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OPTIMISING THE BIOPILING OF WEATHERED HYDROCARBONS WITHIN A RISK MANAGEMENT FRAMEWORK

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Introduction

Thirty years of research into petroleum microbiology and bioremediation have bypassed an important observation – that many hydrocarbon contaminated sites posing potential risks to human health harbour weathered, 'mid-distillate' or heavy oils rather than 'fresh product' (Pollard, 2003). *Ex-situ* biopiling is an important technology for treating soils contaminated with weathered hydrocarbons. However, its performance continues to be represented by reference to reductions in the hydrocarbon 'load' in the soils being treated, rather than reductions in the risks posed by the hydrocarbon contamination (Owens and Bourgouin, 2003; Tien *et al*., 1999). The absence of 'risk' from the vocabulary of many operators and remediation projects reduces stakeholder (regulatory, investor, landowner, and public) confidence in remediation technologies, and subsequently limits the market potential of these technologies. Stakeholder confidence in the biopiling of weathered hydrocarbons may be improved by demonstrating process optimisation within a validated risk management framework.

To address these issues, a consortium led by Cranfield University's Integrated Waste Management Centre has secured funding from the UK Government's Bioremediation LINK programme. Project PROMISE (involving BP, SecondSite Regeneration Ltd., Dew Remediation Ltd., TES Bretby (Mowlem Group), technology translators PERA, and academics from Aberdeen, Cranfield and Lancaster Universities) aims to improve market confidence in biopiling by demonstrating how this treatment may be applied within a risk management context.

Biopiling of weathered hydrocarbons

Bioremediation has developed substantially since the 1980s when it was first promoted as a sustainable technology for the remediation of sites contaminated with organic wastes. There are now a suite of *in-* and *ex-situ* technologies available (Biowise, 2000), which have found international application for a range of organic contaminants (fossil fuel hydrocarbons, organic wood-preserving wastes, high volume industrial organics e.g. polychorinated biphenyls, tetrachloroethylene). Its application for hydrocarbon waste treatment, principally as *ex-situ* engineered biopiling, has been assisted in the US by a shift towards risk-based, remedial design and technology verification (Dupont, 1991; ThermoRetec Consulting Corporation, 2000).

Biopiling is more responsive than many technologies to risk-based remediation because it allows the process control and optimisation of oxygen, nutrient, temperature, and water requirements during treatment. Biopiling also potentially offers a more controlled means of reducing site risk than other methods such as landfarming, windrowing or soil-banking. Engineered biopiling has developed into a mature technology for contaminated soil treatment with leachate, volatile organic compounds (VOC) and odour control (Biowise, 2000). There are applications of this and related technologies to heavier hydrocarbons reported, but detailed information on the specific reduction of risk is rarely reported in the open literature. Many hydrocarbon-contaminated sites (former refineries, coal carbonisation plants, and integrated steelworks) contain (i) oils that are weathered because the source term has aged since release (Pollard *et al*., 1994); (ii) heavy fuel oil residues such as Nos. 4, 5 and 6 fuel oil used in commercial boilers or heavy diesel engines (Uhler *et al*., 2002); and/or (iii) viscous tars and solid bituminous process residues that are difficult to treat biologically (Gray *et al*., 2000). In contrast to lighter gasoline (petrol), diesel and aviation fuels, the literature on heavy oil wastes is not extensive and the risks to human health not well characterised. Understanding the physicochemical and toxicological characteristics of contaminants in these source terms is critical because these factors drive the design of analytical strategies, our understanding of exposure, and selection/operation of remedial technologies (ThermoRetec Consulting Corporation, 2000).

Risk management for contaminated land

The management of risks to human health at contaminated sites is contingent on understanding the characteristics of the source, the existence and relative availability of pathways of exposure, and the relative vulnerabilities of receptors where harm may be manifest. The effectiveness of an environmental technology in treating pollution has historically been expressed as a percentage reduction in the pollutant concentration released to, or found in, a media of concern (Figure 1). Regulators are increasingly concerned however with mass, toxicity and risk reductions within the multimedia, multiphase environment.

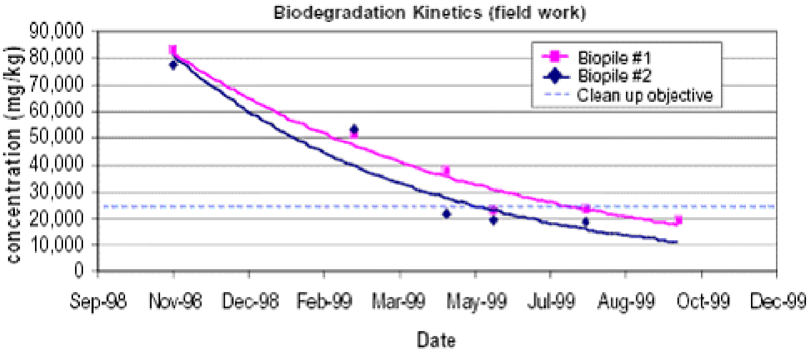

Figure 1: Biopile verification by reference to reductions in TPH load observed in soil (after Berlanger *et al*., 2003)

For weathered hydrocarbon wastes, risk management decisions are complicated by the gross complexity of the source term and the effects of weathering on the bioavailability of risk-critical compounds. There are also significant inter- and intra-variability in site conditions and resulting remediation successes (Pollard, 2003). For the heavy oils (equivalent carbon (EC) >20), losses due to biotic and abiotic weathering processes may result in compounds with increased hydrophobicity and recalcitrance. These compositional changes dramatically affect the affinity of the weathered wastes for risk-critical compounds such as polynuclear aromatic hydrocarbons (PAH) prior to, during and following biological treatment. These chemical processes are only partially understood.

Risk management frameworks

The regulation of site remediation now requires adoption of a risk-based approach. Verification of remediation technologies should take place within this framework. For petroleum hydrocarbons in the soil, international regulatory guidance on the management of risks from contaminated sites is now emerging (e.g. CCME, 2001; MADEP, 2002; NSWEPA, 2002; Environment Agency, 2005). Much of this promotes the use of risk management frameworks to guide decision making, application of reference analytical methodologies and the derivation of toxicological criteria (acute, sub-chronic, chronic) for these wastes. The Environment Agency of England and Wales have recently published their risk management framework for petroleum hydrocarbon in soils (Figure 2; Environment Agency, 2005). Part of this research will be to critically evaluate philosophical differences between US, European and Australian approaches to risk management for petroleum hydrocarbons (Table 1) and implications for selection of analytical and exposure assessment methods.

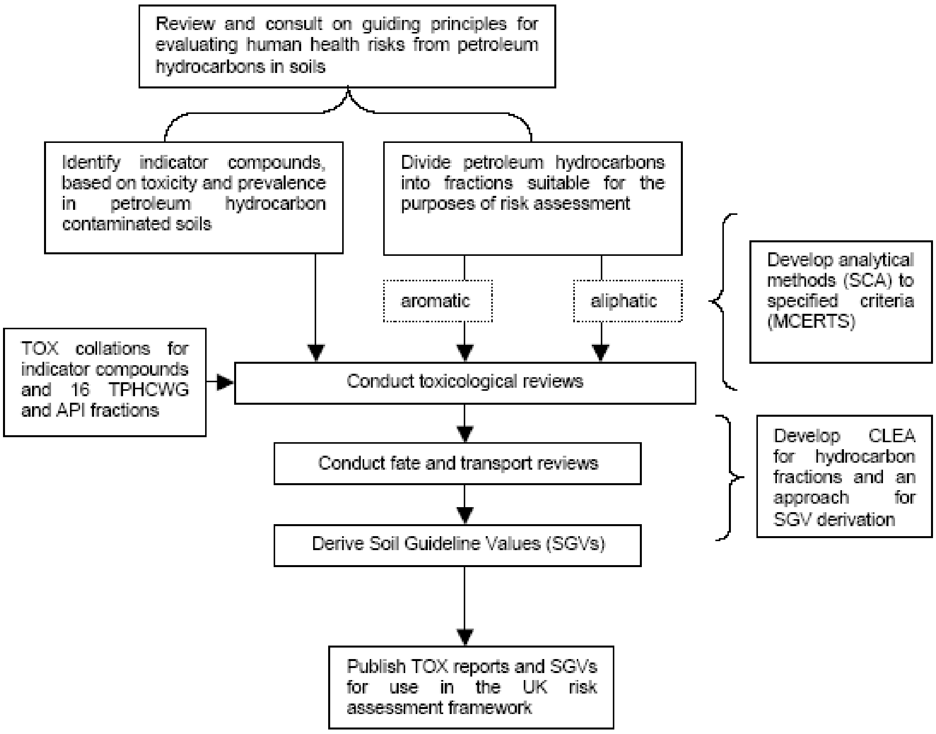

Figure 2: Developing the UK approach to risk assessment of hydrocarbons in soil.

Table 1. Some characteristics of regulatory approaches to evaluating the risks to human health from petroleum hydrocarbons in soil (Environment Agency, 2003)

Basis of approach	TPHCWG / RIVM	MADEP
Staged approach	Total petroleum hydrocarbon criteria working group (TPHCWG) and Dutch Institute for Public Health and Environmental Protection (RIVM) approaches assess indicator compounds first and, if necessary, progress to consideration of the (non-carcinogenic) effects of TPH fractions.	Requires assessors to look at both indicator compounds (target analytes) and (non-threshold) effects of petroleum fractions.
Defining fractions	RIVM and TPHCWG base fractions on equivalent carbon numbers (EC_n)	MADEP base fractions on carbon numbers
Combining fractions	TPHCWG and RIVM combine risk-based screening levels (RBSLs) for all fractions to give an overall petroleum RBSL	Under the MADEP scheme, the RSBL for each fraction is regarded as independent
Indicator compounds	RIVM and TPHCWG consider all compounds (including indicator compounds) in the EC range when assessing the (non-threshold) effects of petroleum fractions	MADEP specifically exclude the indicator compounds from the consideration of the non-threshold effects of TPH fractions

In the US, a substantial research effort has focussed on integrating hydrocarbon fate and transport, petroleum microbiology and environmental diagnostics to inform regulatory processes for site management under the Superfund Program. ThermoRetec Consulting Corporation (2000) provides an authoritative account of the central importance of partitioning within soil-bound hydrocarbons in developing environmentally acceptable remedial objectives. Drawing on a detailed understanding of residual oil fate and behaviour, this work is influencing the development of remediation criteria for petroleum hydrocarbon in soils in the US for human and ecological health. This includes an appraisal of the level of residual petroleum hydrocarbons that can be left at remediated sites without posing unacceptable risks to receptors. However, weathered, mid-distillate and heavier oil sources are generally given a narrow treatment by these reviews and frameworks.

The move towards risk-based corrective action (RBCA) has been slow in the UK and, whilst some progress has been made in integrating the aspects of analysis, exposure assessment and technology verification, there are gaps in the current knowledge base. Specifically: (i) analytical strategies in the UK are not generally targeted on risk-critical components; (ii) risk assessments do not regularly account for highly weathered residues encountered at many sites (API, 2001); and (iii) treatment 'success' is still supported by reductions in hydrocarbon load (Figure 1) in isolation of combined reduction in toxicity, chemical mass and risk.

Analysis of weathered hydrocarbons

Conventional bulk TPH analysis techniques tell the researcher relatively little about the types of contamination, potential toxicity and risks associated with the compounds present (ASTM, 1994; API, 2001; Environment Agency, 2003). These and other problems associated with the use of bulk TPH analysis as an indicator of soil contamination, make the use of solely this type of analysis inappropriate within a risk management framework. Analytical methods to determine concentrations of hydrocarbons in the soil need to be technically and economically feasible and capable of analysing risk-critical compounds (Environment Agency, 2003). With this in mind analytical techniques for the *n*C6 to *n*C40 range involve the extraction and fractionation into aliphatic and aromatic prior to analysis by gas chromatography mass spectrometry (GCMS) (Figure 3), with the *n*C40 to *n*C70 range analysis using high temperature gas chromatography with flame ionisation detection (GCFID).

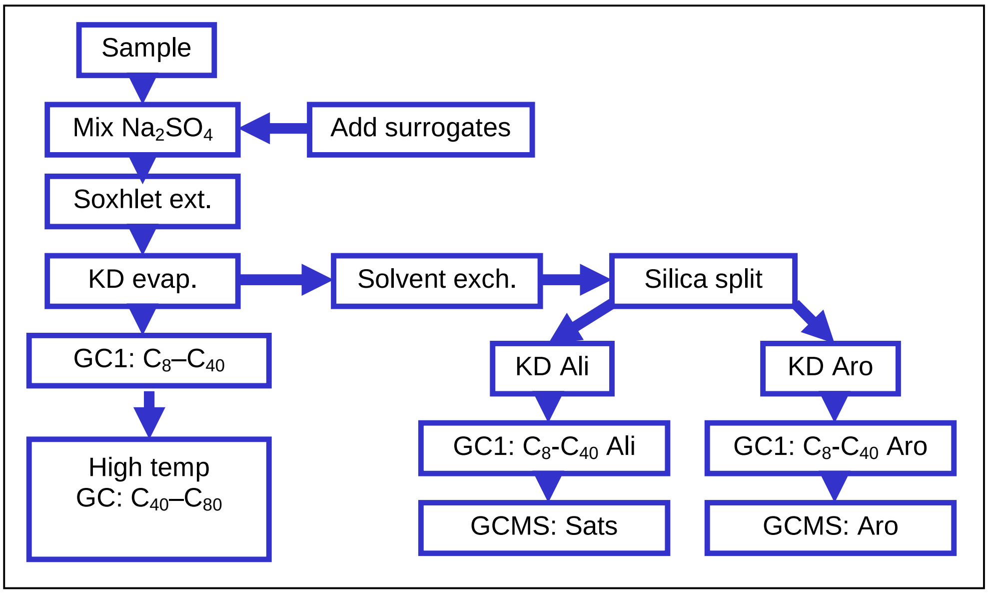

Figure 3: Schematic of preferred analytical approach

Microcosms and fate

Validation of the risk management framework will require treating representative weathered oils in laboratory microcosms. Periodic, sacrificial analysis of microcosm sub-samples will allow mass, toxicity and risk reductions to be quantified within each phase (waste/soil, vapour, leachate) over time. Toxicity will be estimated using a series of bioassays including earthworm survival, seed germination and luminescence-based biosensors (King *et al*., 1990; Layton *et al*., 1998). Measured contaminant concentrations over time will be compared with those predicted using level I and II fugacity models adapted, for the first time, to account for the partitioning behaviour of risk-critical components in the oil phase. The bioavailability of residual saturation within the waste-oil-soil matrix will be assessed using cyclodextrin extraction techniques.

Microcosms are currently being established at Aberdeen University. Microcosms (n = 120) will be split into sterile (control) and non-sterile treatments to distinguish between biotic and abiotic effects. A control (no contaminants) and three environmentally relevant concentrations of the ^{14}C-labelled oils will be added to each of the soils in triplicate. Samples will be analysed using liquid scintillation as well as by GCMS for routine and specialist parameters identified within the risk management framework. ^{14}C-analysis will be undertaken to accurately identify mineralization rates and to quantify soil-bound and bioavailable fractions.

Preliminary studies and method development has made use of model material collected from Kuwait that contains total extractable TPH of 15 %. This material has been mixed with two different control soils (Boyndie (sand, agricultural); industruial (post-remediated oil contaminated soil with residual TPH of 0.2 %)) to produce a series of seven TPH concentrations (%) for each soil (0, 0.175, 0.15, 0.375, 0.75, 1.5, 3). Toxicity of each soil is being evaluated using three different bioassays (earthworm survival; seed germination; luminescence-based biosensors). Currently the earthworm bioassay (*Lumbricus terrestris*) has shown 100 % survival in all soils up to 14 days. Further testing and refinement of the other two bioassays is still required.

Technology transfer

One of the major aims of project PROMISE is to improve stakeholder confidence in bioremediation techniques, with particular emphasis on biopiling. In order to achieve this, PERA Innovation Limited will lead and coordinate an active programme of communication and dialogue with key stakeholders to elicit views, advertise the programme of research and publicise the research outcomes and successes through established fora, targeted workshops and conferences/seminars.

Initial structured telephone interviews have been conducted using template analysis to lead and analyse the conversations. The preliminary results from these have been used to develop a structured investigative on-line questionnaire. Supporting analysis will be obtained through interaction with appropriate organisations and associations, whilst advice will be sought from key contacts in Local Authorities and environmental agencies. The latter two will also be approached with the view of leading user-group discussions. All respondents will be regularly informed of project progress to ensure that enthusiasm and interest is preserved over the course of the work and to incorporate any variable viewpoints.

Summary

For weathered hydrocarbons in particular, the underpinning scientific components of process control, waste diagnostics, environmental fate modelling, and risk assessment have yet to be fully integrated to allow biopiling projects to be verified with improved confidence. The Joint Research Council Review of Bioremediation (BBSRC *et al*., 1999) recognised this in calling explicitly for the positioning of bioremediation within a risk management framework. The PERF report (ThermoRetec, 2000) makes a significant advance but remains limited in its conclusions for weathered hydrocarbon wastes. The PROMISE project aims to increase stakeholder confidence in bioremediation processes, with particular reference to engineered biopiling, by integrating the areas described in this paper, incorporating biopiling into a risk management framework and implementing technology transfer methods to improve stakeholder confidence.

Conclusions

Currently the project is in its initial stages. Early development of a suitable analytical framework and the establishment of methodologies for microcosm experiments have been undertaken. Bioassays to assess toxicity of biodegradation products are in the final stages of development, as are strategies for technology transfer.

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