of all performances with respect to the corresponding criterion. After normalizing, the performances are comparable and the calculation of all score for every option is then possible by weighting all the weights for each criterion as in formula {3}:

$$\mathbf{S(A) = \sum_k w_k A_k} \qquad \{3\},$$

where w_k denotes the weight of k^{th} criterion and A_k the performance of the alternative with regard to k^{th} criterion. The result of the MAUT approach summed from all options compared should give the value as in formula {4}:

$$\mathbf{S(T = A1 + A2 \ldots + An) = \sum_k w_k = 1} \qquad \{4\}.$$

The PROMETHEE I is when alternative A outranks (outperforms) B if there is a sufficiently strong argument in favour of the assertion that A is at least as good as B. The function provides a value between 0 and 1 and indicates the strength of preference of option i over option j regarding criterion k.

The PROMETHEE considers a set of criteria {4a}:

$$\mathbf{C = \{C_{ic}, i_c \in N\}} \qquad \{4a\},$$

The method demands information about each of the criteria (preference function P as in equation {4c}, and among criteria importance weights {4b} and evaluations $c_j(a)$ and $c_j(b)$:

$$\boldsymbol{\omega_i c \equiv \omega(c_i c)} \qquad \{4b\},$$

$$\mathbf{P_j(a,b) = functiona_j[d_j(a,b)], \forall a,b \in A} \qquad \{4c\},$$

The preference function takes as input the amplitude of the deviation between two evaluations within the same criterion j:

$$\mathbf{d_j(a,b) = c_j(a) - c_j(b)} \qquad \{4d\}$$

and yields a preference or indifference (does not outperform) state.

The PROMETHEE calculates the outranking flows defined in {4c and 4d}, the positive outranking flows $\varphi^+(a)$ showing the number of times a chosen alternative outranks all the others and the negative flows $\varphi^-(a)$, where the number of times an alternative is outranked by the others. If the $\varphi^+(a)$ is positive, it is better for the section. At least two versions of the PROMETHEE decision aid exist (Figueira et al., 2005): the PROMETHEE I, which ends by providing the positive and negative outranking flows and the PROMETHEE II with a yield of final ranking, by calculating the net of outranking flow {4e}:

$$\boldsymbol{\varphi(a) = \varphi + (a) - \varphi - (a)} \qquad \{4e\},$$

Thus, the higher is the net flor, the better is the alternative for decision-majers (Figueura et al., 2005).

The ELECTRE or "ELimination Et Choix Traduisant la REalité" (ELimination and Choice Expressing REality) method is similar to the PROMETHEE and has small differences from the mathematical and logical constructions points of view and can be used for validation of other MCDA techniques. It is also described in (Figueira et al., 2005; Böttle, 2011).

The MAUT weighting, the PROMETHEE I, II and the ELECTRE outranking systems (Triantaphyllou, 2000; Geldermann and Rentz, 2007) were used for the preference calculations in the software based Excel model, created by Böttle for coastal engineering decision support needs (2011) and modified by the author regarding the requirements for decision support tool creation exactly for remediation technology choice.

3. RESULTS AND DISCUSSIONS

3.1. Overall characteristics and contamination intensity in research areas

Environmental contamination with heavy metals due to anthropogenic activities in Latvia is present in various amounts and concentration at formerly contaminated areas of historical industrial activities, dumping sites and military areas. Many of these sites have been influenced by anthropogenic pollution for many decades. Legislation standards concerning contaminated soils, as described in the literature review chapter, are important for the appraisal of remedial options and decision-making in planning clean-up activities. However, first the environmental quality must be evaluated and historical data analysis and site research should be performed in order to have the overall characteristics of these sites.

There are 56 sites from the first group contaminated with heavy metals (Fig. 3.1) – 28 of them are situated in Rīga (Fig. 3.2), mostly at the Rīga Freeport Authority, 6 sites are in the Latgale region, 5 in the Vidzeme region, 6 in the Kurzeme region, 4 in the Zemgale region and 7 in the Great Rīga region (Annex I).

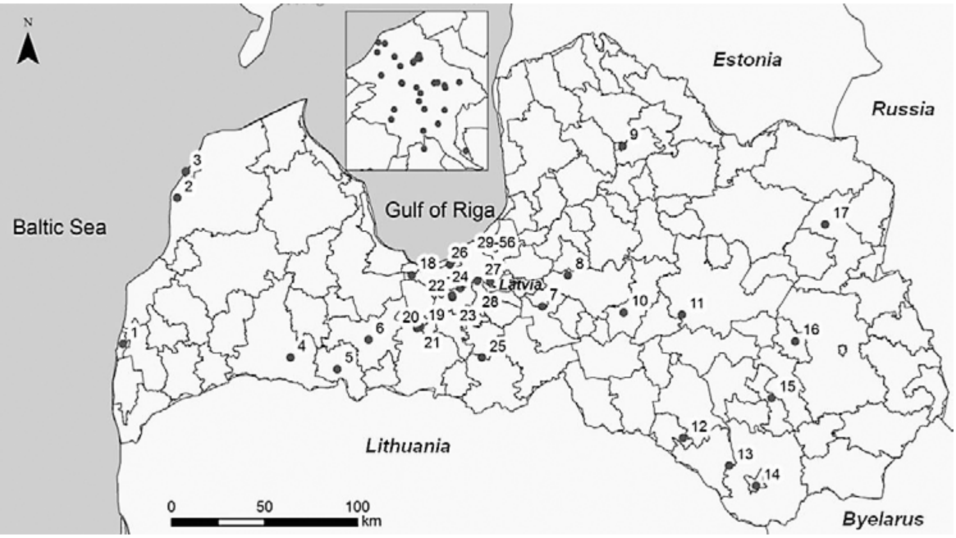

Figure 3.1. The first category sites contaminated with heavy metals in Latvia (NRCT, 2014; Annex I)

The classification of sites contaminated with heavy metals can be done in sub-groups regarding the activities which have dominated as the source of pollutants as well as the contamination intensity. The description of case study results is given according to both classification principles for the ease of understanding and giving further recommendations of potential site clean-up activities, and the logical structuring of the thesis.

Figure 3.2. The first category sites contaminated with heavy metals in Rīga (NRCT, 2014; Annex I)

Source of pollutants. The first sub-group contains the *former dump sites* of mixed waste. In the former USSR, municipal, residential, housing and building waste as well as hazardous substances and materials were often dumped in these sites. *Hazardous dump sites* are, e.g., liquid toxic substances dump site in Jelgava "Kosmoss" (mostly groundwater contamination), biomedical and chemical industry dump site (Olaine), former treatment facilities in Rīga and similar. A more detailed description can be found in the author's previous research (Burlakovs, 2012; Burlakovs et al., 2013e).

In total, 19 sites or 34 % from the list of Latvian National Registry of Contaminated Territories (NRCT) (full list in Annex I) can be classified as dump sites. Some of them contain a high level of contamination with heavy metals and arsenic – five of these sites have been investigated in detail by the author: Kleisti and Deglava municipal dump sites in Rīga city, liquid toxic substances dump site in Jelgava "Kosmoss" and BLB Baltijas Termināls with Vega Stividors in the Rīga Freeport (last two can be considered also as former and still active industrial sites). The case study territories have been the object of research for several years as they contain a wide variety, amount and concentration of different metal and metalloid contamination.

Former military territories constitute the next important sub-group of contaminated sites. After World War II, more than 1,000 units of the Soviet Army were located in about 600 military objects that occupied in total approximately 10 % of territory of Latvia (Military Heritage Map, 2011). The largest firing-grounds were Zvārde, Liepāja Navy port (Karaosta) (Liepaja Navy Port Environmental Research, 1996), Rudbārži missile base, and Lielvārde airfield. Site pre-investigations and remediation have been carried out in some of the former military territories, e.g., Rumbula airfield, where the soil and groundwater have been contaminated with oil products. Contamination with heavy metals, toxic organic substances, and also with oil products was determined in around 11 (20 %) military territories. In spite of the historical contamination, some of these territories have been readjusted for use for other purposes, e.g., the area of the Rīga Freeport. The heavy metal pollution of the soil and groundwater at the potentially contaminated site "Jaunais Mežaparks" and contaminated "Freja" sites at the Freeport of Rīga were investigated by the author during the applied and academic research (Burlakovs and Gorbunovs, 2012).

Areas of *industrial contamination (brownfields)* (26 or 46 %) contain multi-contaminant pollution, including heavy metals, their compounds, inorganic and organic substances. Industrial development has caused site contamination that in many cases is considered as historical contamination. The former agricultural machinery "Selmash" factory area (Fig. 2.2) was researched as solvent and heavy metal contamination was present there at unacceptable levels.

Further land use in brownfields is frequently viable after adjustment activities in these territories, however, the environmental and risk assessment must be done in order to obtain information on the environmental situation and quality of those territories (Burlakovs and Vircavs, 2012).

Detailed pre-remedial pilot studies have been done in Rīga and Liepāja ports, where the economic development is still active. The above sites are included in the NRCT and they are the areas most contaminated with heavy metals and oil products. The studies have shown that the soil and groundwater are strongly polluted with heavy metals. The Liepāja Military Port was studied and an assessment of the sediment quality was carried out in mid-90s (Liepaja Navy Port Environmental Research, 1996). The results have proved that the sediments are mostly polluted with Cd, Cu, Pb, Hg and Zn. The geoaccumulation and pollution load indexes were used in order to compare the contamination levels in Liepāja and Rīga harbours (Vircavs, 2008). The geoaccumulation and pollution load indexes were used in order to compare the contamination levels in Liepāja and Rīga ports (Vircavs, 2008). The geochemical index (I_{geo}) (Müller, 1979) and the pollution load index (PLI) (Sarma, 2011) are the main characteristics of sediment quality: the higher are the values of the I_{geo} and the PLI, the more contaminated are the sediments. The highest I_{geo} values were obtained for Cd (I_{geo}=4.3) and Pb (I_{geo}=4.6) in the Liepāja Military Port and for Cd (I_{geo} = 4.0) in the Rīga Port. According to the geochemical index classification (Müller, 1979), these areas regarding Cd and Pb are considered as strongly or even extremely polluted. As to Cu, Hg and Zn pollution, the areas were defined as moderately to strongly polluted. The maximum PLI values were observed for sediment contamination of the Liepāja Military Port (PLI – 5.0) and the Rīga Port (PLI – 4.5). An uncontaminated state or background level of sediments was observed for Ni and Cr, whose I_{geo}<0. The wide range of I_{geo} of Ni and Cr characterizes their background level. The calculated I_{geo} and PLI show that the sediments of the Liepāja Military Port are the territories most polluted with Cd, Cu, Pb, Hg and Zn, as compared to the Rīga Port sediments (Liepaja Navy Port Environmental Research, 1996). The sediment quality assessment led to the decision that remediation of the sediments must be carried out after the technical economic evaluation in 2010. Pre-research in the Liepāja and Rīga ports (BLB Baltijas Terminals and Vega Stividors areas) has shown that the high groundwater level is the disturbing factor for the application of excavation as well as other *ex-situ* technologies. Therefore, considering the geological and economical obstacles, the application of the S/S technology is the most acceptable development in this case. The remediation of the Liepāja Port sediments after dredging out the water body will be carried out using the S/S technology (Burlakovs and Vircavs, 2011).

Sites selected for contamination research. In total, ten areas were selected for characterizing typical and potentially contaminated sites: nine sites are situated in Latvia, and one in Estonia.

1) *BLB Baltijas Termināls* and *2) Vega Stividors* (both in Fig. 3.3) – the research was done in several stages (Burlakovs and Klavins, 2012). Preliminary research on heavy metal contamination provided information on general situation, but a more detailed analysis was then carried out to prepare the technical economic analysis for testing the chosen S/S remediation technology and performing laboratory experiments for technology application planning.

The decision for the selection of the BLB Baltijas Terminals and Vega Stividors (Annex I, N°54/55) for doctoral research was based on the potentially high actual risk of toxic leachate transfer to the groundwater and the significant negative impact to receptors (the environment and humans) as this area is close to the River Daugava and the Lake Ķīšezers in Rīga. This site has been used intensively from the beginning of the 20th century. In earlier years (1894-1967), the territory was used for several industrial purposes including the manufacturing of superphosphates, with a dump site for tailings made right nearby. Later on, an oil product storage, reloading and transit terminal was established in this area. A factory operated there until the 1960s, but later was replaced by an oil product terminal facility. The main soil pollution source was superphosphate production waste (slag), where the highest concentration was found for lead, copper, zinc and arsenic. The total amount of toxic heavy metals throughout the whole research area was estimated at 1264 t or 15 kg m^{-2} of slag or: 755 t of copper, lead 85 t, zinc 358 t, 66 t of arsenic (Report on…BLB Terminal, 2009). The further studies led to the choice of the S/S technology for possible remediation (Burlakovs and Klavins, 2012).

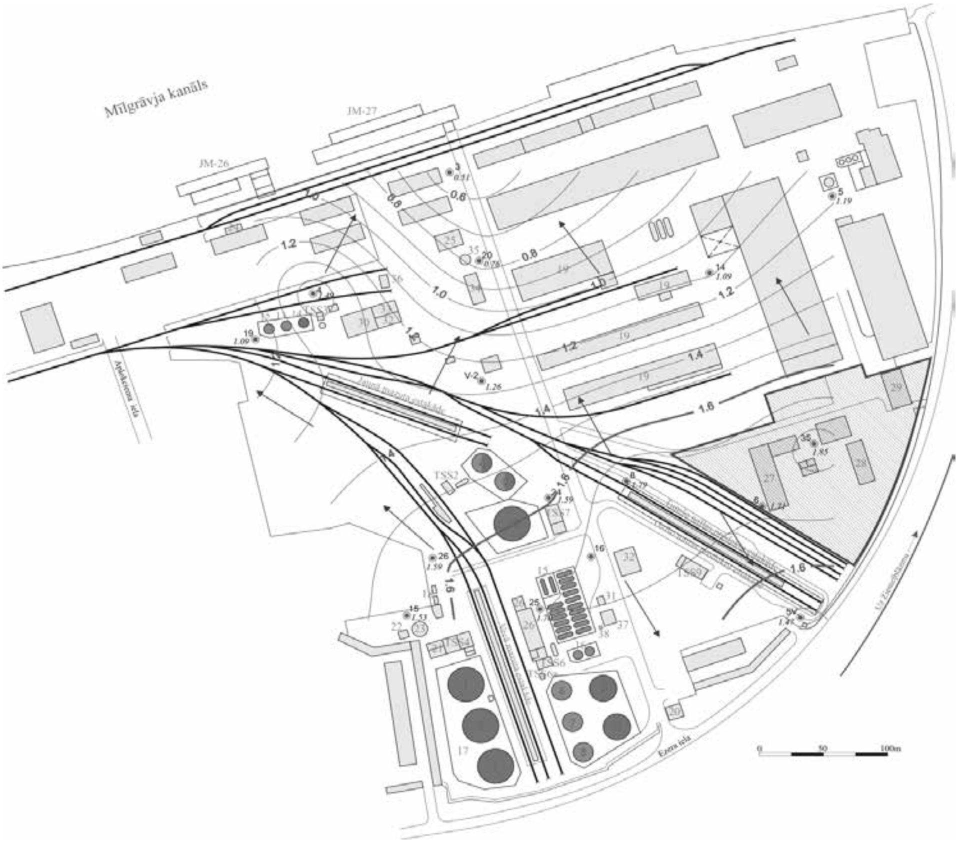

Figure 3.3. Groundwater flow direction determination in BLB Baltijas Termināls and Vega Stividors areas using field levelling and “Surfer 12” software (kriging)

3) *Former agricultural machinery factory “Selmash”* (Fig. 2.2) was studied as solvent and heavy metal contamination was present there in unacceptable levels. Research of the area, which formerly was on the NRCT list, was performed in several stages and following remediation it was shifted to the 3rd group as not contaminated. Construction works have been started and a large commercial area is planned at this site. A disputable question is the removing of such areas from the list of contaminated sites as remediation is not the best solution in all cases – the risk of potential threat to the environment can be expected for many years to come.

4) *Former wooden industry brownfield at 22 Katlakalna Str.* is not included in the list of contaminated sites, but research was done regarding the precautionary means in the area by taking joint samples from the upper soil (0.0-0.5 m) as well as deeper horizons (3-6 m). Heavy metal concentration exceeding precautionary level was detected in average joint samples, however, it does not pose a risk to the environment as no contamination was detected deeper (Tables 3.1 and 3.2).

5) *Former military warehouse area "Jaunais Mežaparks"* is also not included in the list of contaminated areas, however, the soil quality at the research area in 30 ha was determined and results published in (Burlakovs and Gorbunovs, 2012). The area was carefully investigated by analysing joint samples from seven sub-areas. The results showed that some of precautionary levels are exceeded in soil, however, the area can be used for construction works and *gentle* (description at GREENLAND project, 2014) remediation techniques could be a good solution to decrease the mobility of existing pollution with heavy metals (see further chapters).

6) *Former military area in Daugavgrīva "Freja"* is included in the list of contaminated areas (Annex I, N° 35), the soil quality at the research area was determined and results partly published in (Burlakovs and Gorbunovs, 2012).

The results from different contaminated and potentially contaminated sites were obtained during careful environmental soil quality determination projects; the main results are depicted in Tables 3.1 and 3.2 as well as Fig. 3.4. Conventional research techniques by using investigation of different depth soil samples for different subdivided sub-groups were used and a high number of samples were analyzed for heavy metals and metalloids by using analytical tools. Combined data sets mean calculations were considered as most appropriate for representing the environmental situation regarding heavy metal and metalloid concentration in soil.

Table 3.1

Concentration range and mean from combined data sets (*n*=5 in various size areas) concentration of As, Co, Hg in soil samples at various depth obtained from contaminated territories in comparison with limits set by legislation in Latvia

Depth, m		**Concentration (c_{min}-c_{max} (c_{mean})) of element, mg kg^{-1}**		
		As	**Co**	**Hg**
BLB Baltijas Termināls (divided in three sub-areas)				
0.3-1.0		905-1302 (1102)	n.*	0.57-0.79 (0.68)
1.0-2.5		26-1223 (511)	n.	0.4-88.0 (19.2)
2.5-5.0		14-2301 (494)	n.	0.3-13.4 (4.10)
VEGA Stividors (divided in three sub-areas)				
0.3-1.0		115-5679 (2456)	9.4-17.5 (12.4)	0.4-0.85 (0.63)
1.0-2.5		84-3490 (1870)	46.2-49.1 (47.7)	0.7-17.0 (5.2)
2.5-5.0		2-1580 (699)	3.5-5.8 (4.7)	0.0-11.0 (2.3)
Katlakalna str. 22 (divided in three sub-areas)				
0.0-0.5		0.12-18.10 (4.01)	n.	n.
3.0-6.0		0.01-0.04 (0.02)	n.	n.
Limits set by Regulation N° 804 (2005) of Cabinet of Ministers of Latvia**				
Threshold level	**A**	**2**	-	**0.25**
	B	**10**	-	**2**
	C	**40**	-	**10**

**n. – not measured*

***Limits set by Regulations No. 804 (25.10.2005) of the Cabinet of Ministers of Latvia "Requirements for Quality Normative of Top and Bottom Soils"; A – target threshold level, B – precaution threshold level, C – critical threshold level*

Table 3.2

Concentration range and mean values from combined data sets (n=10 in various size sub-areas) concentration of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in soil samples at various depth derived from contaminated territories in comparison with limits set by legislation in Latvia

Depth, m	**Concentration (c_{min}-c_{max} (c_{mean})) of element, mg kg^{-1}**					
	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
BLB Baltijas Termināls (divided in three sub-areas)						
0.3-1.0	2.9-3.5 (3.2)	10.2-15.0 (12.7)	2014-2360 (2190)	6.5-8.0 (7.3)	1350-1680 (1510)	1490-1550 (1513)
1.0-2.5	0.9-7.9 (2.8)	7.7-25.0 (17.2)	231-14011 (3877)	5.2-19.0 (11.6)	262-15033 (3280)	471-1921 (846)
2.5-5.0	0.4-44.2 (9.1)	5.0-21.3 (13.6)	43-8110 (2448)	5.1-22.0 (11.4)	110-2212 (769)	39-2820 (1163)
VEGA Stividors (divided in three sub-areas)						
0.3-1.0	0.3-3.2 (1.2)	<53	350-588 (456)	42-44 (43)	240-2067 (924)	315-1394 (691)
1.0-2.5	2.1-3.0 (2.6)	<53	1013-1120 (1058)	<42	325-383 (353)	1290-1416 (1358)
2.5-5.0	3.1-4.2 (3.7)	<53	403-454 (425)	<42	55-69 (63)	350-421 (381)
Selmash (divided in two sub-areas)						
0.0-0.3	0.09-0.21 (0.18)	4.0-5.3 (4.5)	12-29 (21)	3.2-24.3 (13.5)	25-180 (49)	60-116 (88)
0.3-1.0	0.13-0.19 (0.16)	1.2-8.3 (4.6)	7-19 (14)	1.5-17.4 (7.5)	9-330 (191)	25-89 (48)
1.0-2.5	0.21-0.50 (0.32)	1.7-6.7 (4.5)	7-127 (38)	3.4-16.1 (8.2)	6-100 (54)	22-161 (68)
0.0-0.5 (joint samples)	0.16-1.23 (0.55)	8.2-17.2 (13.3)	39-61 (55)	1.2-18.0 (9.6)	49-170 (96)	189-1352 (496)
1.5-2.5 (joint samples)	0.15-0.56 (0.27)	5.6-18.2 (11.8)	14-176 (73)	5.7-14.3 (9.6)	1-72 (37)	145-1015 (532)
2.5-5.0	0.13-0.33 (0.22)	3.6-9.7 (6.9)	7-16 (12)	3.9-9.3 (7.6)	6-30 (16)	32-49 (44)
Katlakalna str. 22 (divided in three sub-areas)						
0.0-0.5	<0.008	1.1-14.1 (5.1)	2.94-118.05 (39.79)	0.2-5.99 (2.48)	0.04-14.10 (3.32)	9-78 (26)
3.0-6.0	<0.008	0.4-0.9 (0.6)	17.1-38.9 (25.31)	0.2-4.4 (1.54)	0.04-2.10 (0.23)	4-33 (15)
Jaunais Mežaparks (divided in seven sub-areas)						
0.0-0.4	0.22-0.65 (0.29)	11.0-16.3 (12.9)	1-158 (40)	6.2-8.0 (6.6)	6-100 (39)	6-473 (146)
0.4-1.0	<0.20	0.6-15.2 (9.0)	3-145 (44)	6.3-16.1 (10.8)	8-118 (57)	14-79 (38)
Daugavgrīva Freja (divided in two sub-areas)						
0.0-0.4 (joint samples)	0.10-4.56 (1.54)	13.2-45.6 (26.4)	18-103 (61)	0.2-13.0 (5.5)	45-112 (76)	115-458 (270)
0.4-1.0 (drilled samples)	0.15-2.54 (1.03)	14.3-28.4 (20.9)	14-311 (117)	4.7-13.5 (8.8)	12-79 (45)	117-758 (391)
2.0-4.0 (drilled samples)	0.15-0.87 (0.43)	11.1-21.3 (16.4)	5-41 (21)	7.4-12.8 (10.1)	5-20 (14)	75-101 (88)
Limits set by Regulation N°804 (2005) of Cabinet of Ministers of Latvia*						
Threshold level **A**	**0.08**	**4**	**4**	**3**	**13**	**16**
B	**3**	**150**	**30**	**50**	**75**	**250**
C	**8**	**350**	**150**	**200**	**300**	**700**

**Limits set by Regulations No. 804 (25.10.2005) of the Cabinet of Ministers of Latvia "Requirements for Quality Normative of Top and Bottom Soils"; A – target threshold level, B – precaution threshold level, C – critical threshold level*

Tables 3.1 and 3.2 represent data from six territories, and here it can be stated that the most contaminated areas are BLB Baltijas Terminals and Vega Stividors, where As, Pb, Zn, Cu concentrations in the soil are exceeded 10-30 times in some sub-areas. *Gentle* (description at GREENLAND project, 2014) remediation techniques there would not be the best solution for stabilization and immobilization of contaminants. *Gentle* remediation and monitoring or risk assessment techniques can be possible alternatives in other studied cases No.3-6: "Selmash", 22 Katlakalna Str., "Jaunais Mežaparks" and "Freja", regardless of whether the area is on the NRCT List of contaminated sites or not. These areas have spots with soil exceeding allowed contamination norms for heavy metals; joint samples show that on average the level of heavy metals and metalloids is higher than the target threshold level. The reason is the former and active anthropogenic activities that have dominated in the case study areas for decades.

7) *Liquid toxic waste dump site near Jelgava* (Annex I, N°21) – the contamination in this site was researched for more than a decade; the last results were gained with the participation of the author. The results on contamination with heavy metals in soil and waste mass itself in this site as well as referred to next two case studies are given in Fig. 3.4.

8) *Deglava* and 9) *Kleisti waste dumps in Rīga* (Annex I, N°43 and N°37). The Rīga Development Plan 2006-2018 declares that the old former dump sites must be remediated and recultivated considering environmental legislation derived from EU Directives. Two cycles of research were performed for each of these dump sites with a significant contribution of the author. The analysis of field studies indicated that the most contaminated parts are the soft dry waste layer and the part of the soil saturated with leachate under the waste layer. The dry waste layer in both dump sites has been strongly polluted with heavy metals and other pollutants, and research was done in order to assess how much waste should be removed and to give recommendations for environmental impact reduction strategies and remedial and recultivation actions. The above research has been described in detail in the following research paper (Burlakovs, 2012).

In the scope of investigation of the dumps, contamination with heavy metals was detected in the waste mass body as well as in the soil underneath. Researched dump sites have exceeding heavy metal concentrations predominantly in the waste mass (Cr, Cd, Ni, Pb, Cu, Zn). Soil contamination exceeding the threshold was detected only in "Kosmoss" toxic liquid waste dump site; soil in the very vicinity of the dump site was detected regarding Cr. This soil contamination is directly linked to the source – the waste mass. Remediation works at liquid hazardous waste dump site were carried out after detailed studies and planning; contamination was localized, liquid waste was treated by groundwater pump-and-treat technologies, solid waste excavated and removed, and this historically contaminated site is considered as treated. Dump sites in Latvia are mostly recultivated by covering, however, innovative technologies would be recommended such as landfill mining. Removal of the source of metal leaching would diminish the future risks of environmental contamination.

The next chapters provide results of the studies carried out, showing the effectiveness of the *hard* stabilization/solidification technique and *gentle* (description at GREENLAND project, 2014) techniques such as soil amendment use for immobilization, where research is based on the results gained in leaching tests, sorption kinetic studies, speciation analysis and ionometry.

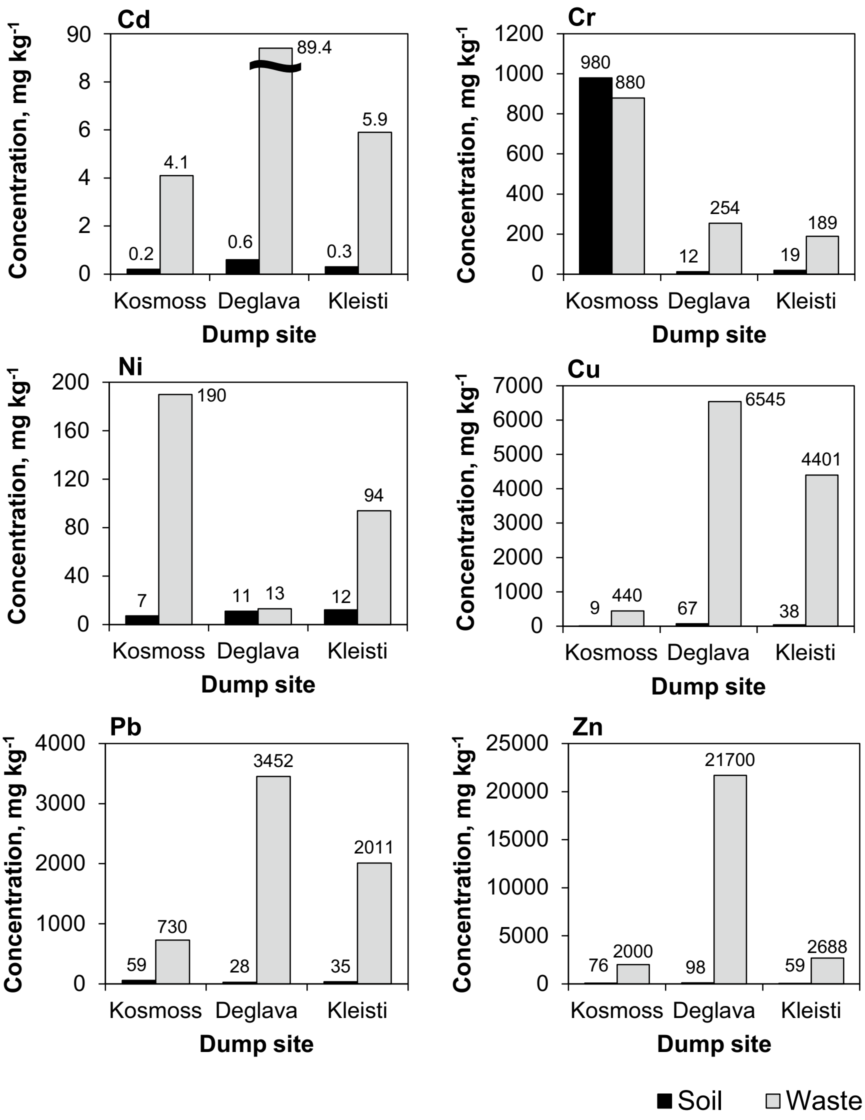

Figure 3.4. Concentration of heavy metals in soil and waste samples from territories of liquid toxic waste dump site near Jelgava, Deglava (No. 8) and Kleisti (No. 9) dump sites

3.2. Soil stabilization with Portland cement

3.2.1. Stabilization/solidification efficiency testing in batch experiments

Stabilization refers to an alteration of waste contaminants to a more chemically stable form, thereby resulting in a more environmentally acceptable waste form. Typically, the stabilization processes also involve some form of physical solidification (Shi et al., 2006). The environmental impact caused by the materials is not determined by their total content of pollutants, but by the amount of pollutants that water can dissolve and leach into the soil, thereby reaching the surface and/or groundwater (Kosson et al., 2002).

A sustainable solution can be found for remediation of industrial areas using the stabilization/solidification (S/S) technology, which refers to binding of waste contaminants to a more chemically stable form and thus diminishing the leaching of pollutants.

The aim of this part of the study was to give an assessment of heavy metal leaching from S/S remediated soils depending on the granulometric composition or soil texture. Thus, leaching behaviour of copper was analyzed by implementing the batch leaching procedure to stabilized samples under laboratory conditions.

Experimental results of soils of known texture spiked with copper were obtained in order to test the efficiency of Portland cement in the stabilization process and diminish leaching of heavy metals from the contaminated soil. The pH during the entire leaching test was alkaline (Fig. 3.5). It is typical when binder agents of building mortar content are added.

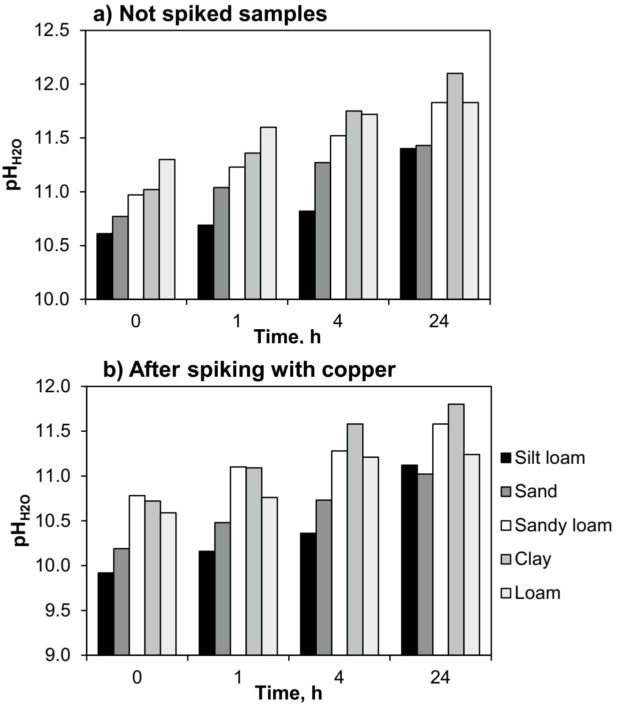

Figure 3.5. Changes of pH in soil samples with various texture by adding 10 % of Portland cement at batch leaching tests: a) without spiking, b) after spiking with copper (300 mg kg^{-1})

As seen from the Fig. 3.5, samples spiked with copper generally have lower pH values than without contamination. However, in both cases the pH increases with the agitation time.

Copper concentration in leachates of crushed and sieved samples, which were agitated for different time periods, increases with time; this trend is obvious for natural samples with the binder as well as for samples spiked with Cu and bound with cement. Fig. 3.6 depicts results with already calculated Cu mass losses from the samples, using the ratio L/S 10:1.

In the Fig. 3.6, the trends of leaching as compared to the length of the agitation period for not contaminated (spiked with Cu and bound with cement) soil can be seen. Copper concentration in the liquid grows with the increasing agitation time. These values can mostly be taken as the reference for evaluation compared to the test results in Fig. 3.6(b), which shows copper leaching from the soil spiked with Cu with the determined concentration of 300 mg kg^{-1} and treated with cement.

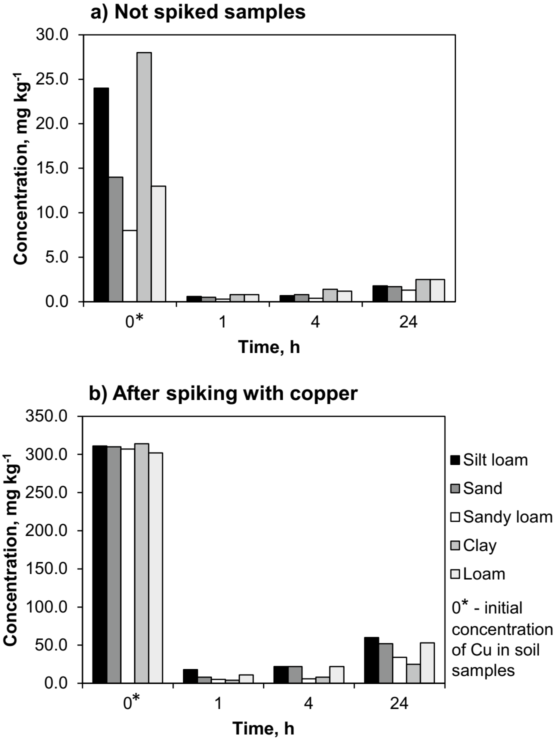

Figure 3.6. Copper leaching with time from soil samples with various texture by adding 10 % of Portland cement: a) for not spiked samples, b) after spiking with copper (300 mg kg^{-1})

Comparing leaching results in a time period, a proportional difference was observed between the results gained from the eluate in 1 h and 24 h both from not spiked and spiked soils bound with cement. The ratio between the leached Cu in 24 h and the amount after 1 h of agitation for not spiked bound soils varies from 2.46 to 3.78 (average

2.97), but for those spiked with Cu – between 3.31 and 6.98 (average 5.38). The difference between the results of 4 h and 1 h agitation has shown that a faster leaching has been detected for samples with different soil particle size distribution. It is possible that the particle size in bound S/S remediated soils has some role in the leaching process.

Nevertheless, according to the description in field notes, sandy loam itself has a very heavy and dense structure as clays do. The leaching results show a trend of diminished leaching for heavy sandy loam and clay. It is possible that contaminants such as copper in this case are leaching less not because of particle size, but it is more due to the presence of more clay minerals in bound matrix.

Further experiments were performed in order to gain more information for field case study samples from the contaminated sites. Physical stabilization provides less leaching because of a less intense groundwater and precipitation impact as compared to the 24 h batch leaching test. Tank tests as well as column leaching tests can be applied in order to get additional results with less extreme leaching results closer to the real environmental model. This experiment has shown that less intense copper leaching is characteristic to soils with texture classes of sandy loam and clay.

3.2.2. Stabilization/solidification efficiency testing for case studies

Natural soils are often complex assemblages of soil fractions, components and possibly contaminants, and S/S treatment introduces new components which react through complex chemical interactions to produce more stable forms with less mobile components (John et al., 2011). However, long-term effectiveness and chemical durability of S/S-treated materials are still not well known. This creates a scenario where evaluations of stabilized material are undertaken without an understanding of the interactions and controlling factors. Leaching time could represent one of the most important factors that influence the release of metals during a batch test. The time may influence the quantity of contaminant leached, unless equilibrium conditions are established.

An important and representative study was carried out as part of pre-investigation in the contaminated area “BLB Baltijas Termināls”. This area has been under anthropogenic industrial impact for 150 years; the results show that the studied territory is contaminated with As, Cu, Zn, Pb and also with Cd, Ni, Cr and Hg. The average soil contamination level exceeds the acceptable legal norms in Latvia: 13.5 times for As, 20.6 times – Cu, 6.6 times – Pb, and the legal acceptable level is also reached for Zn and Hg. Due to extremely high concentrations of heavy metals in the soil of the researched area, the stabilization/solidification technology was chosen as the potential remediation tool because other technologies cannot reach the required efficiency due to the amount and concentration of metals in soil. Area is highly industrial and is a valuable part of the port, so the excavation of soil and transporting is not advisable because in this case activities of port must be stopped, also the area has high groundwater level.

Soil samples from six case study areas (including BLB Baltijas Termināls and Vega Stividors) were taken and representative averages chosen, which were then stabilized with the Portland cement as described in the methodology chapter. Leaching tests were performed and those showed that the *zero sample* (non-stabilized) has unacceptable amounts of leached heavy metals – Cu, Pb and Zn and metalloid As.

Leaching tests were performed for five types – non-stabilized soil, stabilized with 5 %, 10 %, 13 % and 20 % Portland cement. The experiments were done using standard BS EN 12457-2, eluate analysis was performed with ICP-MS. Table 3.3 shows the efficiency of stabilization for soils heavily contaminated with Cu, Pb, Zn and As.

Leaching test results for not stabilized and stabilized/solidified soils (mg kg^{-1}) (samples for S/S testing from BLB Baltijas Termināls and Vega Stividors areas). *N*=10 for each performance (50 in total).

Further experiments were done with contaminated soils from other contaminated areas described in previous chapter where case studies were described and overall characteristics given. Next two tables represent brownfields with less contaminated soil than in BLB Baltijas Termināls and Vega Stividors case.

Leaching test results for not stabilized and stabilized/solidified soils (mg kg^{-1}) (samples for S/S testing from Selmash area). N=10 for each performance (50 in total).

Table 3.3

Leaching test results for not stabilized and stabilized/solidified soil samples derived from contaminated territories

Element	Initial concentration of element in the original sample, mg kg^{-1}	Concentration in leachate, mg kg^{-1}				
		From not stabilized samples	From samples with addition of Portland cement at different rate			
			5 %	10 %	13 %	20 %
Determined pH		3.2-4.3	10.5-10.8	10.7-10.9	11.0-11.3	11.4-11.6
BLB Baltijas Termināls* and *VEGA Stividors**						
As	115-1580	0.02-0.13	0.02-0.43	0.08-0.67	0.08-0.64	0.07-0.69
Cu	231-1120	111-600	1.0-4.2	0.3-1.2	0.1-1.7	0.01-0.85
Pb	55-15033	1-17	0.01-1.17	0.03-0.46*	ND	ND
Zn	471-2820	12-577	1.2-7.2	0.9-3.6	0.2-3.2	0.1-2.1
Selmash**						
Cu	13-176	0.23-0.65	0.01-0.09	0.03-0.15	0.03-0.14	0.01-0.16
Pb	25-180	0.12-0.87	ND	ND	ND	ND
Zn	22-1352	4-342	1.0-11.8	0.5-2.73	0.01-0.45	0.01-0.99
22 Katlakalna Str., "Jaunais Mežaparks" and "Freja" samples**						
Cu	14-158	0.15-1.12	0.01-0.09	0.01-1.2	0.01-1.7	0.01-0.85
Pb	12-100	0.12-0.76	ND	ND	ND	ND
Zn	11-473	0.56-112	0.21-10.7	0.05-2.6	0.03-1.2	0.01-3.1

**ND – not detected*
*** Number of samples: n=5*

Leaching tests have shown that heavy metals such as Cu, Pb and Zn leach from *zero samples* at unacceptable amounts if compared to the, e.g., UK legislation applied for stabilized/solidified soil. Solidification with the Portland cement diminishes leaching, and the results show that the S/S remediation method has a high efficiency on heavy metals. As in general is not very mobile in the low pH as it can be seen in Table 3.4., however,

Table 3.4

Allowed concentration of elements in leachate after the use of S/S method set by legislation of United Kingdom

Element	Concentration set by legislation in United Kingdom, mg kg^{-1}
As	2
Ba	100
Cu	50
Ni	10
Pb	10
Zn	50

leached As can become more mobile outside the soil if washed out from the site and become much more toxic.

The total of 50 samples from BLB Baltijas Termināls and Vega Stividors (site heavily contaminated with heavy metals), 50 samples from the former agricultural machinery "Selmash" factory and 50 – from the former wooden and three military industry areas were analyzed on leaching in case the S/S technology is applied in remediation. Leached eluates from non-stabilized samples and ones stabilized with different proportions of cement, were analyzed after continuous 24 h agitation by using ICP-MS. The pH_{H2O} values of all leachates from bound samples were essentially alkaline in all cases, but not bound samples had much lower values (Table 3.3).

According to the environmental quality research data from *BLB Baltijas Termināls and Vega Stividors areas* given in Table 3.1 and 3.2, it can definitely be seen that the soil in the whole area is contaminated with heavy metals, mainly with Cu, Zn, As and Pb. The S/S technology can be applied for such contaminated areas, especially to elements such as Cu, Pb and Zn, which are most widely distributed in the Freeport and other industrial territories and brownfields. As it can be seen in this and other cases, e.g., "Selmash" factory brownfield, in Table 3.3, stabilization is effective, and for Cu, Pb and Zn leaching from S/S treated samples is 100-1000 times lower than from *zero samples*. Generally it can be stated that diminishing of heavy metal leaching is obvious for some elements, but not so good for other, e.g., As. The selected percentage of the binder material in samples was 5 %, 10 %, 13 % and 20 % to find the best composition. From the environmental point of view, the 10-13 % proportion is good enough as it guarantees sufficient efficiency to deintensify the leaching process. Further studies would be required in the field of leaching analysis and application of the S/S technology for industrial site remediation if the contamination is as high as in BLB Baltijas Termināls case study. Other areas (Table 3.3) can also be treated by the S/S technology in remediation, however, other technologies are probably more applicable such as *gentle* remediation (description at GREENLAND project, 2014) with soil amendments, phytoremediation; excavation at *hot spots* can be done as it is considered to be cheaper and more environmentally friendly.

Geotechnical aspects. Compression tests for contaminated soils in order to research the bearing capacity and find the best proportion of binder material have shown that 5 % cemented soil has sufficiently good properties for using it, e.g., for roads and one-stage warehouses as the bearing capacity is 7MPa after 28 days of testing. Freeze-thaw tests were performed as well. 10 % and 20 % Portland cement additive to contaminated soil increases the bearing capacity and physical strength of the solidified mass and is therefore better to use in applied projects. The physical strength of the solidified blocks means less intense leaching of metals and As.

Compression strength testing in the pilot study provided data that after 28 days the solidified soil with 10 % of the cement had the value of 3.8 MPa. To determine the main aspects and problems for a real case study of S/S technology application in BLB Baltijas Termināls contaminated area, additional compression strength tests were done simultaneously with freeze-thaw resistance studies for solidified samples bound with 5 %, 10 % and 20 % Portland cement (Fig. 3.7). The results are given in Table 3.5.

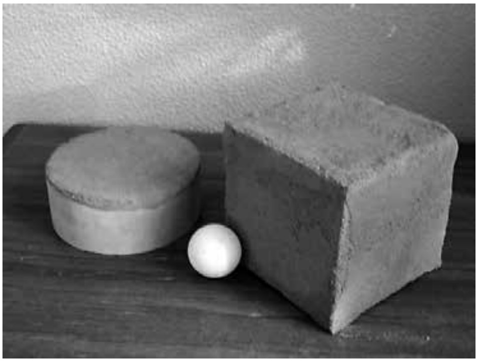

Figure 3.7. Solidified contaminated soil samples stabilized with Portland cement (author's photo)

Table 3.5

Compression strength and freeze-thaw resistance for samples solidified with Portland cement

Content of Portland cement PC500-D20, %	Compression strength (7 days), MPa	Compression strength (28 days), MPa	Compression strength (28 days) after 50 freeze-thaw cycles, MPa
5	0.9	1.6	0.3
10	2.5	3.8	1.5
20	7.1	8.4	8.5

The compression strength of samples is highly dependent on the proportional content of cement, as it can be seen in the testing results given in Table 3.5. Freeze-thaw testing has shown that the physical impact of natural processes will be harmful for 5 and 10 % cemented soil without special additives for improving geotechnical parameters. An interesting detail is that the soil bound with 20 % Portland cement after 50 cycles of freeze-thaw impact shows increased compressive strength. All of the samples after the freeze-thaw impact experienced mass loss, inversely proportional to the content of cement in the sample.

Remediation of contaminated areas by the stabilization/solidification (S/S) technology is closely connected with the development of engineering science and empirical knowledge supported by new research done in this field. Leaching tests provide information about the behaviour of different contaminants in stabilized soils. A series of research was performed in industrial areas with a high, medium and low heavy metal contamination level and improved the effectiveness of the S/S technology in all the cases. Freeze-thaw resistance and compression strength data analysis indicates that the soil bound using only the Portland cement without any other additives does not provide satisfactory geotechnical properties for further solidified land use in construction, therefore additives to improve the binder recipe were studied for leaching parameters and are described in the next sub-chapter.

3.2.3. Municipal solid waste incineration bottom ash as amendment in stabilization

Stabilization/solidification (S/S) technologies for soil remediation have been used for decades in order to get waste contaminants to a more chemically stable form, thereby resulting in a more environmentally acceptable waste form. To ensure the best available technologies for stabilization, additives should be used for increasing the mechanical strength of the contaminated stabilized soil. One of the approaches is to use municipal solid waste incineration (MSWI) bottom ash for increasing the geotechnical stability of the soil, thereby extending the lifetime of immobilized solidified soil. Leaching of heavy metals can be decreased by increasing the physical strength of the stabilized soil. Stabilization of contaminated soils in industrial areas and brownfields has the following benefits: 1) contaminated soils are immobilized; 2) compressive stability of S/S remediated soils improves; 3) MSWI bottom ash as waste material is successfully used in construction. Geotechnical properties of the soil treated with the Portland cement (PC) can be improved when municipal solid waste incineration (MSWI) ash is used as the combined additive. Ash is composed largely of metal oxides and sulphuric compounds so the environmental impact must be evaluated if it is used as amendment in the cement industry.

The use of MSWI ash in the stabilization of contaminated soils was studied to obtain answers to the following questions: 1) does S/S contaminated soil gain a better geotechnical stability if MSWI bottom ash is used as amendment to binder; 2) is it environmentally safe and is leaching of heavy metals from contaminated soil and the ash still at acceptable levels. The aim of this part of research is to provide pilot batch experimental results for leaching of heavy metal compounds when S/S technology is used for contaminated soils using PC and MSWI bottom ash additives.

Stabilized/solidified waste acceptance criteria were used to evaluate the effectiveness of the treatment. This criterion was chosen because the S/S technology is widely used for treatment and two main parameters are measured for determination of the effectiveness of remediation – geotechnical strength (see previous sub-chapter) and leachability limits. Regulatory limits at a disposal site in the United Kingdom (Sollars and Perry, 1989) are given for Cu, which is 5 mg L^{-1} or compared to the results in Table 15, would be 50 mg kg^{-1}, if the L/S ratio 10:1 is applied.

Mineral soil samples from the depth interval of 2-5 m in the Daugava floodplain area in Rīnūži, Rīga City, with the properties 70-90 % sand, 10-30 % silt and cation exchange capacity 0.003 mmol g^{-1}, were spiked with copper pentahydrate (ReagentPlus, >98.0%) in known concentration of 300 mg kg^{-1} and mixed with MSWI bottom ash and PC.

Table 3.6

Concentration of elements in samples of MSWI bottom ash determined using X-ray fluorescence spectrometry method and concentration of elements in leachate from soil samples stabilized by adding 15 % of Portland cement and 35 % of MSWI ash after spiking with copper (300 mg kg^{-1})

Element	Concentration (c_{min}-c_{max} (c_{mean})) of element, mg kg^{-1}	
	In MSWI bottom ash	In leachate from stabilized soil samples
As	0.4-20.9 (4.1)	0.03-0.10 (0.06)
Ba	34-600 (268)	0.07-1.30 (0.54)
Co	6.0-16.3 (11.9)	0.03-0.06 (0.04)
Cu*	26-107 (55)	0.90-13.00 (3.92)*
Mn	48-453 (166)	0.03-0.20 (0.08)
Ni	2.3-19.4 (11.1)	0.04-0.14 (0.08)
Pb	5-241 (70)	0.20-0.60 (0.31)
Rb	4.1-17.8 (11.6)	2.00-5.30 (4.15)
Sr	39-130 (80)	0.40-9.50 (4.05)
V	12.0-32.6 (23.7)	0.24-5.70 (1.44)
Zn	73-2904 (636)	0.03-0.22 (0.09)

**Cu concentration after spiking of soil, stabilizing using MSWI ash and performance of leaching test*

MSW was incinerated at high temperatures in order to get the residual comparable to a real incineration process at an industrial facility. The amount of major elements were found in high concentrations in the MSWI, such as Ca (13.7-21.3 %), Al (1.0-8.0 %), Cl (0.7-10.0 %), Fe (0.5-2.2 %), K (1.1-3.5 %), Mg (3.0 %), P (0.4-1.4 %), S (0.7-3.3 %), Si (3.0-15.0 %), Ti (0.4-3.2 %). The primary purpose of MSWI bottom ash is to improve the physical stability of solidified mass and assist to the Portland cement (PC).

The control samples spiked and not spiked with PC have shown no significant differences in terms of leaching as compared to bound with both MSWI bottom ash and PC. That means that the addition of PC is strong enough to prevent copper (Cu) from leaching without the assistance of ash. The blank has shown no significant amount of heavy metal leaching; the pH level of eluate was 6.7.

The obtained results have shown that the soil stabilized with MSWI bottom ash and PC has diminished levels of leaching and it is at an acceptable level. The results show that the S/S remediation method has high efficiency in respect to heavy metal binding (Table 3.6). The regulatory limits of England and Wales (Statutory Instruments…, 2005) for non-hazardous monolithic waste for metals are not exceeded; the limits are given in Table 3.4 in order to provide a general overview.

The pH level for the eluate from the batch experiment ranged from 10.0-11.5. The soil sample originally does not contain a significant amount of heavy metals nor the PC does, therefore the leaching of heavy metal compounds can be calculated. Arsenic (As) leaching from stabilized samples is not highly dependent of its amount in the parent mass of MSWI bottom ash, the leaching is quite constant and does not exceed 5 % of the permitted level under the UK legislation. The main interest in this study is the amount of copper (Cu) leached from the spiked mass, stabilized with MSWI ash and PC. Leaching is observed in the eluate from some of the samples, but does not exceed the safety threshold. The contamination of Cu is very well immobilized in the mass combined at the batch experiment and is not a subject of concern. The next element of interest from the environmental point of view is lead (Pb); the leaching is also relatively constant and not higher than 8.7 % of the permitted level under the UK legislation. Heavy metals and other elements are also well included in the stabilized mass – the leached mass concentration in the eluate is only 0.009 % for Pb, same as zinc (Zn), which has negligible leaching (0.03 % from the total mass of ash) according to the experimental data. Nickel (Ni) has just 0.006 %, barium (Ba) 0.002 %, As 0.015 %, cobalt (Co) 0.003 %, Cu 0.012 %, manganese (Mn) 0.0006 %, vanadium (V) 0.06 % of the mass leached out from the total mass of stabilized spiked soil.

3.3. 'Gentle' remediation for heavy metal remediation by soil amendments

Different technologies are used for the remediation of diffuse and point sources generated by industrial as well as natural contamination; over the last decades the so-called *gentle* remediation (description at GREENLAND project, 2014) techniques are on the spotline in Western Europe and USA. In the previous chapters, it was already determined that *hard* remediation (stabilization/solidification) shows promising results if applied in contaminated areas, however, this will not always be the best choice from different points of view – environmental, economic, technology and other aspects.

Toxic heavy metal ions are non-biodegradable and tend to accumulate in living organisms causing severe disorders, and this is the reason why areas contaminated with heavy metals even at medium and low levels must be assessed for possible clean-up actions. *Gentle* remediation (description at GREENLAND project, 2014) and particularly soil amendments can often be promising for the rehabilitation process of contaminated soils. Soil amendments can be inorganic or biological, synthetic or natural; combinations are possible as well.

Natural zeolites are one of the options – those are not as good as synthetic ones, but clay minerals can in many cases be used as good sorbents for heavy metal removal – it means the immobilization of heavy metals in soil as well as capture from municipal or industrial wastewaters.

Therefore, in the present study part of the effort was dedicated also to prospective types of optional soil amendments – various clay types, modified species were used with improved sorption properties, and detailed research was dedicated to $CaCl_2$ and hydroxyapatite modified clay due to the novelty aspect and high interest as it is a prospective resource in Latvia. Lead Pb(II) and copper Cu(II) were chosen as model contaminants, as those are the most widespread contaminants among 56 heavy metal contaminated sites in Latvia (NRCT, 2014) and also have similar chemical properties.

Sorption considering the ion exchange mechanism was studied using lead as the model contaminant; copper was used for bioavailability studies using ionometrical research. Lead and copper are pollutants often found in soils of historical contamination worldwide. Cement amendments are used as *hard* remediation in case of the S/S technology, hence clay can be used in the so-called *gentle* (description at GREENLAND project, 2014) remediation as a soil amendment with a lower impact on the soil, used as a sorbent for heavy metals when mixed in soil.

3.3.1. Physical chemical properties of soil amendments

During prior experiments, the physical chemical properties of Quaternary and Devonian clay and modified species were determined. Granulometric, basic mineralogic, cation base saturation, methylene blue sorption analysis was carried out for all the clay used for efficiency testing. Physical chemical properties for most effective soil amendments (clay sorbents) according SEM, BET, FTIR and XRD methods were determined for raw and modified clay species.

The Lielauce Quaternary clay deposit is located in SW Latvia. The thickness of the deposit productive layer is between 1.1 and 5.3 m. Those are mostly illitic clays with the amount of clayey fraction (<0.005 mm) varying between 36 and 43 % (National Research Program, 2010).

The Devonian Liepa clay deposit is located in NE Latvia, the thickness of the deposit varies and it contains illite with chlorite; the deposit contains two types of clay – the red and greyish-blue (National Research Program, 2010). In the present thesis, the red type was used for modification purposes. Further on, the description of important properties for sorption are given for raw and modified species of Quaternary Lielauce and Devonian Liepa red type clay, performed by methylene blue sorption determination and BET surface analyses (Table 3.7).

As can clearly be seen, the surface properties are relatively better for Lielauce Quaternary clay rather than Devonian red clay, however experiments were performed with both stratigraphic types of clay. Raw clay binding capacity according to both methods, further leaching experiments and sorption kinetics studies have proved the hypothesis that modified species have greater immobilization of cations (heavy metals) if amended to soil or used for theoretical heavy metal contaminated wastewater treatment. Increasing of the proportion of Ca by modification (using of $CaCl_2$) increases the binding capacity according to methylene blue and BET specific surface analysis data.

A further SEM analysis was done for HAp modified Lielauce clay in order to determine the structural image for modified species. XRD and FTIR analyses were performed to describe the physical structure of raw clay as compared to HAp modified species.

The topography of the surfaces was studied to confirm modification and characterize differences between the carriers (Fig. 3.8). As the best Pb (II) sorption properties were observed for HAp modified clay, SEM pictures were taken to compare HAp modified Quaternary Lielauce clay and raw clay. The SEM pictures confirm increasing crystalline

Table 3.7

Raw Quaternary and Devonian clay and modified species according to methylene-blue sorption and Brunauer-Emett-Teller (BET) surface tests

Sample	Methylene-blue sorption, mmol g^{-1}	BET surface, m^2 g^{-1} (according to Langmuir isotherm)
Raw Devonian Liepa clay	0.11	24.3
Raw Quaternary Lielauce clay	0.13	49.9
Devonian clay modified with 5wt% FeOOH	0.04	69.2
Quaternary clay modified with $CaCl_2$	0.17	84.8
Quaternary clay modified with NaCl	0.01	23.6
Quaternary clay modified with HAp* 1.67 Ca/P equimolar proportion	0.04	71.0
Quaternary clay modified with HAp 1.5 Ca/P equimolar proportion	0.05	84.4
Quaternary clay modified with HAp 1.0 Ca/P equimolar proportion	0.08	104.6
Quaternary clay modified with HAp 0.5 Ca/P equimolar proportion	0.12	111.2

**HAp – hydroxyapatite*

complexity of the structure within hydroxylapatite crystals on the surface. Those crystals can support the ion exchange at micropore level by the ability to add heavy metal ions. The surface of clay (HAp Ca/P 0.5 equimolar concentration as seen in Fig. 3.8(b) with monetite crystals; these minerals are facilitating the sorption of heavy metals based on ion exchange.

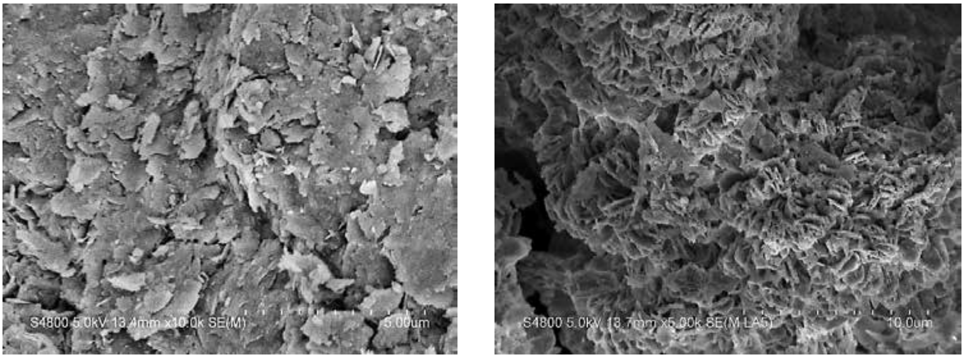

Figure 3.8. The surface of raw (on the left) and HAp modified Lielauce clay sample in 0.5 Ca/P equimolar proportion (monetite) (on the right)

The HAp modified clay in Fig. 3.9 shows that modified clay has XRD patterns characteristic to additional minerals appearing on raw clay.

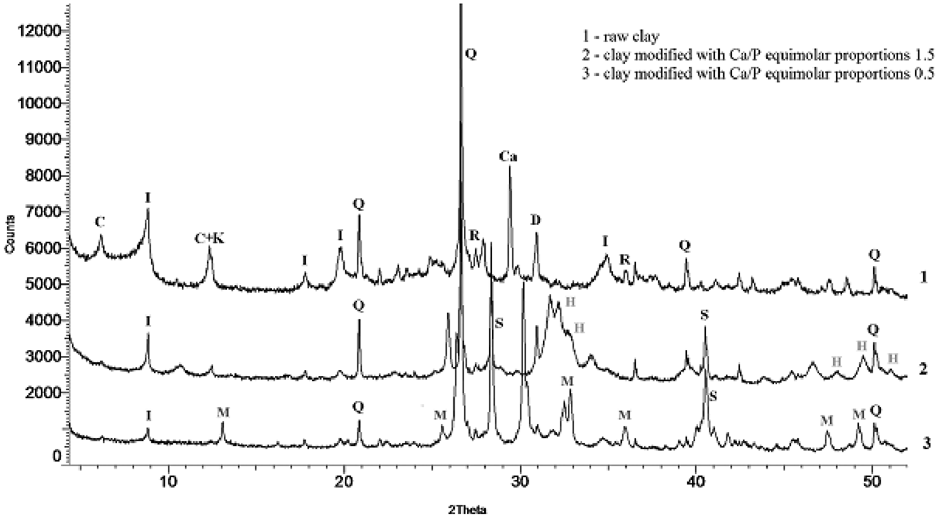

Figure 3.9. The XRD spectra for the raw clay and modified with Ca/P equimolar proportions 1.5 and 0.5, respectively. Q – quartz, D – dolomite, K – kaolinite, I – illite, Ca – calcite, C – clinochlore, R – rutile, H – hydroxyapatite, M – monetite, S – silvite

Raw Quaternary clay – not modified, has a typical clay mineral dominance and no presence of monetite and hydroxyapatite (curve 1). The X-ray powder diffraction pattern for the sample modified in 0.5 Ca/P equimolar proportion shows characteristic diffraction reflections of monetite at 12.9°; 25.5°; 32.8°; 35.7°; 49.2° and 47.5° 2θ scale (curve 3), but the sample modified in 1.5 Ca/P equimolar proportion shows diffraction reflections characteristic to hydroxyapatite at 32.2°; 32.8°; 49.5°; 47.9° and 50.9° 2θ scale (curve 2).

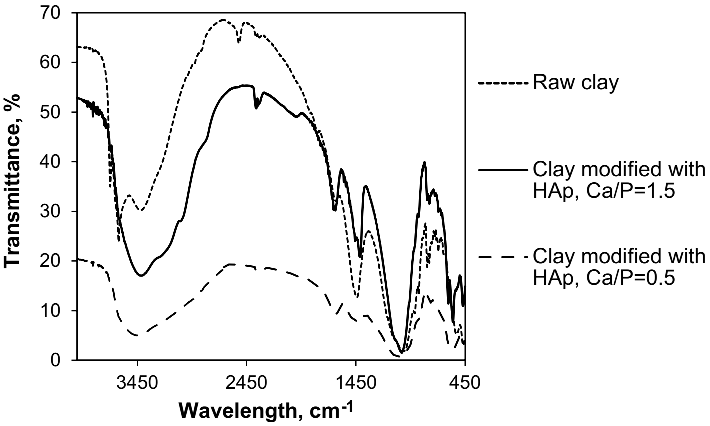

Figure 3.10. The FTIR picture for the raw Quaternary Lielauce clay, modified with HAp with Ca/P equimolar proportions 1.5 and 0.5, respectively

The Fourier transform infra-red spectrosopy (FTIR) performed to Quaternary Lielauce clay samples and modified species was followed by establishing the ratios between the main absorbance peaks; the slopes are rather flat as the clay is composed of a variety of different minerals. Monetite has even more flat spectra as the structure is getting more complex (Fig. 3.10). However, typical for Quaternary Lielauce clay, illite can be determined absorbance peaks in all samples around 3630 cm^{-1}, representing OH-groups of crystalline hydroxyl (hydrated illite). Illite can also be represented in 470, 550, 850, 910 cm^{-1} as it is described in (Oinuma and Hayashi, 1965; Vaculikova and Plevova, 2005). All curves represent water at 1650 cm^{-1}. Carbonates are situated at 1480 and 1420 cm^{-1}, but small peaks at 800 can be Si-O bonds (Vaculikova and Plevova, 2005). Phosphates of hydroxyapatite can theoretically be seen at 600 and 1030 cm^{-1}; however, clay minerals are hiding pronounced view.

3.3.2. Efficiency of soil amendments – sorption kinetics and leaching tests

Leaching experiments and sorption kinetics are experimental methods which allow determining the efficiency of sorption of soil amendments and test it in laboratory conditions in order to promote the further use in field scale and not waste a lot of resources and time if the specific amendment is not effective in the specific circumstances. First, the most widespread contaminant was chosen for sorption kinetics tests – lead.

The Quaternary Lielauce quarry clay was chosen as it is typical resource – it is relatively easy to extract and use for applied industries. Lead was chosen as the model contaminant as it is one of the most widespread contaminants from the range of heavy metals (NRCT, 2014; Annex I).

Kinetic experiment results for raw Quaternary Lielauce clay and its modified species: protonated, $CaCl_2$ and NaCl modified. An experimental test system was designed in order to prove the sorption of lead from 50 mg [Pb] L^{-1} solution obtained by dissolution of $Pb(NO_3)_2$ in distilled water. Three types of Quaternary Lielauce modified clays were compared with the raw clay. Kinetic experiments are a tool for the evaluation of sorption properties for materials, allowing the testing of new sorbents in order to choose the best applicable methods for the remediation process.

In order to determine equilibration, sets of experiments should be performed by using different concentrations of spiked solutions and various temperatures; the amount of sorbent and the pH can be varied. The easiest way is a study of sorption as a function of time. Raw Lielauce clay was compared to protonated, $CaCl_2$ and NaCl modified species.

As it can be seen from graphs in Fig. 3.11, processes reach equilibrium in approximately one to three hours, after which the saturation is reached. The sorption of lead onto raw clay achieves 30-35 mg of lead for g of sorbent under natural conditions. Sodium modified clay achieves higher sorption in the first hour compared to the raw clay, but the effect is not continuously growing with time. The pH of the spiked solution was lower by about 0.2-0.7 units than for distilled water; however, it was adjusted to 5.0. After experimental series, the pH increased for about 0.5-0.7 units compared to the beginning. Around 40 % of lead was sorbed in the first 10 minutes of the experiments.

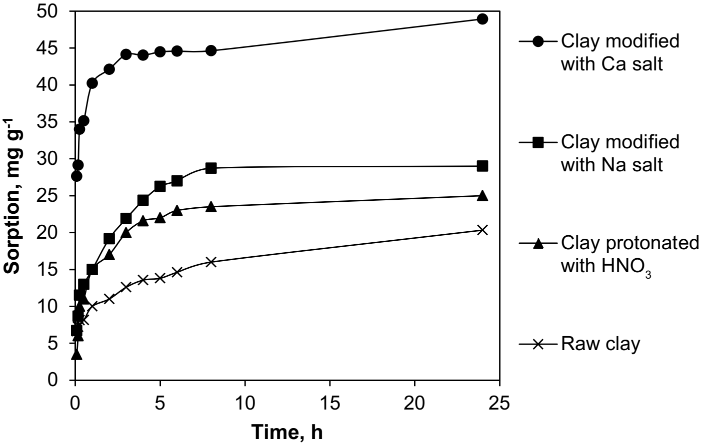

Figure 3.11. Lead sorption kinetics by Quaternary Lielauce raw, protonated, Na modified and Ca modified clay at spiking concentration of Pb 50 mg L^{-1}

There is a slightly lower sorption efficiency for raw than protonated and Na modified clay. In terms of the sorption efficiency process as a function of time, the shape of the curve is more flat, the sorption process is slower, but still continues for a long period of time. The most effective results were obtained from Ca modified clay testing and the effect is significant. Ca modified clay have a growing sorption curve and in 24 h it reaches around 50 mg g^{-1}. 6 % of lead remained in eluate after 24 hours of treatment. Calcium modified clays are reasonable for use as the lead sorption agent for soil amendment production and can probably be tested for industrial wastewater treatment, and can as well be chosen for further analysis of feasibility in different environmental conditions. A further study of sorption kinetics at different temperatures and pH to determine the influence of experimental conditions were done with Ca modified clay.

Sorption kinetics at different temperatures show that sorption are faster if the temperature is higher (Fig. 3.12); pH experiment confirms that pH 4.0-5.0 is the best for the highest sorption efficiency (Fig. 3.13).

100 mg L^{-1} Pb sorption kinetics was additionally tested in order to test the efficiency of Ca modified clay sorbent and compare with the raw clay. The efficiency of Ca modified clay was better than for the raw clay by 20 % (Fig. 3.14). Sorption was lower when tested at 50 mg L^{-1} Pb contamination; if the solution has more lead, the sorption efficiency continues to increase.

Ca modification of Quaternary Lielauce clay showed good sorption efficiency results, however, there are still options for increasing the sorption capacity. Therefore, based on logical assumptions, literature analysis (Corami et al., 2008; Šljivić et al., 2009b; Shaltout et al., 2011; Zhan et al., 2012) and previous research by the author, hydroxyapathite was chosen as the direction of sorption kinetics research.

The test of hydroxyapatite modified clay on 50, 100, 200, 250, 300, 500, 800 and 1000 mg L^{-1} Pb solutions in room temperature and adjusted to pH 5.0 was performed (Fig. 3.15). The experiments showed that hydroxyapatite modified clay has a higher

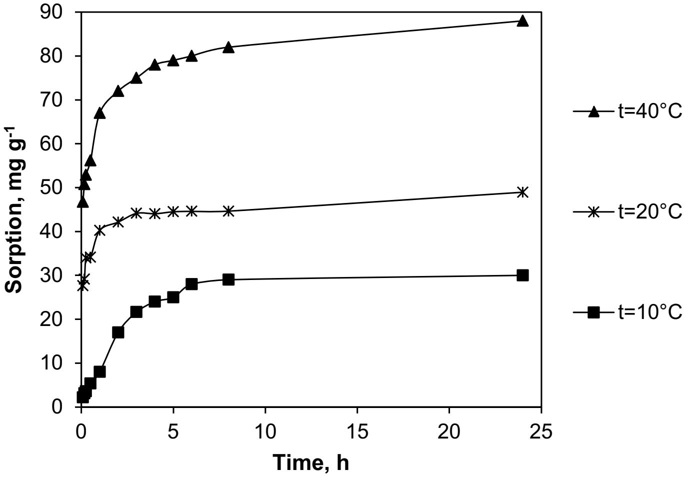

Figure 3.12. Lead sorption by Ca modified clay at spiking concentration 50 mg L^{-1} in different temperatures

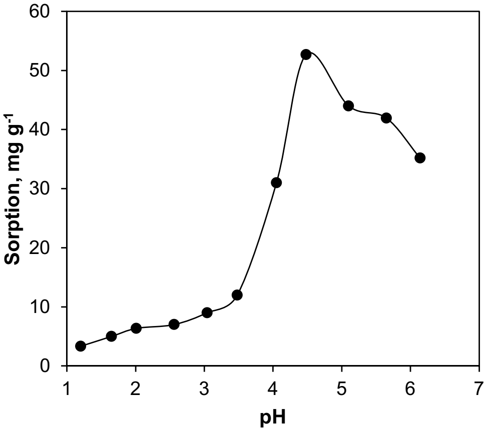

Figure 3.13. Lead sorption by Ca modified clay at spiking concentration 50 mg L^{-1} in different pH environment

efficiency – with the same dosage of sorbent for 50 and 100 mg L^{-1}, the efficiency was nearly 100 % (eluates showed the concentration of Pb under the detection limit even in samples with 5-minute stirring).

Increasing of the lead concentration in spiked solution up to 200, 250, 300, 500, 800 and 1000 mg L^{-1} confirmed that sorption can reach up to 700 mg g^{-1} and equilibrium in terms of concentration is reached approximately within the range of 250-300 mg L^{-1}.

Sorption at 300 mg L^{-1} for raw clay has shown that less than 40 % of lead is sorbed from the spiked solution in total. However, the hydroxyapatite modified clay has better performance as the sorption efficiency is higher (Fig. 3.16).

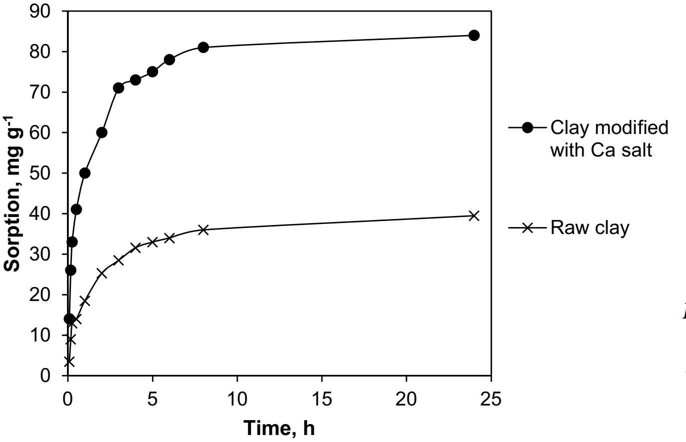

Figure 3.14. Lead sorption by raw and Ca modified clay at spiking 100 mg L^{-1}

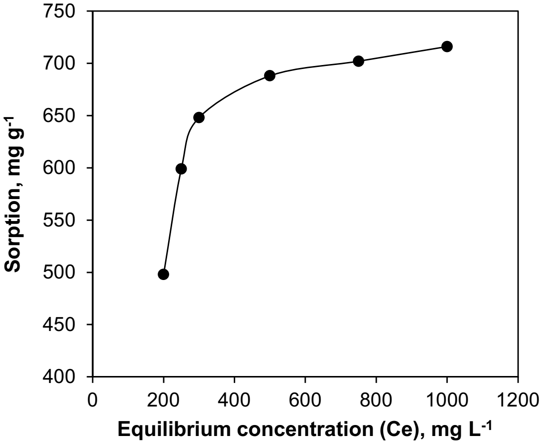

Figure 3.15. Lead sorption by Lielauce clay modified with hydroxyapatite for lead solution at concentrations 200, 250, 300, 500, 800 and 1000 mg L^{-1}

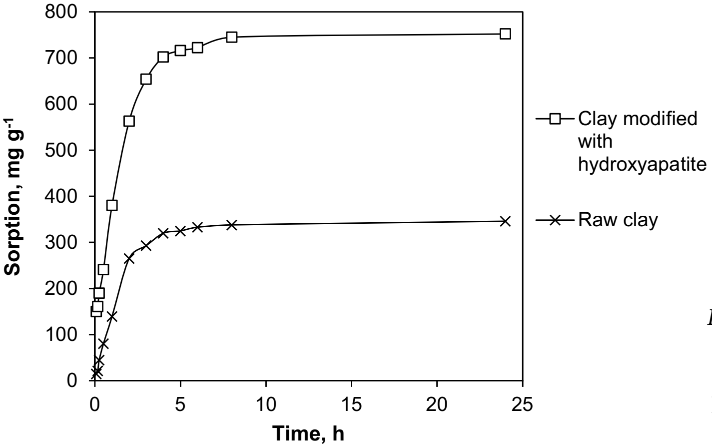

Figure 3.16. Lead sorption by Lielauce clay raw and modified with hydroxyapatite at spiking concentration 300 mg L^{-1}

Sorption efficiency from sorbents described above is highest for hydroxyapatite modified clay compared to others. Sorption reached 700 mg of lead per gram of sorbent thus exceeding the result achieved by raw clay more than two times. Hydroxyapatite crystals can support the ion exchange by the ability to include lead ions into crystal structure.

The reason is a successful Ca exchange as well as formation of Pb-Ca hydroxyapatite as it is described in schematic chemical formulas (formulas 5 and 6). A single Pb (II) cation can substitute Ca(II) in the CaHAp lattice, which leads to distinct geometries, referred to in the following as Pb(Ia), Pb(Ib) and Pb(II), respectively (Ellis et al., 2007).

$$Ca_{10}(PO_4)_6(OH)_2 + 2H^+ \rightarrow 10Ca^{2+} + 6PO_4^{3-} + 2H_2O \qquad \{5\}$$

$$10Pb^{2+} + 6PO_4^{3-} + 2H_2O \rightarrow Pb_{10}(PO_4)_6(OH)_2 + 2H^+ \qquad \{6\}$$

These trends of Ca-Pb exchange were detected also during this study with hydroxyapatite modified clay and solution spiked with initial lead concentration 270 mg L^{-1} (Fig. 3.17).

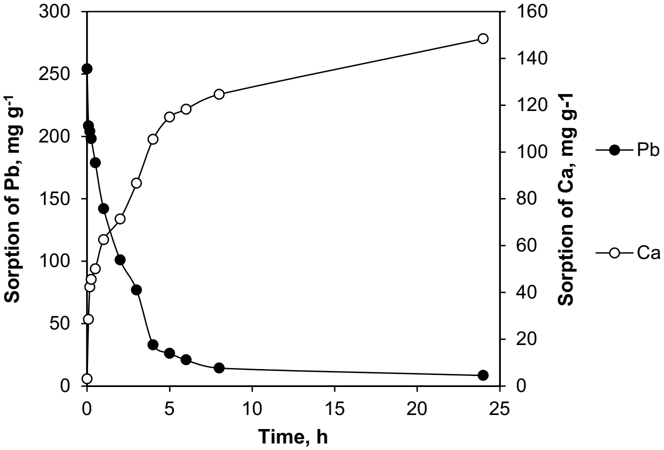

Figure 3.17. Ca-Pb exchange during Lielauce clay modified with hydroxyapatite sorption process (initially spiked solution 270 mg L^{-1})

An experiment was carried out to evaluate disturbances created by the presence of other ions. The spiked solution was prepared with the following initial concentration: Pb 270 mg L^{-1}, Zn 350 mg L^{-1}, Ni 100 mg L^{-1} and Cu 150 mg L^{-1}. The results after three hours of agitation for eluates with hydroxyapatite modified clay sorbent were as follows: the concentration of Cu diminished by 22 %, the amount of Zn and Ni remained almost unchanged, whereas the concentration of lead diminished to 34 mg L^{-1} (87 % were sorbed). Modified clays can be recommended as a reasonable sorbent for use as the lead and probably copper sorption from industrial wastewater, and can be chosen for further analysis of feasibility in different environmental conditions. Based on the present study, hydroxyapatite modified species can be defined as the most applicable ones and further research is highly recommended.

Sorption experiments alone are not enough to be used for describing the efficiency of heavy metal immobilization in soil; therefore, leaching experiments for different types of clay and its modified species as well as various concentrations of contaminants in soil were performed. After that, sequential extraction and ionometry were used as additional methods for gaining extra proofs.

Leaching tests for soil amendment studies were performed with raw Quaternary and Devonian clay from various quarries; some types of clay were modified with hematite (FeOOH), similar to sorption experiments protonation (HNO_3), Na and Ca modification was performed and in the end, various Ca/P equimolar concentrations with hydroxyapatite were tested.

Leaching experiment results for FeOOH modified Devonian clay. Leaching experiments for lead were performed in the same manner as with stabilized soils described in the previous chapters. The pH_{H2O} values of all samples were common for natural conditions 5.0-6.7 and during the agitation pH_{H2O} was increasing or not significantly changing in all cases. This trend is dictating the behaviour of lead during the leaching experiment.

Table 3.8 depicts the results of leaching from soils of different texture, where no amendments, raw Devonian clay and two different types of clay modified with FeOOH were added. Soil with a higher content of silty and clayey particles with no amendment diminishes the leaching of lead under natural pH conditions, so, basically, there is no practical need to amend it with special additives.

A small increase of immobilization of lead ions in soil happens if Devonian clay modified with FeOOH is added. The immobilization efficiency increases by 5-10 %. There is no significant change of immobilization efficiency if more FeOOH is applied in the clay, however, in general leaching of lead from spiked sandy soil samples with 100 mg kg^{-1} contamination is significantly diminished when Devonian clay is amended and the efficiency increases if modified Devonian clay with FeOOH is applied.

The benefits of Devonian clay modification with FeOOH for lead immobilization efficiency in soil under natural pH conditions are not high and the feasibility of this soil amendment is disputable. This discovery required for a search for other ways of modification for potential applied environmental soil remediation projects.

Leaching experiment results for different amendments. Experiments were performed in order to find out the efficiency of different sorts of raw and modified clay from various geological sites as soil amendment material for immobilization of heavy metal contamination in soil. The data has partly published in articles (Burlakovs et al., 2013c, d); the study also provides the comparison of soil amendment quantity, i.e., quantitative differences for the leaching of lead when raw Sātiņi clay is amended in a different amount. The quantitative amount of lead leached from soil significantly decreases when 5% of clay is added. When a larger amount of clay amendment is added (10 %), it plays a less significant role. 25 % of clay amendment immobilizes all of contamination in the given concentration of 100 mg kg^{-1}. 10 % amendment is added in all cases to dry soil mass, results are given in Table 3.9.

Table 3.8

Leaching experiment results for lead from soils of different texture amended with raw and modified Devonian clay

Soil texture	pH_{Cl} mean value	Leaching of lead*, mg kg $^{-1}$			
		In soil without amendment	After raw Devonian clay amendment	After modification (5% FeOOH) Devonian clay amendment	After modification (10% FeOOH) Devonian clay amendment
Sandy loam	4.88	2.08	1.65	1.45	1.58
Loam	6.54	0.64	0.49	0.47	0.49
Silt loam	5.24	0.39	0.48	0.31	0.31
Clay	5.75	<0.2	<0.2	<0.2	<0.2
Sand	4.23	2.45	1.67	1.55	1.46

** Leaching of lead from filtered soil samples found in eluates was measured in units mg L^{-1}; in Table 3.8 it is given recalculated with the rate L:S 10:1 and is therefore given for comparison also in mg kg^{-1} by arithmetically multiplying with 10*

Table 3.9

Leaching experiment results from soils (S1 – sand, S2 – silt loam, S3 – sand) of different texture treated by various clay amendments*

Type of amendment (10% of dry sample mass added)	pH_{KCl} start value / pH_{H2O} end value			Pb concentration in leachate from soil, mg kg^{-1}		
	S1 (silt content 2-5%)	S2 (silt content 80%)	S3 (silt content 0%)	S1 (silt content 2-5%)	S2 (silt content 80%)	S3 (silt content 0%)
Quaternary Sātiņi quarry clay	4.6/4.8	4.9/4.9	4.7/4.9	2.77	0.17	2.67
Zeiļu lake clay	5.7/5.7	5.7/5.9	5.8/5.6	40.2	0.38	36.8
Borovichi varved clay	5.2/5.1	5.7/5.9	5.4/5.6	29.3	0.26	24.8
Quaternary Lielauce clay modified in 1.6 Ca/P equimolar proportion (hydroxyapatite)	5.9/6.4	6.2/6.5	5.8/6.3	0.10	<0.02	<0.02
Quaternary Lielauce clay modified in 1.3 Ca/P equimolar proportion	5.5/6.2	6.2/6.2	6.0/6.1	<0.02	0.08	<0.02
Quaternary Lielauce clay modified in 1.0 Ca/P equimolar proportion	5.3/5.8	5.4/5.9	5.2/5.8	<0.02	<0.02	<0.02
Quaternary Lielauce clay modified in 0.5 Ca/P equimolar proportion (monetite)	5.4/5.5	5.3/6.0	5.2/5.4	<0.02	<0.02	<0.02
Devonian Liepa clay modified with 5% FeOOH	5.2/5.4	5.1/5.6	5.3/5.3	0.45	0.39	0.40

Devonian Liepa clay modified with 10% FeOOH	5.7/5.8	5.7/5.7	5.6/5.7	0.49	0.36	0.33
Raw Devonian Liepa red clay	4.8/5.1	5.2/5.2	5.1/5.0	32.3	<0.02	39.7
Raw Devonian Liepa grey-blue clay	4.6/4.9	5.1/5.4	5.0/5.3	42.1	0.06	39.2
Devonian Liepa clay modified with Ca salt	5.5/5.9	6.0/6.2	5.7/6.1	<0.02	<0.02	<0.02
Devonian Liepa clay modified with Na salt	5.0/5.2	5.3/5.5	5.0/5.2	0.04	<0.02	0.03
No amendment	4.8/4.9	5.1/5.0	4.7/4.7	54.2	2.15	52.7

** Leaching of lead from filtered soil samples found in eluates was measured in units mg L^{-1}; in Table 3.9 it is given recalculated with the rate L:S 10:1 and is therefore given for comparison also in mg kg^{-1} by arithmetically multiplying with 10. Standard deviation for AAS values varies in the range 0.89-8.9 %*

The pH_{H_2O} value for samples was mostly of natural neutral conditions pH 4.6-6.5 and during the 24 h agitation, pH_{H_2O} for eluates was not significantly changing. The soil sample with a higher content of silty particles (80 %) diminishes the leaching of lead even with no clay amendment. Sātiņi clay amendment increases the immobilization rate greatly for lead in spiked soils compared to Borovichi and Zeiļu clay.

All the modified clay amendments have a good lead immobilization efficiency, but most efficient are species modified with Ca, Na salts and hydroxyapatite. Unmodified Devonian Liepa clay as well as natural Borovichi and Zeiļu Lake clay decrease the leaching of lead from sandy soil with a low silt content, but the efficiency is not satisfactory.

To provide information about the leaching behaviour of heavy metal ions in a multi-component system, a leaching test was performed for soil spiked with Pb, Cu, Cd and Cr. Pure sand was chosen as the soil to disregard the influence of natural soil sorption capacity (a negligible influence exists anyway). Different Devonian and Quaternary raw and modified with various methods clay was used as 10 % amendment (Tables 3.9 for lead and 3.10 for multi-contaminants). The results are given and the best sorption on modified clay particles is reached in case of hydroxyapatite modification; therefore sorption kinetic data was confirmed.

The general results show that lead ions are more strongly immobilized in case of modified species as well as when more clay is added quantitatively, thus proving the general trend that lead ion immobilization is better in soils with a higher cation base saturation value. Immobilization of heavy metals in contaminated soil *in-situ* by using clay as amendment is an effective method for diminishing environmental hazards with low and average target concentrations and a relatively stable environment. Clay is a well-known immobilizing agent for heavy metal contaminants, and the most effective results for lead immobilization were achieved by using as soil amendment the Lielauce quarry clay modified by hydroxyapatite and Ca salts. In cases of contamination with different heavy metals, the highest soil amendment efficiency was reached for immobilization of Pb and Cu; a less effective treatment of soil was gained for Cd and Cr contamination, however, the results are promising also in multi-contaminant systems.

Table 3.10

Leaching intensity of Pb, Cu, Cd and Cr from sandy soil after soil amendment addition (10 wt %)

Clay material description	Extraction site	Raw / Modified	Element concentration in eluate*, mg kg^{-1}			
			Pb	Cu	Cd	Cr
Devonian clay – illitic with significant content of kaolinite	Liepa quarry, Priekuļi region, Latvia	Raw	123.5	136.3	34.3	46.0
		Modified with Fe-oxyhydroxide	8.5	35.6	27.9	44.1
Quaternary clay – mainly illitic	Sātiņi quarry, Saldus region, Latvia	Raw	99.2	87.9	38.3	44.4
		Modified with Fe-oxyhydroxide	10.3	42.4	41.0	39.3
Quaternary clay – mainly illitic	Lielauce quarry, Auce region, Latvia	Raw	99.1	101.3	34.8	45.9
		Modified with Ca salts	14.1	71.3	34.0	25.9
		Modified Na salts	18.4	24.7	40.0	38.9
		Modified with protonation by HNO_3	17.3	67.2	44.4	39.0
		Modified with hydroxyapatite	<0.02	5.7	11.4	18.5
Quaternary glaciolacustrine clay – illitic, silt content up to 30%	Zeiļu Lake, Ludza region, Latvia	Raw	78.2	104.2	33.3	40.2
Quaternary glaciolacutstrine varved clay – illitic, structure varved, summer layers with significant silt amount	Borovichi, Novgorod Oblast, Russia	Raw	94.2	115.6	39.0	41.3
Sandy soil, without amendment			112.2	128.7	46.2	44.9

** Initial concentrations for spiked soil: Pb and Cu 150 mg kg^{-1}, Cd and Cr 50 mg kg^{-1}, measurements in triplicates. Standard deviation for FAAS measurements varied in range 0.8-28.8 %*

3.3.3. Bioavailability and speciation of metals in soil

The selective concentration of trace elements can lead to overexposure and metal speciation as well as bioavailability can be defined as important indicators for environmental risk assessment. Trace elements are bioavailable if in soil environment the mobility of metals such as dissolution and precipitation, sorption, ion exchange and oxidation-reduction reactions do not stop the uptaking by plants and animals. This chapter provides experimental data and field soil analyses done with a set of methods to evaluate the potential hazard which can affect humans and the environment. Ecological risk assessment is a step forward and metal speciation, bioavailability of heavy metals and ionometry can be tools to give useful information which cannot be gained by total concentration measurement techniques.

Ionometry and bioavailability of metals. Case study 1. Stability constants are well-known tools for solution chemists, biochemists and chemists in general to help determine the properties of metal-ligand reactions in water and biological systems. Stability constants for the copper spiked soil were determined and compared with constants in soil treated with different amendments. During this study, natural zeolites and humic substances were used as amendments. Two types of Devonian clay from Liepa quarry were used as natural zeolites.

Table 3.11 shows results with already calculated Cu stability constants for 49 samples. In this study, the ion selective electrode approach was used to determine the conditional stability constants of a number of Cu^{2+} complexes with zeolites (alumosilicates) and organic ligands (humic acids in this case).

Table 3.11

Calculated stability constants (min-max, mean values) for soils spiked with copper of 500 mg kg^{-1} concentration and different amendments applied: no amendments, humic acids, red Liepa clay, gray Liepa clay and both clays and humic acids together

Soil without amendment	**Type and rate of soil amendment**			
	Humic acid 1:100	**Red Liepa clay 1:100**	**Gray Liepa clay 1:100**	**Both Liepa clays and humic acids* 1:100 each**
3.56-6.58 (5.50)	4.14-6.48 (5.72)	6.59-8.53 (7.68)	7.03-8.37 (7.65)	4.37-7.02 (5.66)

* *pH during electrode potentiometry measurements was adjusted to 6.0±0.2*

When comparing stability constant results for samples without any amendments to samples treated by humic acids, some effect was observed, however, significant changes appeared in both cases with clay as amendment. Both clay types were effective to increase the stability of the formed complexes which basically means that heavy metals lose their mobility. Both additives – zeolites and humic acids – together have shown that the picture becomes more complicated when sorption of metals is increased by the clay, whereas humic acids lower the values by diminishing the pH. Sophisticated interactions are also possible as humic acids form various complexes together with metals and at the same time can increase values of the stability constant.

The ratio between the stability constant in spiked soils without amendments varies from 3.68 to 6.52 (average 5.5); for spiked soils with humic acid amendments alone – between 4.13 and 6.48 (average 5.7); for samples with the red and gray clay addition – between 6.59 and 8.53 (average 7.65); whereas when both agents are added, the interval is between 4.37 and 6.72 (average 5.7). Adding humic acids does not change the stability constants significantly, the complex use of zeolites and humic acids at the same time also does not effectively diminish the free copper ion amount and thus the contamination remains biologically available and the soil remains with increased toxicity for the healthy environment. On the other hand, addition of the Gauja Formation Liepa quarry mined clay at a concentration of 1:100 significantly diminishes the biologically available copper within the soil pH of 6. Zeolite addition diminishes the biological availability of copper significantly and thus can be used for remediation purposes as a soil amendment.

Soil amendments and metal speciation. Case study 2. This study experiment has shown that copper ions and substances in case of the presence of zeolite amendment have diminished the ability of leaching. Compared to Case study 1 described above and in (Burlakovs et al., 2012b), the metals have lower bioavailability; the first method described above has proved that the stability constant of copper is higher for soils with zeolite amendment, but here the speciation analysis was performed with various chemicals in order to test the strength of metal immobilization in soil.

Spiked sandy loam soils from the Ap horizon were chosen for speciation analysis. The results have shown that the increasing of the amount of humic substances (HS) additives allows diminishing the amount of copper and lead ions that are biologically available and increasing the content of more stable metal complexes (Fig. 3.18 and 3.19). When characterizing the interaction of HS with heavy metals, it is essential to assess the factors which determine the process of binding. Influential factors include soil texture and mineral composition – the process is dependent on the type of soil, as well as the ability of soil-forming minerals to interact with both metals and HS. The amount of freely exchangeable copper and lead cations generally decreases if HS amended up to 20 g L^{-1}. A significant increase of the HS amount in sandy soil decreases easily available free exchange forms (Fig. 3.20 and Fig. 3.21). Metals in the Ap horizon has been bound in more stable complexes than in the beginning before the HS amendment – the stable fraction has increased for both Cu and Pb. By adding HS, the stability of metal complexes increases even further (Fig. 3.18 and 3.19).

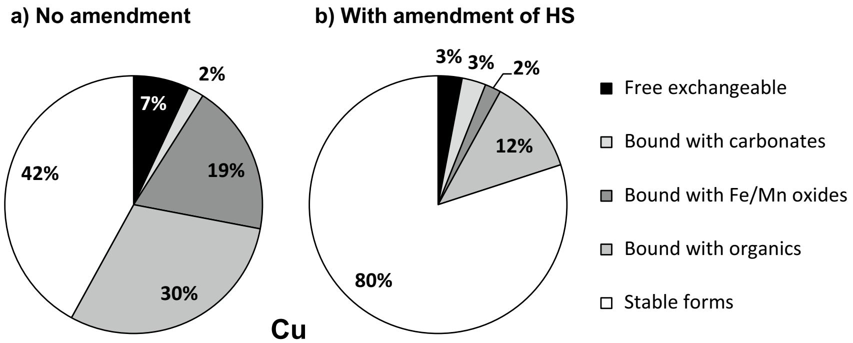

Figure 3.18. Speciation of copper in sandy loam soil (Ap horizon) without amendment (a) and with amendment of HS solution at concentration 20 g L^{-1} (b)

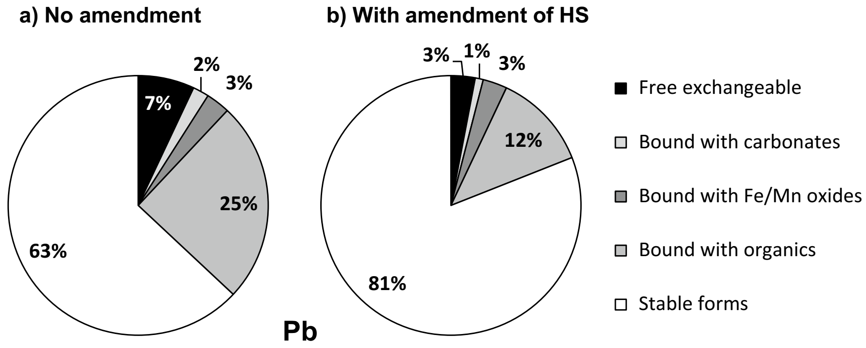

Figure 3.19. Speciation of lead in sandy loam soil (Ap horizon) without amendment (a) and with amendment of HS solution at concentration 20 g L^{-1} (b)

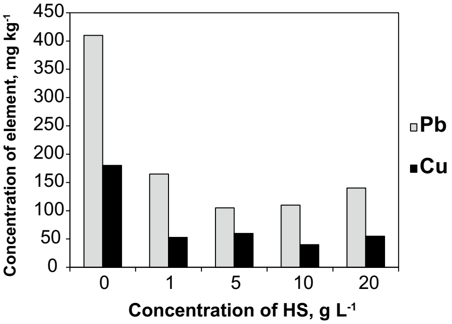

Figure 3.20. Amount of free exchangeable lead and copper in sandy soil (E horizon) at various concentrations of HS solution amendment

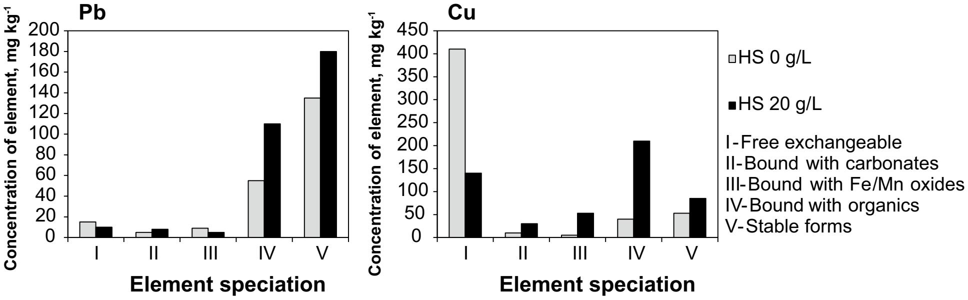

Figure 3.21. Influence of HS amendment on lead and copper speciation in sandy soil (E horizon) (without amendment – HS 0 g L^{-1} and at concentration of HS 20 g L^{-1})

Adding HS for both types of soil improves the forming of stable metal complexes where both lead and copper are less available for plants. Compared to the ionometrical study with zeolite and HS amendments, this experiment gave more clear results that the amendment of HS increases the complex stability thus diminishing biological availability of metals and confirms the hypothesis that HS as well as zeolites can be used as immobilizers of heavy metal contamination. Results of this study in details are described in (Burlakovs et al., 2013a).

Metal speciation studies in contaminated soils from field study. Case study 3. Two case studies with the use of humic substance and natural zeolites as amendments indicate a trend that bioavailability for copper and lead can be significantly diminished and amendments can be effective for the treatment of contaminated soils with medium to high concentration of metals in soil. Further on, the BLB Baltijas Termināls and Vega Stividors area soils were studied with partly done speciation analysis to determine the easily extractable fraction of heavy metals in this strongly contaminated area. The sample analysis results of the total concentration in samples, leaching test data and speciation tests are given in Table 3.12.

Table 3.12

Total concentration, speciation and leaching of heavy metals and metalloids from BLB Baltijas Termināls and Vega Stividors contaminated soil samples

Element	Initial concentration of element in the original sample, mg kg^{-1}	Eluates extracted in analyses, mg kg^{-1}				
		Leaching tests performed (L:S=10:1)	Speciation analysis (fractions)			
			exchangeable	acid soluble	reduced forms	residual (calc.)
BLB Baltijas Termināls* and *VEGA Stividors						
As	96	0.04	7.06	2.3	14.0	72.64
Cu	283	56	13.2	11.0	92.0	166.8
Pb	449	48	0.25	8.6	190	250.15
Zn	430	231	32.2	35.0	140	222.8
Cr	5	n.d.*	0.19	0.04	2.4	2.37
Ni	4	n.d.	0.75	1.6	0.7	0.95
Cd	2.9	n.d.	0.56	0.47	0.57	1.3
Te	5	n.d.	1.03	0.90	0.96	2.11

**n.d. – not done*

This study was necessary to arrive at a decision on the use of *hard* or *gentle* remediation, or a combination of both. Case study 3 reported results that are similar in trend with those gained from leaching tests and heavy metal speciation studies in Case 2. A proportionally significant part of metals such as Zn, Cu and Pb is found in relatively mobile (exchangeable) fractions, which means it needs to be immobilized, transformed into a form not available to plants and stopped from travelling within the biogeochemical cycle. In the previous chapters, significant attention was paid to the study of soil amendments such as the Portland cement and different clay and its modified species. The question is not in doubt as to whether remediation is needed if we take into account expert opinion and formal norms of legislation regarding the elements of concern. However, the question is not so easy to answer if environmental risks are taken into account, and the feasibility of different remediation technologies should be evaluated.

3.4. Landfill mining as remediation technology

3.4.1. Re-cultivation with fine fraction material

The landfill mining (LFM) approach provides a unique opportunity to close landfills and at the same time use their own material for covering them with fine fraction. The research in the Kudjape LFM field project gave the possibility to analyze the potential of the landfill material. Only the fine material is described in this part of the case study in order to keep the scope of the thesis on the immobilization of contaminants during remediation projects.

The research of fine fraction from the landfill itself was performed by the author in order to pinpoint the opportunity of using such type of waste as the covering material in landfill mining projects in future. The relatively (for landfills) fine fraction of the Kudjape landfill in 0–40 mm was identified, with 80 % <10 mm, and 20 % 10-40 mm particle size. Metals that were possible to identify in the fraction of 0-40 mm were calculated at ~0.6 % (mostly Fe, Al, Cu). The fraction of fines <10 mm was prepared for analysis in order to analyze heavy metal content, speciation and concentrations of rare metals if those could be used as recovery material in distant future. The main purpose was to analyze leaching properties for this fraction as it is important to determine if this fraction of waste is to be used for closure of landfills as the covering material. Sequential extraction was performed to analyze the bioavailability of heavy metals when stored in a landfill covering after its recultivation.

Figure 3.22. Sample extraction at the landfill – excavated, trommeled, shredded, sieved, manually sorted and fine fraction separated samples; derived for homogenization and analytical applications (from 16 tons to 16 grams) (author's photos)

Table 3.13

Concentration of heavy metals in fine fraction of landfill waste material measured by AAS technique

Element	Concentration of element (c_{min}-c_{max} (c_{mean})) at sampling points (H1-H4), mg kg $^{-1}$			
	H1	H2	H3	H4
Cd	0.96-1.62 (1.32)	0.63-1.94 (1.05)	0.69-1.03 (0.85)	0.83-1.27 (0.99)
Co	5.5-7.6 (6.1)	4.3-8.1 (5.3)	6.2-17.4 (9.4)	5.5-6.7 (6.1)
Cr	47-79 (62)	43-102 (65)	43-104 (70)	63-219 (210)
Cu	133-464 (312)	132-383 (269)	114-793 (305)	123-303 (178)
Mn	329-365 (341)	241-519 (340)	259-352 (313)	338-406 (359)
Ni	24-34 (27)	13-55 (36)	30-60 (45)	27-42 (32)
Pb	201-238 (216)	99-1063 (377)	78-251 (154)	120-383 (229)
Zn	1124-2776 (1858)	744-1864 (1168)	835-3887 (1952)	1037-2305 (1431)

The results of the fine fraction research have shown that the elemental content is of great concern if compared to the legislation standards for soil quality (e.g., in Latvia); this study showed that Cu and Zn and in some cases Pb had the threshold concentration exceeded. Therefore, additional research of metal speciation in the fine fraction of waste as well as the leaching behaviour under various pH should be performed if this fraction is to be used as the covering material in landfills. The content of other major, trace and rare earth metals was measured by accurate analytical ICP-MS techniques (Figs. 3.23-3.25).

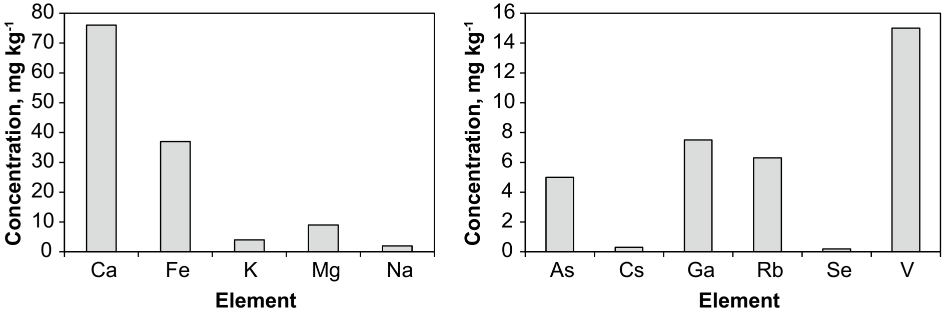

Figure 3.23. Major and trace metallic and metalloid elements detected in fine fraction from Kudjape landfill; mean concentration from 16 average homogenized samples analyzed by ICP-MS (K and Na values are approximate due to the interference)

It was confirmed that the elemental content of major and trace metals is high enough to be of concern in terms of leaching and worth to be debated if extraction by landfill mining technology is applied.

3.4.2. Laboratory vs. field data comparison

A large part of sites contaminated with heavy metals in Latvia is dump sites. In order to perform remediation works, a fast analysis with express methods is highly recommended. It has been reported that the data quality measured by the field portable X-ray fluorescence (FPXRF) instrument can be affected by soil moisture and organic matter content as well as particle size distribution (Argyraki et al., 1997). The field moisture content in Kudjape case study varied between 25-39 %; a correction of 32 % was applied for FPXRF raw data. The organic matter content in the samples varied in the range of 15.6-24.7 % (18.8 % on average). The application of express measurements with FPXRF deals with the non-homogeneous solid matrix and moisture content in fine fraction samples gained and sorted from the landfill.

The ICP-MS method was used more for determination of trace and rare elements, which are under the detection limits for other analytical tools (FAAS and FPXRF). The comparison of the two laboratory methods was done when comparing Cu and Ni results between FAAS and the ICP-MS. The difference was negligible (34.9 vs. 37.7 mg kg^{-1} in case of Ni and 266.0 vs. 250.1 mg kg^{-1} for Cu, respectively). A further comparison for major and trace elements was done by using FAAS and FPXRF. Fig. 3.24 shows that express analysis for major metallic elements in the fine fraction of the landfill mass can be done in a good quality, especially for iron. Standard deviation in Fig. 3.24 and 3.25 means that elemental distribution in various analyzed samples in the landfill (*n*=16) is still highly variable, although the homogenization of samples was done very carefully. It can especially be seen in FPXRF columns of Fe, Ca, Zn and Cu and FAAS columns of Fe, Zn and Cu. The FPXRF method can be used with a high rate of trust to determine the general distribution of major and trace elements for samples rapidly prepared in field conditions, as the general trend compared to AAS is similar – uncertainties of landfill composition are clearly seen by using both analytical techniques (Fig. 3.24 and 3.25).

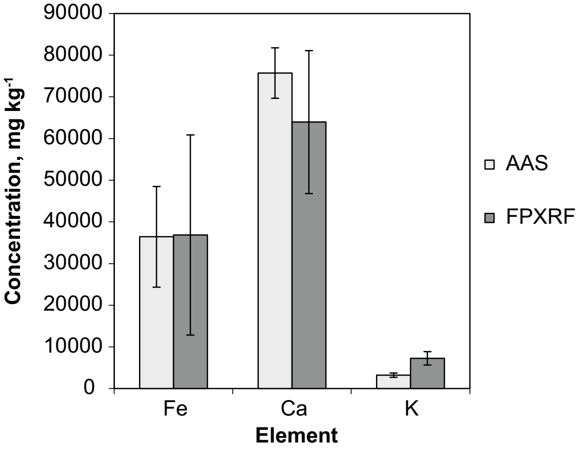

Figure 3.24. Average content of major metallic elements dominating in landfill detected by AAS and FPXRF (*n*=16)

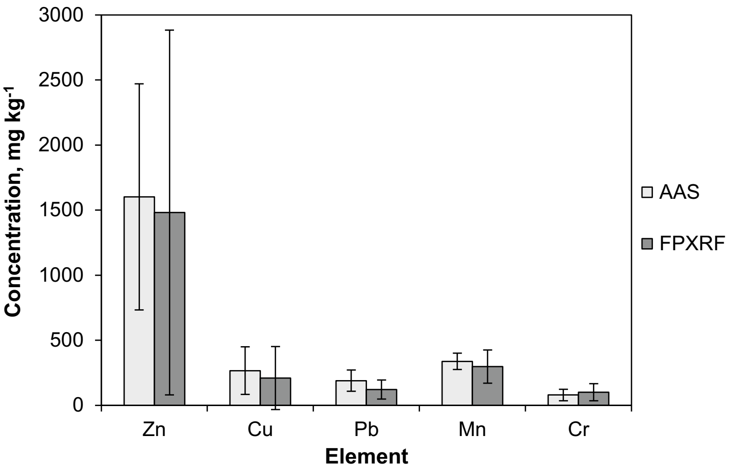

Figure 3.25. Average content of trace metallic elements dominating in landfill detected by AAS and FPXRF (n=16)

However, spectral interferences can disturb the quantification of major elements such as Ca, K, and trace elements Cr, Pb, Cd and Ni. The comparison of the precision and accuracy of quantitative measurements derived by different analytical techniques (FPXRF, AAS, ICP-MS) is not possible in this case with certified LFM reference materials; AAS and ICP-MS wet digested sample analysis can be assumed as much more precise for such elements as Cd, Co, Cr, Pb, Cd, Ni etc. compared to the FPXRF method.

FPXRF is a relatively fast and quantitative method, and the equipment is portable. Precision and accuracy of the results provided by using the express method is acceptable for quick analysis of the content of major and trace elements in field projects for landfill mining purpose; however, large unconformities of data should be avoided by maximal homogenization of samples, analysing large quantities of field measurements, using the data treatment, calculating moisture and sample matrix corrections.

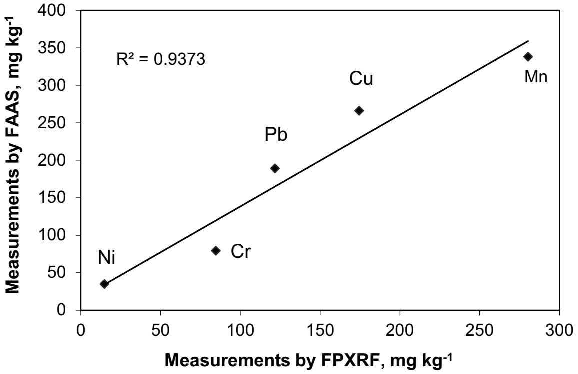

Figure 3.26. Correlation between data obtained by FAAS and FPXRF for five trace metallic elements dominating in landfill (n=16)

The correlation shown in Fig. 3.26 affirms that correlation is strong enough between FAAS and FPXRF results, thus the method can be advised as a rapid analysis tool during LFM projects in future. The data quality for Sr and As between ICP-MS and FPXRF was also reasonable (170.0 vs. 216.8 mg kg^{-1} in case of Sr and 5.0 vs. 5.1 mg kg^{-1} for As, respectively). The quantitative analysis of some trace elements such as Co, Cd and Rb has for some reason shown wrong unrealistic values; the possible influencing factors can be spectral interferences, the properties of the measurement X-ray tube itself and organic matrix.

It can be suggested that a rapid quantitative analysis of trace and major elements (except for volatile elements) in contaminated samples is possible with FPXRF if the accuracy of measurements is needed for environmental or economic evaluation of the fine fraction of landfill mass in general. Environmental studies by express method provide information about the total content of elements for finding general trends. The presence of heavy metals as well as arsenic can be proven and the results are comparable with AAS and ICP-MS data. FPXRF data can be obtained in large amount for a large number of samples and does not demand time-consuming sample preparation procedures. A more accurate analysis should be done for the chosen samples to improve project quality control and labour safety. Similarly, the FPXRF technique can be considered as a good tool for evaluation of contaminated sites elsewhere, not only in dump sites.

3.4.3. Comparative studies of soil fine fraction quality

The speciation of elements is important for two main purposes: to know the bioavailability and potential threat to the environment within the changing environment, and technological ways to recover resources – exchangeable fractions are easy to be extracted.

Bioavailability of trace elements (Fig. 3.27) is the highest for elements important in biogeochemical cycles such as Sr, Rb and Mg, for Fe, Ba, Cu, Pb, Cr and other elements,

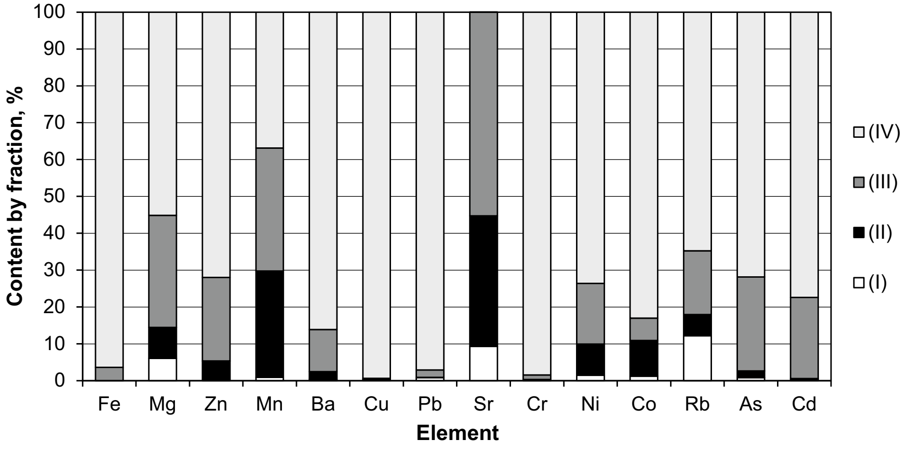

Figure 3.27. Element distribution by fractions in H1-4 combined samples (I – exchangeable fraction; II – acid soluble fraction; III – fraction of reduced forms; IV – residual fraction)

including potentially toxic heavy metals; the exchangeable fraction is comparably low in percentage. Pb, Cr and Cu have a very low amount of bioavailable fraction; the residual fraction is of dominating proportion. Zn, Ni and Co have the proportion of acid soluble fraction higher than for others, meaning that those can be present if intense leaching with changing pH to acid takes place. For other elements, reduced forms also contain significant portion, these are of environmental concern as can be transformed during excavation if a large amount of oxygen becomes available (during digging works). The residual part of metals is not easy to extract; the environmental concern is therefore negligible. Here, an important question arises as to whether this fraction can be used for recycling of elements during landfill mining (LFM) or whether it should better be left buried and used as part of the soil's fine fraction covering material (FFCM).

Excavated and sorted material from landfill mined dump sites can be used as the remediation material itself, in case amendments such as clay with its modified species or humic substances can be added. The FFCM may consist of landfill material; amendments described in the previous chapters improve immobilization and metal complex forming thus preventing the leaching and diminishing the presence of potentially toxic and bioavailable elements.

3.5. Choice of remediation technology

3.5.1. Decision drivers and option appraisal

Legislative aspects, environmental quality assessment, costs, risk assessment and detailed remediation and post-remediation planning should be performed as well as a comparison of technologies done in order to start the process of remediation.

An indicative model roadmap is given in Fig. 3.28 that would be a useful tool for application of the right and feasible actions regarding heavy metal contaminated sites.

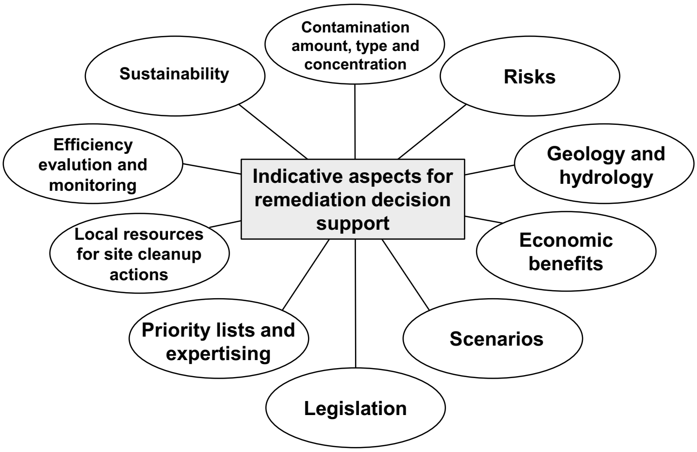

Figure 3.28. Indicative model roadmap as remediation decision support system tool (author's illustration)

Many aspects should be considered in selecting a proper remediation solution to a contaminated land problem. The core objectives must be considered, e.g., costs and benefits, technical suitability, efficiency and feasibility, risk management, aesthetic and environmental aspects as well as social and economic conditions. The criteria and manner how the decision can be reached is also very important. A large number of approaches described in the literature review chapter as examples can be used, however, balanced and systemic principles are important if the decisions are to be accepted by authorities and the public. Decisions about the option(s) most appropriate for a particular site are to be analyzed as a complex system. The key factors are depicted in Fig. 3.29.

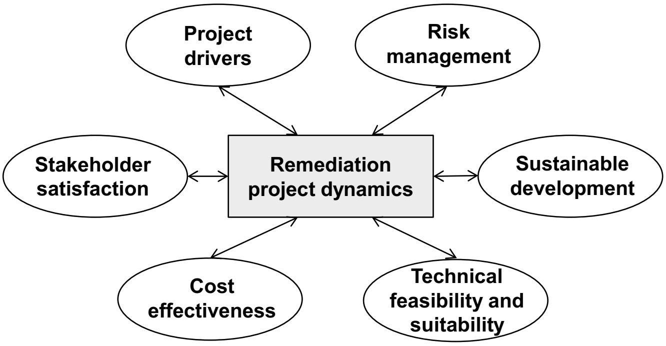

Figure 3.29. Reverse dynamic system of decision support for remediation (author's illustration, after CLARINET, 2002)

Initial data is a key source for developing the list of indicators as well as the potential remedial action list from which the choice can be made. The very beginning of evaluation is stakeholder involvement in the decision option appraisal process. If remedial actions are needed, technical and sustainability aspects are evaluated and preliminary calculations of the cost efficiency are done together with risk analysis. The contamination level often has a certain degree of uncertainty as it can be seen from case study research in the previous chapters (i.e., only some data points are usable for the assessment of contamination in larger areas). A decision is therefore required as to whether more detailed information is needed or state-of-the-art approach can be performed.

Fig. 3.30 provides an example of how the author of the present thesis would recommend initial key questions to be answered to go further with option appraisal in general.

The first and initial question is about the necessity of remediation in general. If authorities have generated the list of contaminated or potentially contaminated territories, this question is not automatically answered by the inclusion of this unit on the list. Sometimes risk assessment can lead to an obligatory monitoring process; however, it is always possible to recommend the best choice of remediation technology useful for every site. If heavy metal contamination dominates, the first important question that arises automatically is whether the metals are hazardous from hydrogeological and bioavailability point of view. While the geological structure is usually evaluated during a conventional

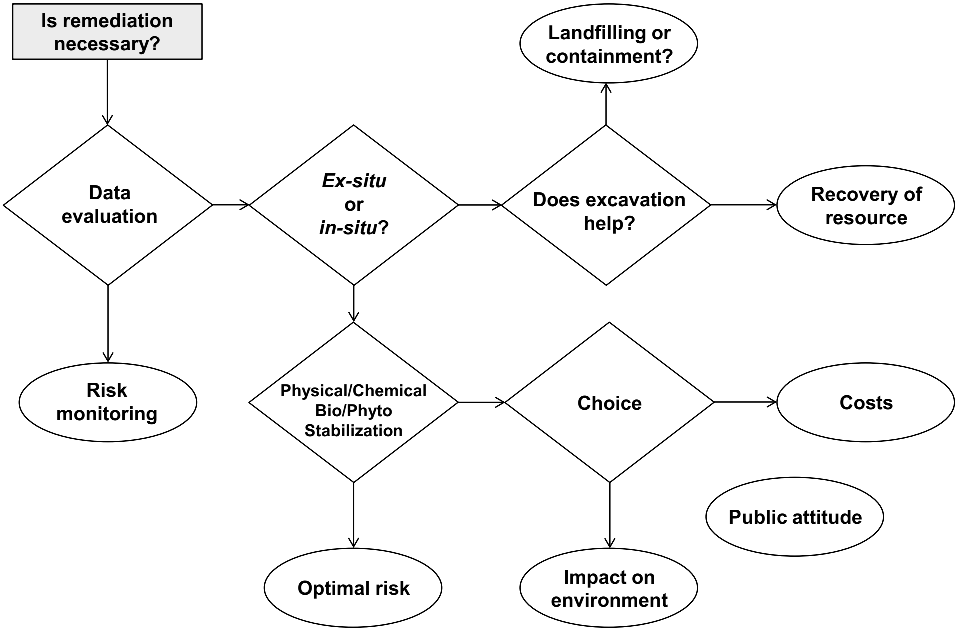

Figure 3.30. Simple algorithm leading to option appraisal for remedial decision choice (author's illustration)

environmental pollution assessment project, the second aspect is very often neglected and remains as an unknown factor. Fig. 3.31 shows the bioavailability process in soil including interactions with living organisms. Mostly the indirect study of bioavailability is used, and one of the easiest methods is the sequential analysis for metal speciation that allows determining the potential behaviour of heavy metals in distinct environments.

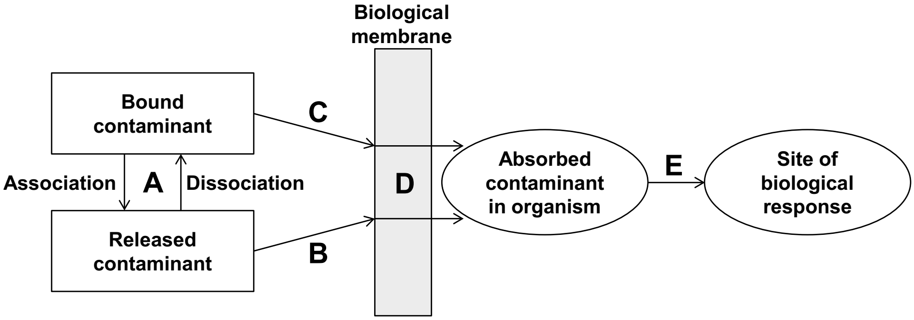

Figure 3.31. Bioavailability processes in soil including: A – release of a solid-bound contaminant and B – consequent transport; C – transport of a solid-bound contaminants; D – uptake across physiological membrane; E – incorporation into a living system. A, B, and C can occur internal to an organism such as in the lumen of the gut (author's illustration, according to US NRC, 2002)

Sequential extraction performed for heavy metals was evaluated in two case studies of the present thesis, and the results show that a certain risk of increased bioavailability is present. In such cases, *gentle* remediation (description at GREENLAND project, 2014) techniques would be highly recommended if the contamination level were not too high. It is derived from literature studies, practical case studies all around the world, EPA recommendations, experts and more. This approach was also tested in experimental research, and soil amendments made of clay and its modified species are one of the options that could be proposed if *hard* remediation (stabilization/solidification, electrokinetic, excavation and other heavy affecting) technologies are environmentally unfriendly, contradict public opinion or have too high costs.

The next diagram in Fig. 3.32 shows the simplified version of the decision support scheme if *gentle* remediation is under question.

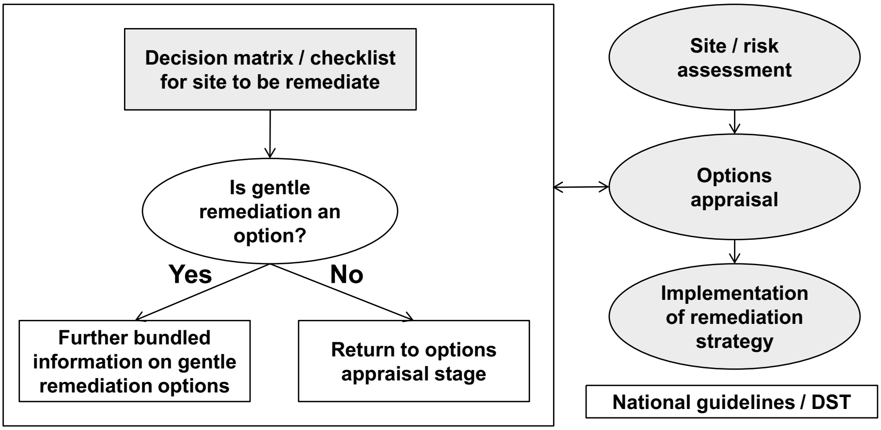

Figure 3.32. Decision support tool for *gentle* remediation choice (author's illustration, after EUGRIS and SUMATECS, both 2008)

The decision matrix and indicators must be clear and easy to use, including data on the level of contamination, main pollutant sources and types, timescales, depth and other criteria as well as exclusion criteria considering economic and/or practical considerations. The remediation decision support system itself should be included in the national legislation or at least in the Guidelines for different level authorities. This decision matrix or checklist should clearly define the capabilities of each set of methods applicable for specific contaminated site. The author's opinion based on practical environmental quality assessment and remediation planning projects is to divide larger areas into smaller ones to decrease the heterogeneity of the contamination level, geological and hydrogeological conditions, land-use aspects and other important factors that can exclude one or another remediation option if formal evaluation is applied.

The next chapter is providing results of a case study research based on multi-criteria decision support analysis (MCDA) for BLB Baltijas Termināls and Vega Stividors areas (case studies No. 1 and No. 2). Situation is analyzed from the potential remediation point of view, where options should be evaluated by decision makers. The MCDA is the method that is based on chosen options and criteria with weighed importance done by experts, the case study as the model specimen is given.

3.5.2. Multi-criteria based decision analysis of remediation options

Any multi-criteria decision analysis (MCDA) starts with the choice of options for resolving the problem or a set of problems. According to Asafu-Adjaye (2007), problem solution through the MCDA must be done in eight steps at least (remediation choice in this case, with comments in brackets given by the author):

1) Identification of the problem (classification and choice of contaminated sites);
2) Identification of the alternatives (assumptions done to make the options list possible for evaluation);
3) Identification of the criteria (should be performed by stakeholders and experts, balanced choice is desired);
4) Scoring of the alternatives (stakeholder involvement necessary – scoring should be performed through surveys among target groups);
5) Assignment of weights to the criteria (expert group decides through discussions);
6) Evaluation of the alternatives (Excel model created by the author of the thesis modified from (Triantaphyllou, 2000; Geldermann and Rentz, 2007; Böttle 2011);
7) Sensitivity and risk analysis (should be performed after the use of evaluation of scenarios);
8) Ranking the alternatives (final ranking results for a specific project is promoted for decision-makers).

Problem definition. The main problem is that many contaminated sites pose threats to the environment and human health; one case was chosen for MCDA model description: BLB Baltijas Termināls and Vega Stividors (sites No. 1 and No. 2, Figs. 2.1, 3.3. and 3.33.). These sites are located in the northern part of Rīga city, approximately 5 km from the estuary of the River Daugava in the Riga Gulf. The study area has been economically active from the beginning of the 20th century. In earlier years (1894-1967), the territory was used for several industrial purposes including the manufacturing of superphosphates, with a dump site for tailings made nearby. Later on, an oil product storage, reloading and transit terminal was established in this area. In the 1960s, a factory operated there, but later on the oil product terminal facility replaced it. The main soil pollution source was superphosphate production waste (slag), where the highest concentration was found for lead, copper, zinc and arsenic. The total amount of toxic heavy metals throughout the whole research area was estimated at 1264 t or 15 kg m^{-2} of slag or: 755 t of copper, lead 85 t, zinc 358 t, 66 t of arsenic. The ground and groundwater in the territory is heavily contaminated with heavy metals, and isolated areas – also with oil products. The area is included on the list of contaminated and potentially contaminated areas, and the future of the contaminated industrial territory depends on sound decision-making and the financial situation as well as the actual estate market development in high-cost port areas and lower-cost marginal ones. The geological situation: the technogenic contaminated sediments cover marine sediments with muddy layer mixture with silt, which can support the immobilization of heavy metal contaminant migration further downwards. The area covers 20 ha, and technogenic sediments are used as the soil for supporting the logistic areas and the oil terminal. Roughly estimating 20 % of the area is covered by grass and trees, which possibly provide rhizofiltration and immobilization of toxicants within their root system. The terminal area is near the river, and the geological organic silty layers as well as the ecosystem helps prevent the spread of contaminants to the river and further to the Baltic Sea. The main ecosystem services (vegetation and soil) in zero scenario (so called *doing nothing*) only partly prevent leaching of toxic heavy metals and oil products outside to the neighborhood and into the river.

The MCDA approach. The MCDA approach is important as the main stakeholders are the national government, municipality, owners (in this case – users) of the polluted land, inhabitants in the neighborhood, and the controlling authorities. Therefore the decision should be made by using a balanced choice and taking many aspects into account.

The fate of contaminants must be estimated before the choice of remediation technologies can be proposed; historical information and data from previous research stages give the main core for decision-making to establish a set of potential options and criteria. The main concerns are related to the costs and legislative peculiarities when those contradict business interests. Decision-makers should be strict about the process of pre-investigation, research and remediation, but the decision must allow some flexibility in order to avoid too high costs and the ensuing stagnation of the remediation process because of this reason. The environmental feasibility of different remediation technologies should be evaluated case by case: environmental quality assessment, risk assessment and detailed technology analysis by using an indicative model described in the previous chapter. For example, for dump sites, feasibility studies of the LFM can be promoted in the context of the developing economic processes and the opportunities to recycle raw resources. Financial feasibility such as the costs of technology itself, market situation, industry needs, incineration capacities and many other factors should be analyzed before the beginning of the process. The last but not the least aspect is that EPA, EURODEMO and other guidelines of similar importance should be taken into account when using the model for planning any type of remedial actions.

The model can be constructed as the continuation to decision support option appraisal scheme depicted in Fig. 3.30, developed by taking into account aspects in Fig. 3.28 and 3.29; specific adjustments should be used in specific cases. Model criteria are generalized so as to have a balanced view and evaluation opportunity, e.g., dominating areas not covering each other must be chosen (in this case – environmental, social and economic blocks).

This means that questions from specific domains such as geological circumstances, changes in biodiversity, aesthetic aspects and labor wages from different sectors must be taken into consideration as sub-criteria and included in dominating criteria. In some cases many criteria can be implemented, but then the mainstream analysis can become too detailed and non-transparent. As it was already mentioned in the theoretical description in Chapter 1.5, the advantage of MCDA is that it can cover spheres with seemingly incomparable criteria, but the main disadvantage is multidisciplinarity, which demands participation of numerous expert groups and stakeholders with different viewpoints and levels of knowledge, experience, viewpoints and interests.

Identification of alternatives and criteria. The MCDA was performed as the decision support tool by dividing this area into four sectors considering the contamination level, geological and land-use principles (Fig. 3.33). Three main blocks of indicators for remediation choice evaluation were chosen specific to this site: economic (construction costs), social (aesthetic and public acceptance) and environmental aspects (importance of remediation). The MCDA model was created in MS Excel format; the number of areal segments, criteria (aspects), weighting of criteria and additional information on segmental remediation costs can be manipulated to adjust the model through possible discussions.

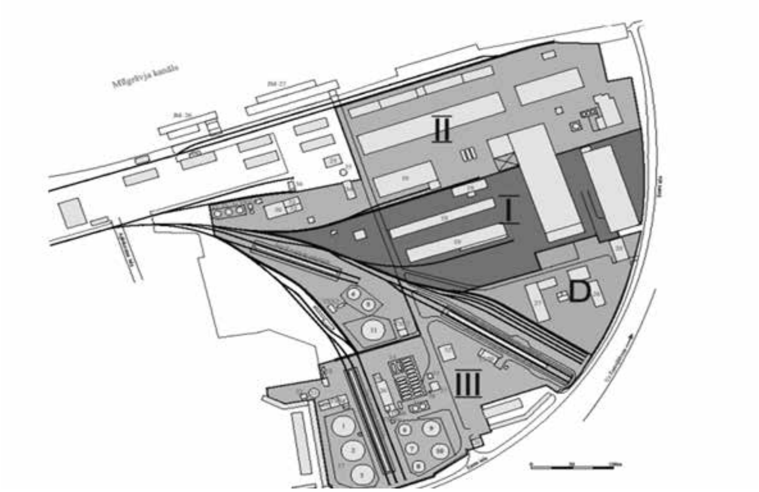

Figure 3.33. Case study of BLB Baltijas Terminãls for MCDA analysis: the area of 21 ha was divided into 4 sectors and several indicators were chosen for mathematical calculations of applicable site remediation technologies

The following potential remediation technologies were chosen as options: excavation, separation, stabilization/solidification, phytoremediation and soil amendment use (example shown in Annex II, Fig. A-1). Options can be changed by the user of the model and further properties added for each option as the model allows input of values for estimated remediation costs in EUR for each area (segment) with the known area in cubic meters regarding the chosen remediation technology spectra in each segment (example shown in Annex II, Fig. A-2).

Weighting of scores regarding criteria. Different weighting is applied and can be varied as different scenarios are disputed and played among experts, authorities, public and other stakeholders (as shown in Annex II, Fig. B-1). Thus the use of the decision support tool is transparent, and decision-makers can perform assessment of different scenarios under the control of the Advisory Board organized specifically for this case. A questionnaire can also be a solution, and averages of weighted criteria are chosen if many people are involved in the process of weighting. The author in (Burlakovs, 2010 and Burlakovs et al., 2014) shortly analyses this particular case study.

Scoring of the alternatives. One of the outputs of the mathematical model is a decision matrix, which is mathematically normalized (Annex II, Fig. B-2).

Evaluating and ranking of alternatives and calculations. The MCDA output was the choice from three theoretical options to be used; in the thesis, the simplified model is shown to propose the description of the approach, which can be adjusted to any of the specific projects evaluated. The algorithmic principles of MAUT and PROMETHEE II provide the numerical result for given parameters in the model (aggregation technique), whereas PROMETHEE I and ELECTRE provide outranking of options (concordance analysis). As shown in the model example (Annex II, Fig. B-3) the final output is that for areas with the highest contamination level, the S/S technology is the best option, but for sites with a medium and low contamination level *gentle* techniques such as phytoremediation and/or soil amendments (description at GREENLAND project, 2014) are more applicable. The option C in the example outranks both A and B, and the numerical values of option C by PROMETHEE II and MAUT are also higher. Therefore, option C with given parameters in the best solution based on the MCDA approach.

The performance of the MCDA analysis is not the remedy for clearing all doubt about the only and best decision possible in this or that particular case; however, it can help considerably if a large package of information is applicable for multi-criteria analysis; additional input of information can be performed providing new actual option appraisal in the decision-making process.

CONCLUSIONS

1) Environmental contamination with heavy metals in Latvia is mainly of historical – former industrial and military origin. In total, 19 sites or 34 % from the list of the Latvian National Register of Contaminated Territories can be classified as dump sites, 26 sites or 46 % are areas of industrial contamination (brownfields) and 11 sites or 20 % are former military areas. Among the 244 contaminated sites of the first category included in the list of Latvian National Register of Contaminated Territories there are 56 sites contaminated with heavy metals and half of them are located in the Rīga city. Remediation is necessary where concentrations exceed the prescribed risk based on numerical criteria or standards and conditions defined in the legislation.
2) The stabilization/solidification technology is the most effective solution for remediation of contaminated sites with high, medium and low target concentration of metals. Detailed work in the BLB Baltijas Terminināls and Vega Stividors areas with performed feasibility studies through logical and multi-criteria analysis lead to the conclusion that main project drivers for practical application of stabilization techniques is the potential to reuse the land in an economically feasible way and rehabilitate ecosystem services.
3) Studies of innovative soil amendments revealed that their applications are among the most effective methods for the reduction of environmental hazards with low and average target concentrations of contaminants in a relatively stable environment. The results of batch tests revealed that modified clay with iron oxyhydroxide and hydroxyapatite are far more effective agents for immobilization of heavy metal contaminants compared to raw clays. The best results were achieved for copper, lead and multicomponent cases.
4) The experimentally developed and examined soil amendments with an efficient qualitative and quantitative composition for the immobilization of heavy metals by *hard* remediation are cement and cement mixed with municipal solid waste incineration ash, while for *gentle* remediation raw clay, modified clay with iron oxyxydroxides, modified clay with hydroxyapatite, humic substances and clay combined with humic substances. Soil amendments improved the quality of contaminated soil by immobilizing metals and decreased the proportion of exchangeable fraction.
5) Dump sites constitute a large part of heavy metal contaminated sites and innovative technology such as landfill mining can be used for the recovery of valuables and restoration of degraded environments using its own resources on the site. The fine fraction of landfill-mined soil can be used as the landfill covering layer. Fast preliminary research of the quality of the landfill fine fraction mass for this purpose can be performed by screening with field express methods.
6) Remediation technology choice depends on legislation, economic situation and the entire environmental cost-benefit structure. EPA, EURODEMO and similar guidelines should be respected in general aspects. Complex contamination of metals can be remediated stage by stage by using various remediation technologies depending on the land use activities, social aspects, contamination level and economic feasibility.
7) The performance of a multi-criteria decision analysis is not the remedy for clearing all doubts about the possible decisions, but it can be a helpful tool to make the right choice if a large amount of incomparable quantitative and qualitative data has to be assessed and taken into account by the decision-makers planning environmental clean-up or remediation of the polluted site.

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LVS ISO 11047:2003 Soil quality – Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc in aqua regia extracts of soil – Flame and electrothermal atomic absorption spectrometric methods (in Latvian: Augsnes kvalitāte – Kadmija, hroma, kobalta, vara, svina, mangāna, niķeļa un cinka satura noteikšana augsnē, ekstrahējot ar karaļūdeni. Liesmas un elektrotermiskās atomabsorbcijas spektrometrijas metodes).

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ANNEXES

ANNEX I
Contaminated sites in Latvia and short characteristics of contamination

Nº	Contaminated site	Number in the list of Latvian National Registry of Contaminated Territories (NRCT Nº)	Characteristics of contamination and scale of problem
1	Liepāja Port channel	17004/5138	Metals and oil products in sediments of harbour (78 ha, 600,000 m^3)
2	Bangas, former Soviet Army missile base, former military area	98788/3471	Oil products and metals in soil and groundwater
3	Ventspils fishing port, fuel base	27004/2086	Oil products and metals in soil, oil products in groundwater
4	Zvārde tank polygon, former military area	84988/1437	Metals in form of unexploded ordnance, oil products
5	“Lāčkalni” dump site	46055/1668	Mixed contamination (50,000 t in 1.8 ha)
6	“Lemķini” dump site	46468/1679	Mixed contamination (400,000 t in 5.4 ha)
7	“Ķilupe” dump site, Ogresgals	74808/3638	Mixed contamination (320,000 t in 0.5 ha, up to 5 m deep)
8	“Priedītes”	74888/5198	Metals and metalloids (Cr, As), fluorides (3 ha)
9	Recultivated dump site “Misas”	96015/2214	Mixed contamination
10	“Cenši” dump site	32468/2816	Mixed contamination (12,000 t in 0.75 ha, up to 2 m deep)
11	“Siliņi” dump site	70628/3034	Mixed contamination (0.87 ha)
12	Former dump site “Bubuļi”	56448/1352	Mixed contamination (0.1 ha)
13	Ilūkste dump site	44075/828	Mixed contamination (56 000 m^3)
14	JSC “Lokomotīve”, Daugavpils, industrial area	05004/1046	Metals and oil products

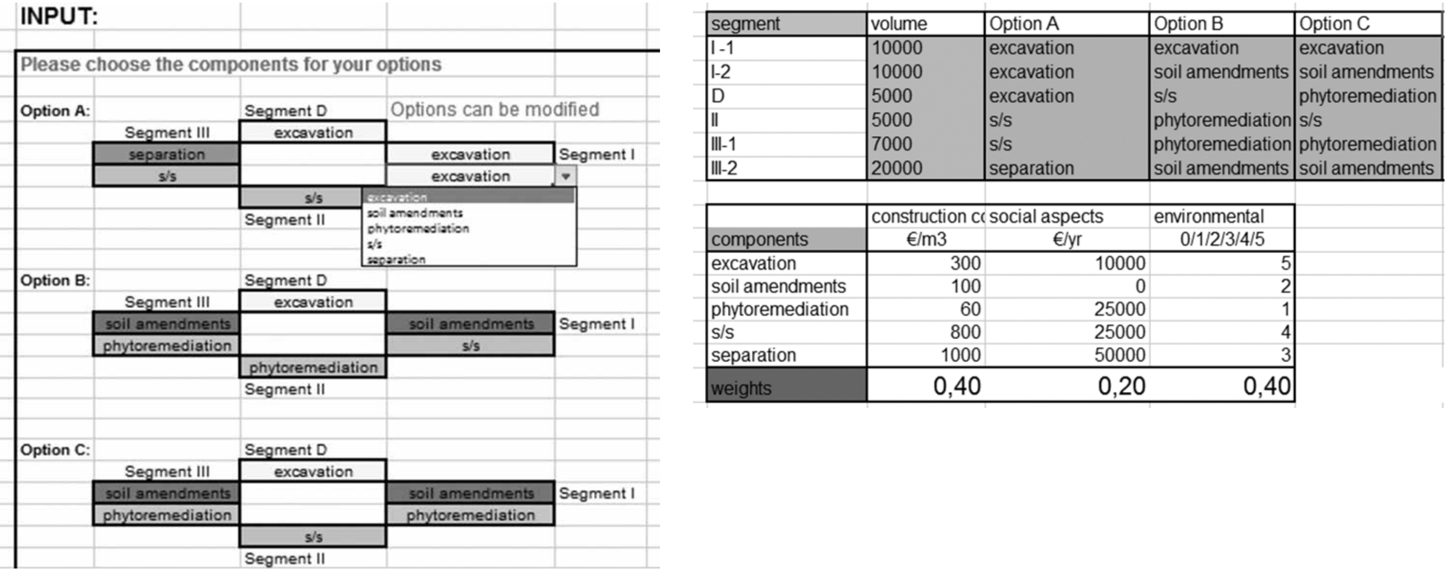
Nº	Contaminated site	Number in the list of Latvian National Registry of Contaminated Territories (NRCT Nº)	Characteristics of contamination and scale of problem
15	Preiļi Municipal Landfill	76015/813	Mixed contamination (0.4 ha, up to 2 m deep)
16	Former Pesticides Warehouse, Viļāni	78175/3584	DDT, pesticides, metals and metalloids (Cd, Cr, As, Pb) (>200 t in 0.67 ha, up to 1.5 m deep)
17	Gasoline fill station in Balvi	38015/2539	Oil products and metals in groundwater (0.41 ha)
18	“Kūdra” former dump site	80888/1524	Mixed contamination (10 ha, up to 9 m deep)
19	“Klāšķini” dump site	54628/2352	Mixed contamination, metals (Cr) in groundwater
20	“Brakšķi” dump site	54628/2350	Mixed contamination (5.8 ha), metals (Pb, Cd) (80 ha)
21	Liquid toxic substances dump, Jelgava	09004/2259	Anionic substances, oil products, metals (2.3 ha), deeply contaminated groundwater
22	“BIOLAR” dump of toxic substances, Olaine,	80808/3672	Toxic hazardous substances and metals (600 ha), groundwater contamination
23	Olaine dump site	80808/1430	Mixed contamination (150,000 t in 3.5 ha, up to 5 m deep)
24	Mārupe landfill	80768/916	Mixed contamination (11.6 ha, up to 2 m deep)
25	“Grantiņi” dump site	40648/1965	Mixed contamination, Cd, Zn (4 ha)
26	Municipal landfill “Priedaine”	13004/705	Mixed contamination (17 ha, up to 16 m deep)
27	“Tilpums” gasoline fill station	80708/1481	Gasoline, metals (Zn) in groundwater (1.8 ha)
28	“Getliņi” dump site	80968/1404	Mixed contamination (150 ha, up to 30 m deep), 2 km contamination plume to the River Daugava
29	“KRS” Ltd., Rīga Port industrial area	01924/624	Oil products, metals (Hg) (1.7 ha, up to 4 m deep)
30	“Vižņi” Ltd.	01924/3827	Metals (Cu, Zn) in groundwater (0.5 ha)
31	“Mekora” Ltd., former 145 military factory,	01924/585	Oil products and metals (Zn, Cu, Pb, Ni) in groundwater (3.5 ha, up to 5 m deep)

Nº	Contaminated site	Number in the list of Latvian National Registry of Contaminated Territories (NRCT Nº)	Characteristics of contamination and scale of problem
32	Bolderāja ship repair yard, Rīga Port, brownfield	01924/618	Oil products and metals (Zn, Cu, Cd) in groundwater (3 ha, up to 5 m deep)
33	“Jūras vējš” Ltd.	01924/3826	Oil products and metals (Zn) in groundwater (0.9 ha)
34	“Lacon” Ltd., former Soviet Army fuel base, Rīga Port	01924/666	Oil products and metals in groundwater (300 t of oil, up to 5 m deep)
35	“Freja” Ltd., former Soviet Army territory, Rīga Port	01924/665	Oil products, metals (6.9 ha, up to 5 m deep)
36	JSC “Bolderāja”, former sewage treatment system, Rīga Port	01924/668	Anions, metals in groundwater (15 ha, up to 4 m deep)
37	Kleisti dump site, Riga	01924/673	Mixed contamination in the waste and leachate (4.6 ha, up to 10 m deep)
38	JSC “Latvijas Krāsmetāli”, Rīga, brownfield	01934/623	Metals and oil products in soil and groundwater (0.3 ha)
39	“Russo-Balt” Ltd., Riga former military factory	01934/638	Metals (Pb, Zn, Cd) in soil, oil products (2 ha, up to 3 m deep)
40	Jugla trading centre	01944/3780	Sewage system deficiencies, technogenic soil contains heavy metals and phenols (2 ha, up to 5 m deep)
41	Former “Alfa”, area 2, Rīga, brownfield	01944/606	Metals (Pb, Cu, Zn), oil products (0.65 ha, up to 4 m deep)
42	State AS “Latvijas nafta”, 9 Sporta Street 9, Rīga	01944/662	Oil products, metals (Pb, Zn) in soil and groundwater (0.2 ha, up to 3 m deep)

Nº	Contaminated site	Number in the list of Latvian National Registry of Contaminated Territories (NRCT Nº)	Characteristics of contamination and scale of problem
43	Deglava Street dump site	01944/675	Mixed contamination (18.5 ha, up to 7 m deep)
44	Former “Alfa” area, Rīga, brownfield	01944/677	Trychlorethylene, metals, oil products (1 ha, up to 5 m deep)
45	Former factory “Kosmoss”	01944/712	Metals and oil products (1.2 ha, up to 3 m deep): excavated and site shifted to the 3rd category (not polluted)
46	“Viva Color” Ltd., Riga, brownfield	01954/609	Oil products, metals (Pb, Zn), phenols in soil and groundwater (1.2 ha, up to 5 m deep)
47	Bieķengrāvis, former hazardous waste dump	01954/669	Oil products, metals (Pb, Cu) in soil and groundwater (2.5 ha, up to 8 m deep)
48	“Eko Osta”, Rīga Port, former Soviet fuel base	01964/4411	Metals, oil products in soil and dredged sediments (3-5 ha)
49	Rīga gardenery pesticide warehouses	01964/5418	Metals, oil products in soil and groundwater (3 ha, up to 3 m deep)
50	“Grand” Ltd., former light bulb factory, brownfield	01964/626	Oil products, metals (Pb) in soil and groundwater (3 ha, up to 5 m deep
51	SJSC “Latvenergo” TEC-1, Rīga, brownfield	01964/621	Oil products, metals (Pb, Cu), ammonia, fluorides in soil and groundwater (5 ha, up to 5 m deep)
52	JSC “Starts”, Rīga, industrial area	01964/625	Oil products, metals (Pb) in soil and groundwater (1.8 ha, up to 5 m deep)
53	“Magnāts” Ltd., Rīga Port, industrial area	01964/627	Oil products, metals (Pb) in soil and groundwater (0.5 ha, up to 5 m deep)
54	“BLB”, Rīga Port, industrial area	01964/611	Metals and metalloids (As), oil products in soil and groundwater (10 ha, up to 10 m deep)
55	“Vega Stividors”, Rīga Port, industrial area	01964/629	Metals and metalloids (As), oil products in soil and groundwater (5 ha, up to 10 m deep)
56	”Energoautomātika” former industrial area, Rīga	01964/634	Metals and metalloids (Pb, As) in soil (1.9 ha, up to 3 m deep)

ANNEX II

Examples for the inputs and application of multi-criteria analysis model



(A-1)

INPUT:

Please choose the components for your options

Option A: Segment D Options can be modified

Segment III: separation, s/s

Segment D: excavation

Segment I: excavation, excavation

Segment II: s/s

Option B: Segment D

Segment III: soil amendments, phytoremediation

Segment D: excavation

Segment I: soil amendments, s/s

Segment II: phytoremediation

Option C: Segment D

Segment III: soil amendments, phytoremediation

Segment D: excavation

Segment I: soil amendments, phytoremediation

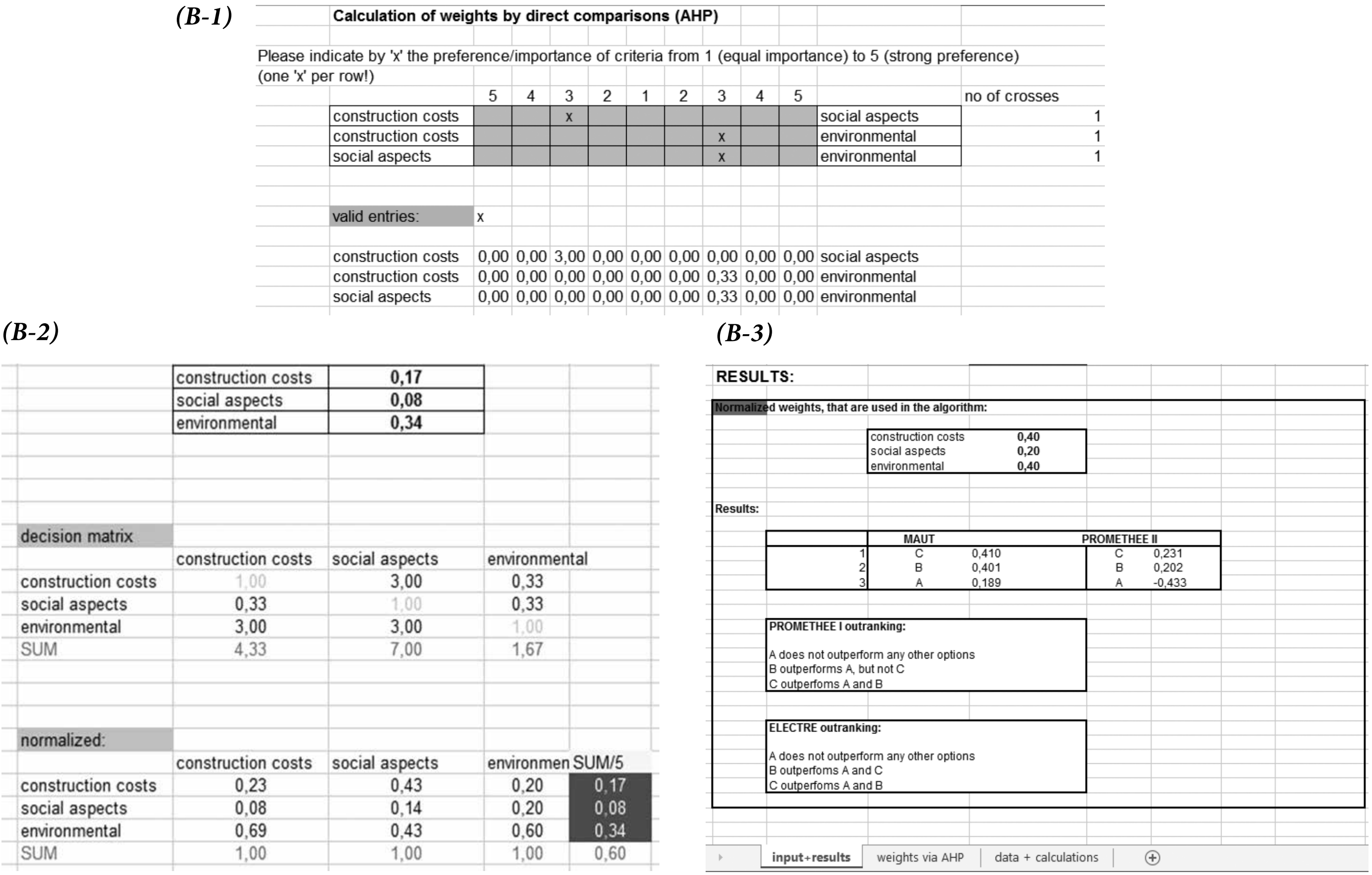
Segment II: s/s

(A-2)

segment	volume	Option A	Option B	Option C
I -1	10000	excavation	excavation	excavation
I-2	10000	excavation	soil amendments	soil amendments
D	5000	excavation	s/s	phytoremediation
II	5000	s/s	phytoremediation	s/s
III-1	7000	s/s	phytoremediation	phytoremediation
III-2	20000	separation	soil amendments	soil amendments

	construction c(	social aspects	environmental
components	€/m3	€/yr	0/1/2/3/4/5
excavation	300	10000	5
soil amendments	100	0	2
phytoremediation	60	25000	1
s/s	800	25000	4
separation	1000	50000	3
weights	0,40	0,20	0,40

Figure A. An example for remediation technologies option appraisal in multi-criteria analysis for different areal segments (A-1) and input options and costs in areals D, I, II and II (segments I and II are divided in two parts regarding contamination intensity and depth) (A-2) for the case study of BLB Baltijas Termināls and Vega Stividors



(B-1)

Calculation of weights by direct comparisons (AHP)

Please indicate by 'x' the preference/importance of criteria from 1 (equal importance) to 5 (strong preference)
(one 'x' per row!)

	5	4	3	2	1	2	3	4	5		no of crosses
construction costs			x							social aspects	1
construction costs							x			environmental	1
social aspects							x			environmental	1

valid entries: x

construction costs	0,00	0,00	3,00	0,00	0,00	0,00	0,00	0,00	0,00	social aspects
construction costs	0,00	0,00	0,00	0,00	0,00	0,00	0,33	0,00	0,00	environmental
social aspects	0,00	0,00	0,00	0,00	0,00	0,00	0,33	0,00	0,00	environmental

(B-2)

construction costs	**0,17**
social aspects	**0,08**
environmental	**0,34**

decision matrix

	construction costs	social aspects	environmental
construction costs	1,00	3,00	0,33
social aspects	0,33	1,00	0,33
environmental	3,00	3,00	1,00
SUM	4,33	7,00	1,67

normalized:

	construction costs	social aspects	environmen	SUM/5
construction costs	0,23	0,43	0,20	0,17
social aspects	0,08	0,14	0,20	0,08
environmental	0,69	0,43	0,60	0,34
SUM	1,00	1,00	1,00	0,60

(B-3)

RESULTS:

Normalized weights, that are used in the algorithm:

construction costs	**0,40**
social aspects	**0,20**
environmental	**0,40**

Results:

	MAUT		PROMETHEE II	
1	C	0,410	C	0,231
2	B	0,401	B	0,202
3	A	0,189	A	-0,433

PROMETHEE I outranking:

A does not outperform any other options
B outperforms A, but not C
C outperfoms A and B

ELECTRE outranking:

A does not outperform any other options
B outperfoms A and C
C outperfoms A and B

Figure B. An example for decision matrix normalization for criterions (B-1, B-2) and MCDA output for three given options (B-3) for the case study of BLB Baltijas Termināls and Vega Stividors