

**SOCIETY OF BROWNFIELD RISK ASSESSMENT
SUMMER WORKSHOP REPORT 2012**

**RISK ASSESSMENT OF PETROLEUM HYDROCARBONS
IN GROUNDWATER**

PUBLICATION

This report summarises the key technical issues relevant to the risk assessment of petroleum hydrocarbons in groundwater as presented and discussed at a SoBRA (Society of Brownfield Risk Assessment) workshop in June 2012.

Whilst every effort has been made to ensure the report is an accurate account of workshop proceedings, neither SoBRA nor the authors of the report accept any liability whatsoever for any loss or damage arising in any way from its use or interpretation, or from reliance on any views contained herein.

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PREFACE

The Society of Brownfield Risk Assessment (SoBRA) was established in December 2009 with the principal aim of promoting technical excellence in land contamination risk assessment in the UK.

As part of achieving this aim, SoBRA undertook to host regular conferences and workshops on technical subjects of interest to UK risk assessors.

SoBRA's first summer workshop was held in June 2010 in York where the human health risk assessment of polycyclic aromatic hydrocarbons in soil was considered.

SoBRA's second summer workshop was held in June 2011 at the Mechanics Institute in Manchester. It addressed the assessment of the risks associated with lead contamination in soil.

The current report describes the proceedings of SoBRA's third summer workshop, which considered the risk assessment of petroleum hydrocarbons in groundwater. The event was held at Armada House in Bristol on 28th June 2012. Following the same thematic format established by previous events, the day was structured around four key themes:

- 1) site investigation and sampling;
- 2) laboratory analysis and environmental forensics;
- 3) groundwater risk assessment modelling and the development of guidance; and
- 4) assessment of the vapour risk from groundwater.

Delegates heard presentations from expert speakers on the four topics and participated in separate afternoon workshops on the same themes. During the morning proceedings, delegates also heard a presentation from the Environment Agency on the policy issues surrounding hydrocarbon contamination in groundwater and a progress report from the leader of SoBRA's working group on vapour risks.

Eighty delegates, including expert speakers and SoBRA Executive Committee members, attended the 2012 summer workshop. Feedback provided by delegates electronically after the event was extremely positive with 100% of responding delegates rating the event as "excellent" or "good", with similar high scores awarded to the individual afternoon workshops. Overall, therefore, the 2012 summer workshop consolidated SoBRA's commitment to hosting high quality and stimulating meetings on technical topics of relevance to its members.

This report fulfils an undertaking given by SoBRA to produce a formal record of the proceedings of the workshop. It summarises the expert presentations given on the day, records current views on the main technical issues within each subject area and describes the challenges identified by risk assessors in dealing appropriately with petroleum hydrocarbons in groundwater.

ACKNOWLEDGMENTS

SoBRA wishes to thank the following individuals for their considerable assistance in the successful delivery of the SOBRA 2012 summer workshop and associated report.

Trevor Howard	Environment Agency	Expert Speaker
Jon Parry	SLR Consulting	Expert Speaker & Workshop 1 Facilitator
Hazel Davidson	Derwentside Environmental Testing Services	Expert Speaker & Workshop 2 Facilitator
Mike Carey	AMEC	Expert Speaker & Workshop 3 Facilitator
Robert Ettinger	Geosyntec Consultants	Expert Speaker
Simon Clennell-Jones	WSP Environment and Energy	Expert Speaker & Workshop 4 Facilitator
Ed Stutt	WCA Environment	Workshop 1 Facilitator
Charles Bacon	University of Bristol/Golder Associates UK Ltd	Workshop 1 Rapporteur
David Megson	University of Plymouth	Workshop 2 Rapporteur
James Rayner	Geosyntec Consultants	Workshop 3 Rapporteur
Natasha Glynn	Atkins	Workshop 4 Rapporteur
Mary Harris	MRH Consultants Ltd	Report Editor

Special thanks are due to Ed Stutt (WCA Environment) and Rob Ivens (Mole Valley District Council) of SoBRA's Executive Committee for the smooth organisation and running of the event and to David Hall (Golder Associates UK Ltd and SoBRA's treasurer) who looked after financial matters.

Finally, SoBRA wishes to acknowledge the contribution to the overall success of the event made by individual workshop delegates for attending and enthusiastically participating in the day's proceedings.

Workshop delegates are listed in Appendix 1 to this report.

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1 INTRODUCTION

1.1 Background

Hydrocarbons are organic compounds with molecules comprising only hydrogen and carbon atoms and are naturally occurring in all organisms and in their geological derivatives: crude oil, natural gas and coal.

Soil and water contamination by petroleum hydrocarbons is a common occurrence in the UK due to the widespread use and transport of these compounds as fuels and lubricants, and their presence in industry in the form of raw and waste materials. Hydrocarbons are hazardous substances (former List 1) and include individual substances, such as benzene, toluene, ethylbenzene and xylenes (BTEX) and groups of substances, such as polycyclic aromatic hydrocarbons (PAHs).

In addition to the health and environmental impacts associated with some of the more toxic compounds, a range of other harmful and negative aesthetic effects may result from uncontrolled releases of petroleum hydrocarbons. For example, they can taint water supplies, create visual impact (e.g. the fouling of soils and surface waters) and produce unpleasant odours.

Petroleum hydrocarbons comprise a large group of compounds that have a range of different chemical and physical properties. They can exist in a number of physical states and exhibit different behaviours once they are released into the environment. Hydrocarbon pollution can occur as a dissolved phase in the water environment, or as free product, also known as non-aqueous phase liquid (NAPL), which is typically lighter or less dense than water (LNAPL). Some low molecular weight compounds are readily soluble and/or volatile, and can be highly mobile in the environment moving rapidly away from a release site into all compartments (solid, gas and liquid phases) of the subsurface. High molecular weight compounds tend to be less soluble, volatile and mobile, and they can be highly resistant to degradation so persisting in the subsurface environment for many decades.

The contamination of groundwater by petroleum hydrocarbons can present particular problems, not least because certain parts of the UK rely on groundwater sources for a significant proportion of their potable water supply. Even if groundwater is not used directly for drinking water purposes, it may contribute to the base flow of rivers and streams, so contamination can have major implications for the quality of surface waters used for drinking water purposes, and for any animals, plants and ecosystems reliant on the quality of surface water for their well-being.

The chemical complexity of petroleum hydrocarbons presents additional practical difficulties for risk assessors involved in groundwater contamination projects. For example:

- it is important to ensure that individual or groups of hydrocarbon compounds, particularly the so-called 'risk-driving' compounds (e.g. those which are particularly toxic or mobile in the subsurface environment) are correctly identified - this has implications for consistency in the use of the chemical nomenclature and for the selection of appropriate field and laboratory based diagnostic techniques;
- the physical and chemical properties of individual or groups of hydrocarbon compounds, and their likely behaviour in the subsurface environment, must also be correctly anticipated - this is essential to ensure that groundwater contamination is properly conceptualised at the outset so that site

investigation and monitoring effort delivers the reliable, good quality data needed for risk assessment purposes.

Despite much progress over recent years, groundwater contamination by hydrocarbons also continues to present a challenge for the development and use of appropriate modelling tools for both the aqueous and vapour phases.

The varied and challenging nature of the topic selected for the 2012 SoBRA Summer Workshop provoked much discussion and debate amongst participants as described in the remainder of this report.

1.2 The SoBRA Workshop

The 2012 SoBRA Summer Workshop aimed to define current understanding of the key issues surrounding the risk assessment of petroleum hydrocarbons in groundwater, to identify key uncertainties in current approaches, and to establish where there is (and is not) consensus on how best to manage and resolve uncertainties.

A specific goal of the workshop organisers was to produce a formal workshop output that summarised the proceedings, consolidated ideas and made recommendations on the work required to support risk assessment efforts in the future. This report is that written output.

1.3 Structure of the Report

Following this introduction, section 2 of the report sets the scene for the workshop proceedings as a whole by providing an account of the UK policy and legal background relevant to groundwater contamination by petroleum hydrocarbons. This section also sets out the key technical issues relevant to each workshop topic as described by expert speakers.

Four key themes were addressed:

- site investigation and sampling;
- laboratory analysis and environmental forensics;
- groundwater risk assessment modelling and the development of guidance; and
- assessment of the vapour risk from groundwater.

Sections 3 to 6 summarise workshop discussions on each of the four themes.

Section 7 of the report draws on the outcome of the workshop discussions, identifies some common issues and highlights key recommendations.

Reference documents used to support presentations and workshop discussions are shown as footnotes to the text, and are collated as a complete list in section 8 of the report.

Appendix 1 gives details of the workshop groups including names of individual participants. Appendix 2 sets out a list of the abbreviations used in the report.

2 EXPERT PRESENTATIONS

2.1 Policy and Legal Background

2.1.1 Policy Issues for Hydrocarbon Contamination in Groundwater

Trevor Howard of the Environment Agency presented a summary of the European and UK groundwater policy hierarchy and the status of four UK legislative regimes that aim to protect and/or improve groundwater quality. He highlighted key differences between these regimes and some of the issues to be overcome through the development of new guidance, tools and methodologies.

Effective management and protection of groundwater quality is of national importance. The Environment Agency indicates groundwater provides nearly one third of drinking water; some parts of the country are more dependent still, using groundwater resources for up to 80% of potable supply. Surface waters are partly fed by groundwater; some rivers, wetlands and associated ecology are completely dependent on it. Some aquifers even provide ecological habitats of their own in the form of groundwater macrofauna or stygofauna¹.

Pollution puts resource and aquatic ecosystems under pressure. Many impacts to groundwater have resulted historically, some of which are many decades old. More recent legislation has sought to prevent pollution or improve groundwater quality but impacts continue to occur that are potentially detrimental to groundwater and surface water quality. The relative invisibility of groundwater means that the effects of land contamination on it are sometimes overlooked.

2.1.2 Groundwater Policy Hierarchy

Groundwater policy is made at three levels:

- The highest level, European Legislation (EU Policy), includes many Directives that aim to protect or improve groundwater. The Water Framework Directive and Groundwater Directive define key objectives for groundwater that include achieving “Good Status”, preventing and limiting pollution, reversing trends in declining water quality and protecting drinking water.
- UK government legislation (Government Policy) either directly or partly implements EU Directives that consider groundwater protection. The latter group includes Anti-Pollution Works², Environmental Permitting³, Part 2A⁴ and Town and Country Planning⁵ legislation.
- The Environment Agency’s viewpoint on groundwater is provided in the guidance document GP3 (Groundwater Protection: Principles and Practice)⁶.

GP3 aims to provide a framework for consistent regulation, encourage co-operation between stakeholders, promote Environment Agency positions, influence the decisions of other organisations on pertinent issues, ensure sustainable groundwater protection into the future and provide information on groundwater for England and Wales.

¹ Environment Agency Wales. 2012. Presentation on subterranean aquatic ecology of the Vale of Glamorgan. Accessed at South East Wales Biodiversity Records Centre, www.sewbrec.org.uk

² The Anti-Pollution Works Regulations. 1999. SI No. 1006

³ Environmental Permitting (England and Wales) Regulations. 2010. SI No. 675

⁴ Environmental Protection Act 1990 c. 43 Part 2A Contaminated Land

⁵ Town and Country Planning Act 1990 c. 8

⁶ Environment Agency. 2012. GP3, Groundwater protection: Principles and practice, LIT 7562, Version 1

Note that GP3 has recently been revised (November 2012). The new document and further details are available at: <http://www.environment-agency.gov.uk/research/library/publications/144346.aspx>.

While the overall objective of groundwater protection is similar across this policy hierarchy, the aims and approaches of individual regimes are subtly different and subject to details of the legislation; policy decisions made at all levels of government; and our society's changing expectations.

2.1.3 UK Legislation & Policy

Trevor described the current status of four sets of policy/legislation that aim to protect and/or improve groundwater quality.

Planning Policy

Planning Policy Statement 23 (PPS 23) was withdrawn in March 2012 and superseded by the National Planning Policy Framework (NPPF) as part of the government's reforms to make the planning system less complex, more accessible and to promote sustainable development.

With regard to surface and groundwater, the NPPF aims to "prevent both new and existing development from contributing to or being put at unacceptable risk from, or being adversely affected by, unacceptable levels of....water....pollution" and improve the environment by "remediating.....contaminated land, where appropriate".

Stakeholder responsibilities under the new NPPF are similar to those in the previous planning policy PPS23:

- The developer or landowner should ensure that development is safe and that the land is suitable for the use intended, or can be made so through remediation. By ensuring that developers reduce or remove the risk or consequences of pollution of surface and groundwater, the planning regime should aid the realisation of Water Framework Directive objectives.
- Local Authorities take responsibility for development management policies and decisions regarding contamination, taking account of ground conditions, pollution arising from previous uses and any proposals for remediation.
- The Environment Agency is a statutory consultee for local plans, certain types of planning application and developments requiring an Environmental Impact Assessment, chiefly concerning the water environment.

For the purposes of determining planning applications, the NPPF follows the same risk-based approach, concepts and principles for land contamination management as is used for the Part 2A regime and should not therefore require any significant development or application of new methods for groundwater pollution assessment.

Note that the Environment Agency has produced quick guides to the NPPF - further information is available at <http://www.environment-agency.gov.uk/research/planning/139631.aspx>

Part 2A

Part 2A of the Environmental Protection Act (EPA) 1990 defines "pollution of controlled waters" as the entry into controlled waters of any poisonous, noxious or polluting matter or any solid waste matter. Section 86 of the Water Act 2003 changed how Part 2A applies to cases of water pollution. It introduced two tests for the determination of land on water pollution grounds that differ from the

Water Framework Directive and conventional Environment Agency interpretation of pollution:

- “Significant Pollution of Controlled Waters” - being pollution that is currently occurring; and
- “Significant Possibility of Significant Pollution of Controlled Waters” (SPoSPoCW).

The new category 1-4 system introduced by the revised Part 2A Statutory Guidance⁷ is designed to aid the determination of cases of a Significant Possibility of Significant Pollution of Controlled Waters:

- Category 1 or 2 = SPoSPoCW
- Category 3 or 4 ≠ SPoSPoCW

The guidance gives examples of what levels of pollution might represent each category as set out in Table 1 below.

Table 1: Examples of levels of pollution in each SPoSPoCW Category

Category 1	Category 2	Category 3	Category 4
Environmental Damage Regulations (EDR) damage Drinking water requiring treatment Statutory surface water Environmental Quality Standards (EQS) exceeded Upward trends in groundwater concentrations	Whether a particular case is Category 2 or 3 depends on whether there are significant concentrations at appropriate compliance points Categorisation is subject to cost/benefit considerations		“Minor Entry” Concentrations not discernible Authorised discharge

It is anticipated that the determination of Categories 1 and 4 cases could be relatively straightforward. The boundary between Category 2 and 3 cases is greyer, however, and is intended to be resolved through risk assessment coupled with cost/benefit analysis. This matter will be the subject of an Environment Agency project that is due to start later in 2012. A key question to be answered is whether existing risk assessment tools and methodologies are suitable for the task and what new guidance will be required to support application of the revised Statutory Guidance.

Environmental Permitting & Industrial Emissions Directive (IED)

The Integrated Pollution Prevention and Control (IPPC) regime provides an integrated environmental approach to the regulation of certain industrial

⁷ Department for Environment, Food and Rural Affairs (Defra). 2012. Environmental Protection Act 1990: Part 2A Contaminated Land Statutory Guidance. www.defra.gov.uk

activities. The IPPC Directive is implemented in England and Wales by the Environmental Permitting Regulations 2010 (EPR) - see Defra guidance on EPR⁸.

Environmental Permitting adopts a Site Condition Report (SCR) approach to prevent pollution and provide documented evidence to this effect. On this aspect Environmental Permitting is not a risk-based policy, as it aims for there to be “no deterioration” from baseline in land or groundwater quality as a result of industrial activity.

Defra acknowledges this approach is potentially onerous but states that:

“This may be significantly stricter than the ‘suitable for use’ test of the contaminated land regime in Part 2A of the Environmental Protection Act 1990 and similar controls on redevelopment [NPPF]. While ‘suitable for use’ is appropriate for pre-existing contamination, it is not the right test for the preventative environmental permitting regime”.

Where deterioration has occurred, contamination should be removed unless it is unsustainable or not practical to do so. In these cases the Environment Agency allows for the use of risk assessment and cost/benefit analysis to understand what would be reasonable action.

Defra is currently considering implementation of the Industrial Emissions Directive as a replacement for the IPPC regime. The IED is similar to IPPC in that it adopts a “no deterioration” approach to new contamination (not risk-based). It will require baseline setting for soil and groundwater quality in some circumstances with minimum frequencies for soil and groundwater monitoring also stipulated.

Environmental Damage Regulations (EDR)

These regulations aim to prevent serious environmental impacts or ensure that remediation is completed to restore the environment and provide compensation for major harm following operational failures.

The regulations apply a “*no deterioration*” policy and specify three types of land damage, including “*water damage*”. The threshold for water damage is high. EDR cases are therefore likely to be among the most serious cases of pollution, which currently relates to only a small number of sites in the UK.

2.1.4 Summary

UK groundwater policies share the common goal of groundwater protection and/or improvement but the approaches to achieve this differ. Part 2A and NPPF address existing contamination to ensure suitability for use currently or in the future through risk assessment. Environmental Permitting and Environmental Damage Regulations aim to prevent pollution by not allowing deterioration of groundwater quality.

While there are differences in the aims, objectives or approaches of the various regimes, much of the existing guidance, methodologies and tools can be used or adapted for all, and many of the uncertainties and evidence gaps are the same.

2.2 Site Investigation and Sampling

2.2.1 Introduction

Jon Parry (SLR Consulting Ltd) gave a presentation on site investigation and sampling, conceptual models (CMs) and data quality objectives.

⁸ Defra. 2012. Environmental Permitting Guidance – Core Guidance for the Environmental Permitting (England and Wales) Regulations 2010, Revised March 2012, Version 4.0

Jon began by stating that the site investigation phase is likely to be the most expensive element of any risk assessment project involving hydrocarbons in groundwater and that it is crucial that the dataset obtained from site investigation is robust and reliable to ensure the validity of risk assessment findings and conclusions. Groundwater occurs in shallow and perched aquifers in intergranular porosity within made ground and unconsolidated superficial drift deposits and also in deeper rock aquifers within intergranular and fracture porosity.

A range of petroleum hydrocarbons may be present at a site, each with different parameters that govern their fate and transport in the environment. Partitioning between the soil, water and vapour phases is determined by key contaminant-specific parameters including solubility, vapour pressure (volatility) and the organic carbon to water partition coefficient (K_{oc}). For example, the aromatic compounds benzene and toluene both have low partition coefficients and high solubility values, which give a high overall risk rating compared to other hydrocarbons. Lighter-end aliphatic hydrocarbons are also very mobile and can be widely distributed over a site. An appreciation of these different factors is needed when planning any site investigation involving hydrocarbons in groundwater. Note that fraction of organic carbon of the aquifer matrix is also a key control on partitioning of hydrocarbons and so aquifer-specific values of fraction of organic carbon should be obtained during the site investigation, for use in the subsequent risk assessment.

2.2.2 Key Design Issues

Any site investigation should be driven by clearly stated aims and scope of work which are informed by the risk assessment data requirements of a project, as well as any future widening of its scope. It is essential that critical pathways are identified in advance and targeted by the site investigation. Furthermore, a system of QA/QC must be built in at an early stage to prevent false positive or negative results, for example due to changes in the type of groundwater sampling technique chosen.

Before any intrusive works commence, a good estimate is required of the piezometric surface elevation(s), flow direction and gradient of the groundwater body being assessed. These should be obtained from available references or through desk-based review.

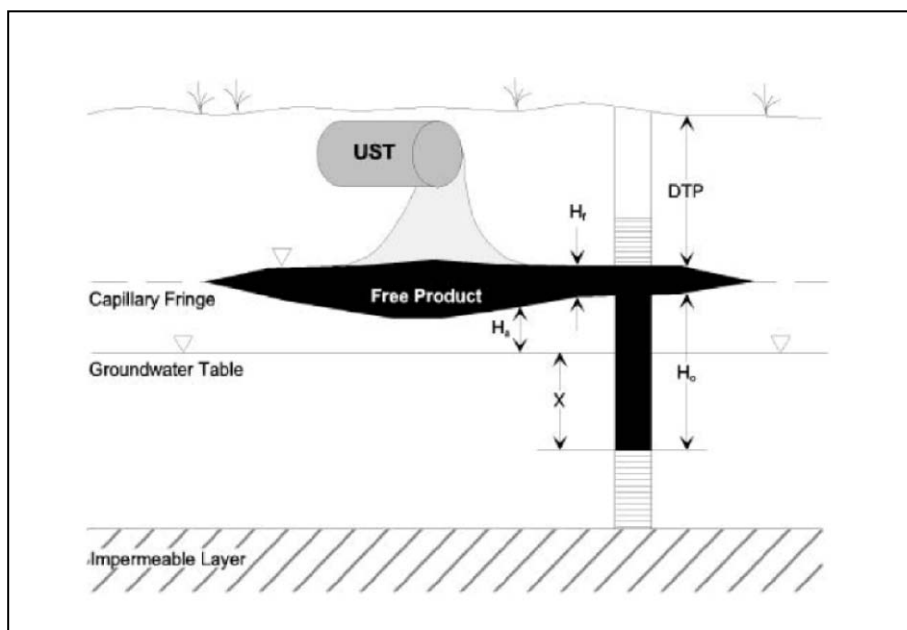
All CMs involving hydrocarbon contamination of groundwater must include a consideration of: the possible hydrocarbons present; the type of source involved (e.g. pipeline, underground storage tank (UST), above ground storage tank (AST)); the release history, as far as it can be established from desk study; and the likely partitioning behaviour of the hydrocarbons given the geology and hydrogeology of the site. Likely partitioning between the solid soil matrix, groundwater (vadose zone, sub water table) and soil air must be considered and factored into the planning of any site investigation work.

The 'Tank and Pancake' model of subsurface light non-aqueous phase liquid (LNAPL) dispersal has been repeatedly shown to be too simplistic in reality (see Box 1)⁹. The shortcomings of this model include the fact that lateral flow is often rather limited and LNAPL is often found to be trapped in secondary porosity fractures, or perched on any low permeability layers present, so that the LNAPL has a stepped vertical profile. Monitoring well location and design can improve the

⁹ United States Environmental Protection Agency (USEPA). 1996. How to effectively recover free product at leaking underground storage tank sites: A guide for state regulators, EPA 510-R-96-001 - available from: <http://epa.gov/OUST/pubs/fprg.htm>

detection and delineation of any LNAPL present^{10,11}. By contrast, poor well design or installation can lead to misleading results. For example, well screen length and location can significantly affect the apparent thickness of LNAPL. In particular, in low permeability formations, the well can act as a sump for LNAPL, drawing it down below its actual level, and giving erroneous data.

Box 1: The classic 'Tank and Pancake' conceptual model of subsurface LNAPL dispersal



Well screens should be as short as possible and targeted in order to improve resolution of data, in terms of both the heterogeneity of the site hydrogeology and contaminant concentrations. Complex sites benefit from multi-level well designs that give greater data resolution.

Investigating the source zones and mass of NAPL (non-aqueous phase liquid) present is complex and requires both horizontal and vertical data¹². The observation of NAPL in a monitoring well will depend on many factors governed by the aquifer heterogeneity, the well installation design and NAPL distribution in the aquifer. For example in a fractured aquifer two nearby wells may record different NAPL thicknesses due entirely to variations in the fracture orientation and connectivity to each well. Another consideration is that NAPL flow into monitoring wells might be temporally variable depending on hydraulic conditions and seasonal fluctuations.

2.2.3 Site Investigation Tools and Techniques

Many site investigation tools are available, covering a range of data resolutions. Tools include field analytical equipment and techniques such as:

- ¹⁰ Environment Agency. 2006. Guidance on the design and installation of groundwater quality monitoring points. Science Report – SC020093
- ¹¹ International Standards Organisation (ISO). ISO 5667-1. 2006. Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques
- ¹² Environment Agency. 2009. Petroleum hydrocarbons in groundwater: Supplementary guidance for hydrogeological risk assessment

- MIP (Membrane Interface Probe), LIF (Laser Induced Fluorescence), PID (Photoionization Detector), FID (Flame Ionization Detector); and Waterloo profiler¹³;
- borehole geophysics;
- cored boreholes;
- multi-level installations¹⁴; and
- traditional monitoring wells.

These tools and techniques can complement each other and direct the course of the investigation as it progresses. Each tool also has limitations that should be acknowledged in the investigation design. Sufficient training and experience is required for the correct and successful use of every type of tool/technique.

Monitoring well gravel packs should be developed prior to sampling by rapid removal of groundwater using air-lifting or surge pumping techniques. Well development information should be included where data objectives require it, as drilling operations could clog the gravel pack and aquifer as drilling progresses, which may render the well obsolete. Gravel packs may also bridge without careful installation followed by well development, resulting in loss of well integrity. This is often overlooked or not documented in traditional investigations.

Well development is not simply a matter of extracting three well volumes, and other tools exist for determining appropriate extraction volumes such as turbidity/suspended sediment tests. Often, the best approach is surging and airlifting. Differences in well performance measured on a pre- and post-development basis can be pronounced and an example of this for a chalk well was shown during the presentation. The maximum pumping rate of the developed well increased from 8 litres/min to 35 litres/min, with a 2m settling of the gravel pack (which required the use of 20 additional bags of gravel after development) and the suspended sediment content dropped from >300mg/litre to <50mg/litre.

2.2.4 Groundwater Sampling Techniques

A range of groundwater sampling techniques were described in the presentation. The best choice should be a reflection of the contaminants considered to be present and the data objectives. Well design will also influence the method selected. Low flow groundwater sampling methods that avoid stripping out volatile hydrocarbons by causing laminar rather than turbulent flow in the well are usually believed to give representative samples, but need to target the impacted zone or sample multiple depth zones. Sampling protocols need to be appropriate for organic chemicals, this includes containers, headspace, storage temperature and journey time to the laboratory. As for every step of the investigation, the rationale for each decision needs to be documented.

2.2.5 Case Study Example

A case study was presented of a NAPL plume that was detected using a variety of methods including headspace readings from vapours emitted from core samples. A correlation between groundwater elevation and LNAPL thickness was observed, with measured LNAPL accumulations occurring over a repeated seasonal cycle over a 2-year period. LNAPL reduced in thickness or disappeared in the wells

¹³ Pitkin, S.E., Cherry, J. A., Ingleton, R.A. & Broholm, M. 1999. Field demonstrations using the Waterloo Groundwater Profiler. Ground Water Monitoring and Remediation, Volume 19, Issue 2, pp122-131

¹⁴ Contaminated Land: Applications in Real Environments (CL:AIRE). 2002. Multilevel sampling systems. Technical Bulletin TB02

during the seasonal cycle indicating a dynamic relationship with groundwater elevation. High resolution sampling helped in the development of the CM.

The presentation ended with a summary that stressed the need to:

- define the objectives of the site investigation and design according to the conceptual model, which needs to be continuously up-dated as more information is obtained;
- document the sampling rationale;
- attempt to estimate source mass and distribution whilst indicating where the main uncertainties lie; and
- consider heterogeneity.

2.3 Laboratory Analysis and Environmental Forensics

2.3.1 Introduction

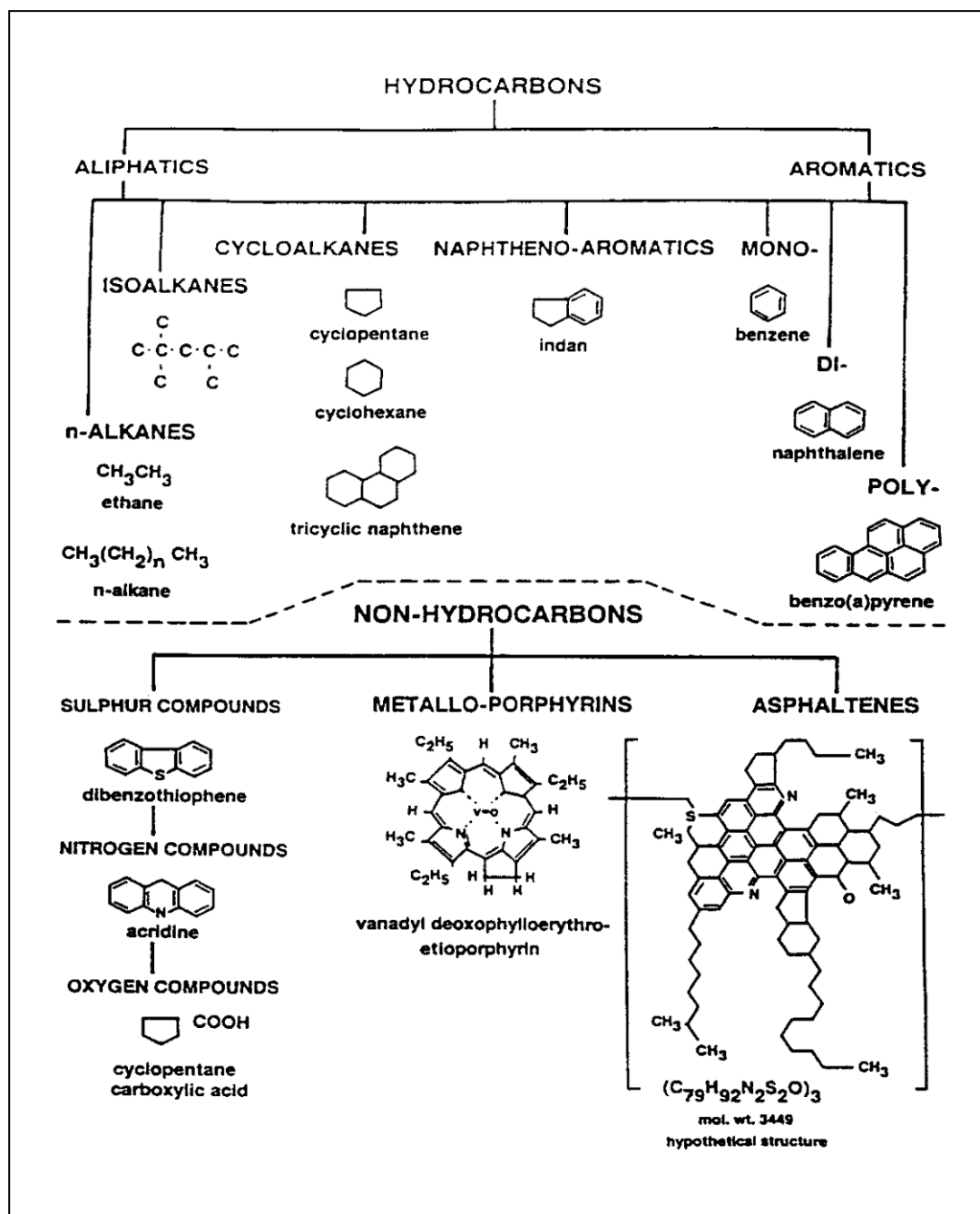
Hazel Davidson of Derwentside Environmental Testing Services provided an introduction to the chemistry of petroleum hydrocarbons and gave an overview of the techniques commonly used in their laboratory analysis. She also addressed the environmental forensics techniques available for source identification and age dating. A summary of the key points from the presentation is given below.

2.3.2 Composition of Petroleum Hydrocarbons

Petroleum hydrocarbons include thousands of different individual compounds derived from crude oil. These compounds can be placed into groups based on their chemical structure; some of the major groups are presented in Box 2.

Note that the toxicity, mobility and environmental persistence of these different compounds are highly variable. Generally with an increasing molecular size (carbon number) there is an increase in boiling point, density and adhesion to soils, and a decrease in vapour pressure and solubility.

Box 2: Overview of the major groups of compounds found in crude oil



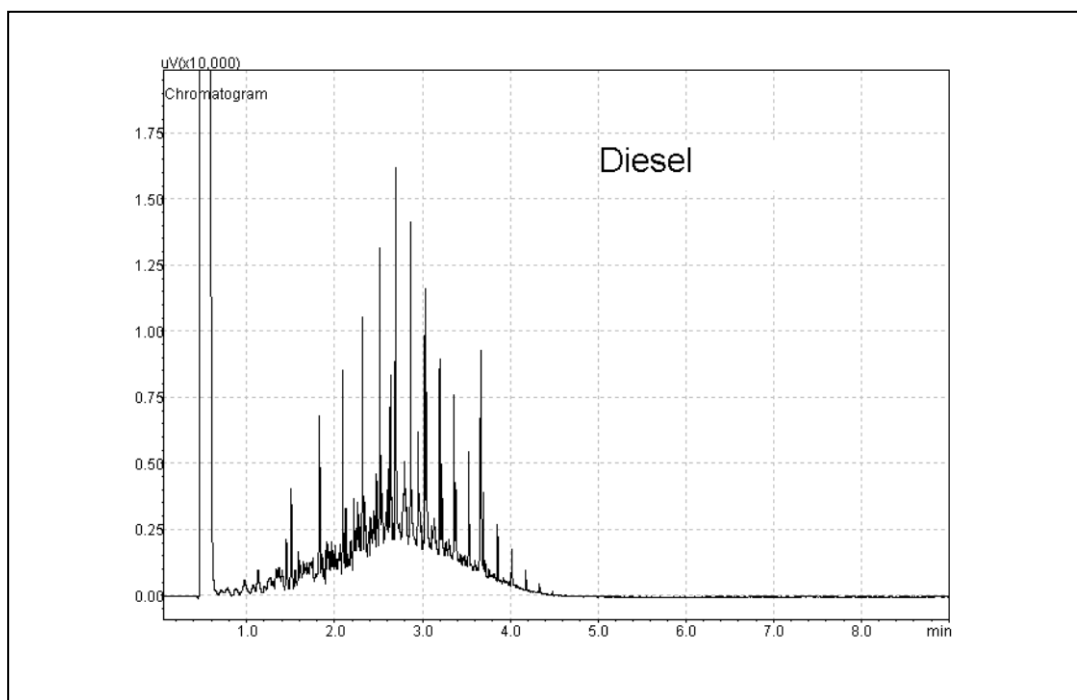
2.3.3 Methods of Analysis

Two main instruments are commonly used for the analysis of petroleum hydrocarbons:

- Gas Chromatography Flame Ionisation Detector (GC FID) – used for initial screening and bulk identification of compounds in relatively high concentrations.
- Gas Chromatography Mass Spectroscopy (GC MS) – used for the more detailed analysis and quantification of individual compounds at relatively low concentrations.

Both techniques use gas chromatography, which allows for the separation of compounds by partitioning between a stationary phase (the column) and a mobile phase (carrier gas). Samples are injected into the instrument where they are vaporised and pass into the column. This is located in an oven where the temperature is increased at a set rate. The columns used for the majority of hydrocarbon analyses allow separation to be based primarily on boiling point; this means that the lighter hydrocarbons tend to elute (leave the column and reach the detector) before the heavier hydrocarbons. Box 3 shows an example chromatogram where the 'x' axis represents time and the 'y' axis is the response from the detector.

Box 3: Example chromatogram



Under the same instrumental conditions, the same compound will always elute at the same time. The time at which a compound elutes is called the retention time. Identification of compounds by FID is by retention time only which can lead to errors due to co-eluting compounds (2 or more compounds with the same retention time). Identification by MS uses retention time data along with interpretation based on the mass of the compound. This makes MS a more accurate detector as it is able to resolve co-eluting compounds with different masses.

Different laboratories may use slightly different sample preparation methodologies; for example, they may use different solvents and different extraction techniques. This may explain some variability in the data produced by different laboratories analysing the same sample. However, each laboratory should undertake strict quality control procedures to monitor the performance of their chosen method and make improvements where necessary.

The concentrations of petroleum hydrocarbons may be reported in a variety of different ways. Each method usually involves reporting the concentration of groups of hydrocarbons that elute at a given time window on a chromatogram,

e.g. the sum of all compounds eluting between carbon numbers C₅ to C₁₀. The following groups are often used when analysing petroleum hydrocarbons:

- GRO – Gasoline Range Organics, sometimes also known as Petrol Range Organics (PRO) or volatile petroleum hydrocarbons (VPH). GRO include around 400 different compounds with carbon numbers ranging from around C₅ to C₁₀; however, the exact range of analysed compounds varies slightly between different laboratories. Analysis of GRO is usually by the headspace method that involves analysis of the volatile compounds, which have diffused into the air (headspace) above the sample. This technique generally has a rapid turnaround, is relatively inexpensive and gives detection limits of about 10ppb.
- EPH – Extractable Petroleum Hydrocarbons. EPH include hundreds of aliphatic and aromatic compounds with carbon numbers ranging between C₁₀ to C₄₀; however, the exact range of analysed compounds varies slightly between different laboratories. As the name suggests, an extraction procedure is required for the analysis of this suite of compounds, which makes analysis more time intensive. A 'cleaned up' EPH includes non-polar compounds (aliphatics) and slightly polar compounds (aromatics) but does not include polar compounds (NSOs - nitrogen, sulphur and oxygen containing compounds) such as carbazole. The term 'Mineral Oil' is sometimes reported; this refers to the non-polar compounds that are collected from the EPH fraction.
- TPH screen – The Total Petroleum Hydrocarbon screen. This measure is now largely obsolete in risk assessment due to improvements in the understanding of the toxicity of individual hydrocarbons. It refers to a combination of the GRO and EPH.
- TPHCWG suite – Total Petroleum Hydrocarbon Criteria Working Group suite. This is the recommended analytical suite for assessing the risks from petroleum hydrocarbons and includes bands of aliphatic and aromatic hydrocarbons in the carbon number range C₅ to C₄₄.

2.3.4 Forensic Analysis

Forensic analysis is often used to answer four main questions arising from a contamination incident:

- what is it [the contaminant]?
- what was its source?
- when did it happen?
- who was responsible?

Forensic analysis is highly case specific and no one set of analytical methods will answer all the questions. Forensic investigation is usually undertaken following a tiered approach, which provides multiple lines of evidence to allow decisions to be made on the balance of probability.

Double ratio plots are commonly used to help identify the source of PAH (polycyclic aromatic hydrocarbons) contamination. PAHs can be produced from a variety of different processes that can be split into biogenic, petrogenic and pyrogenic processes. These different formation processes can give a specific diagnostic profile, which can be identified using double ratio plots and alkylated homologue profiles.

Age dating techniques usually focus on the fact that some compounds are more resistant to degradation than others. Several weathering processes can cause

degradation including evaporation, dissolution and biodegradation, and each will change the hydrocarbon mixture in its own specific way. Depletion of the lighter alkanes and the presence of an unresolved complex mixture (UCM) are key signs that degradation has occurred. Some compounds are known to be particularly resistant to degradation and so the concentrations of these compounds do not alter significantly with time. These more resistant compounds are present in approximately the same proportions as the day they were released to the environment and so have an application for source identification. They also provide a benchmark by which the extent of degradation can be established through comparison with less resistant compounds. Knowledge of degradation rates for different compounds in different environments can be used to help age-date a spill event. Pristane phytane, nC_{17} and nC_{18} are commonly used compounds for age dating diesel spills.

As mentioned previously, petroleum hydrocarbons are made up of thousands of different compounds. The compounds selected for risk assessment purposes (US EPA 16 speciated PAH and TPHCWG) have been selected based on their toxicity and are often of little diagnostic value for forensic investigations. They may be able to provide some basic information for simple scenarios; however more detailed analysis of a different set of compounds is often required. Compounds commonly used in the forensic investigation of petroleum hydrocarbons include alkylated homologues of PAHs, hopanes, steranes and terpanes. By examining the relative proportions of these compounds, and using a variety of statistical techniques, it is possible to solve the complex problems faced in forensic investigations.

2.4 Risk Assessment Modelling for Petroleum Hydrocarbons in Groundwater

Mike Carey of AMEC gave a presentation, which described the drivers for hydrocarbon risk assessment, key fate and transport processes, and some of the problems that can arise in modelling these processes. He also set out some of the challenges yet to be overcome in risk assessment and approaches for evaluating non-aqueous phase and dissolved phase impacts on groundwater.

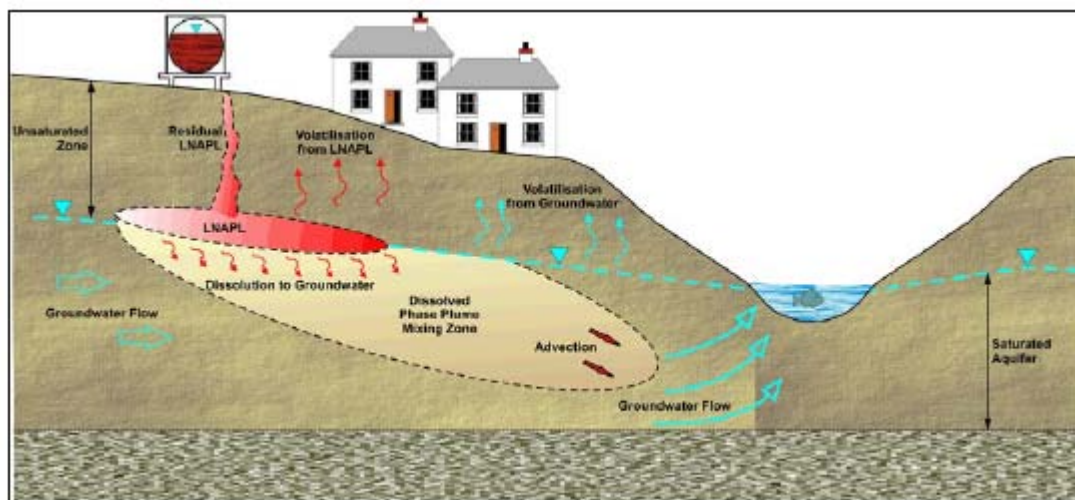
Hydrocarbons have numerous uses including vehicle and heating fuels, lubricants and chemicals. Large volumes are stored and/or transferred in storage tanks (both over and underground), and are transported by pipeline and road/rail tankers. Spills and leaks can introduce hydrocarbons to the subsurface that have the potential to impact groundwater either directly as free-product (non-aqueous phase) or as dissolved product.

Risk assessment is required to better understand the fate and transport of petroleum hydrocarbons in groundwater and the potential risks to water resources and environments. Risk assessment models should help to predict when pollutants will arrive at a point of compliance, and at what concentration, and to explain what processes are likely to operate along a pathway to reduce the risk of adverse effects. However the varied nature of hydrocarbons, and the complexity of the relevant fate and transport processes, means that groundwater risk assessment presents assessors with unique challenges.

2.4.1 Analysis, Fate and Transport for Risk Assessment and Modelling

Conceptual models for petroleum hydrocarbon fate and transport in groundwater can be complicated, incorporating multiple phases (dissolved, vapour, non-aqueous) and numerous attenuation processes (dissolution, sorption, degradation, dilution, volatilisation) - see Box 4.

Box 4: Typical CM showing groundwater contamination by hydrocarbons



The conceptual model is a simplification of reality that can be tested and enhanced through modelling. For the purposes of hydrogeological risk assessment, the conceptual model will often consider and quantify the nature, extent and magnitude of the source term, phase partitioning and attenuation processes using a combination of site-specific and literature data and assumptions.

Laboratory 'Screening Analysis', which indicates the source and total concentration of hydrocarbons, can be used to determine the presence and extent of contamination. However many hydrocarbon products, for example gasoline, diesel, kerosene and bunker fuel, are complex mixtures of aliphatic and aromatic compounds. 'Detailed Analysis' provides information on the concentration of individual compounds, carbon bands or fractions¹⁵, which will always be required for hydrogeological risk assessment.

The mobility of hydrocarbons in groundwater is governed by solubility, vapour pressure (volatility) and the potential for adsorption to aquifer solids such as organic matter, as indicated by the organic carbon to water partition coefficient (K_{oc}). As compound Equivalent Carbon Number (ECN) increases, the pure phase aqueous solubility decreases and K_{oc} increases. Aliphatic compounds are typically less soluble and mobile than the equivalent aromatic compounds. In general, low molecular weight compounds, such as benzene, tend to dissolve in groundwater easily and are less retarded compared with larger, higher molecular weight compounds (see Box 5).

Risk assessment of hydrocarbon pollution in the water environment utilises contaminant fate and transport modelling, which requires assigning values to many input parameters that are contaminant-specific, aquifer-specific and scenario-specific. There are no agreed contaminant-specific values for hydrocarbon screening analysis results and modelling 100s of individual substances would be impractical. Fortunately in 1997 a practical tool for hydrocarbon risk assessment was provided when the US Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) agreed a range of physico-chemical parameter values for carbon banding analysis results that could be used

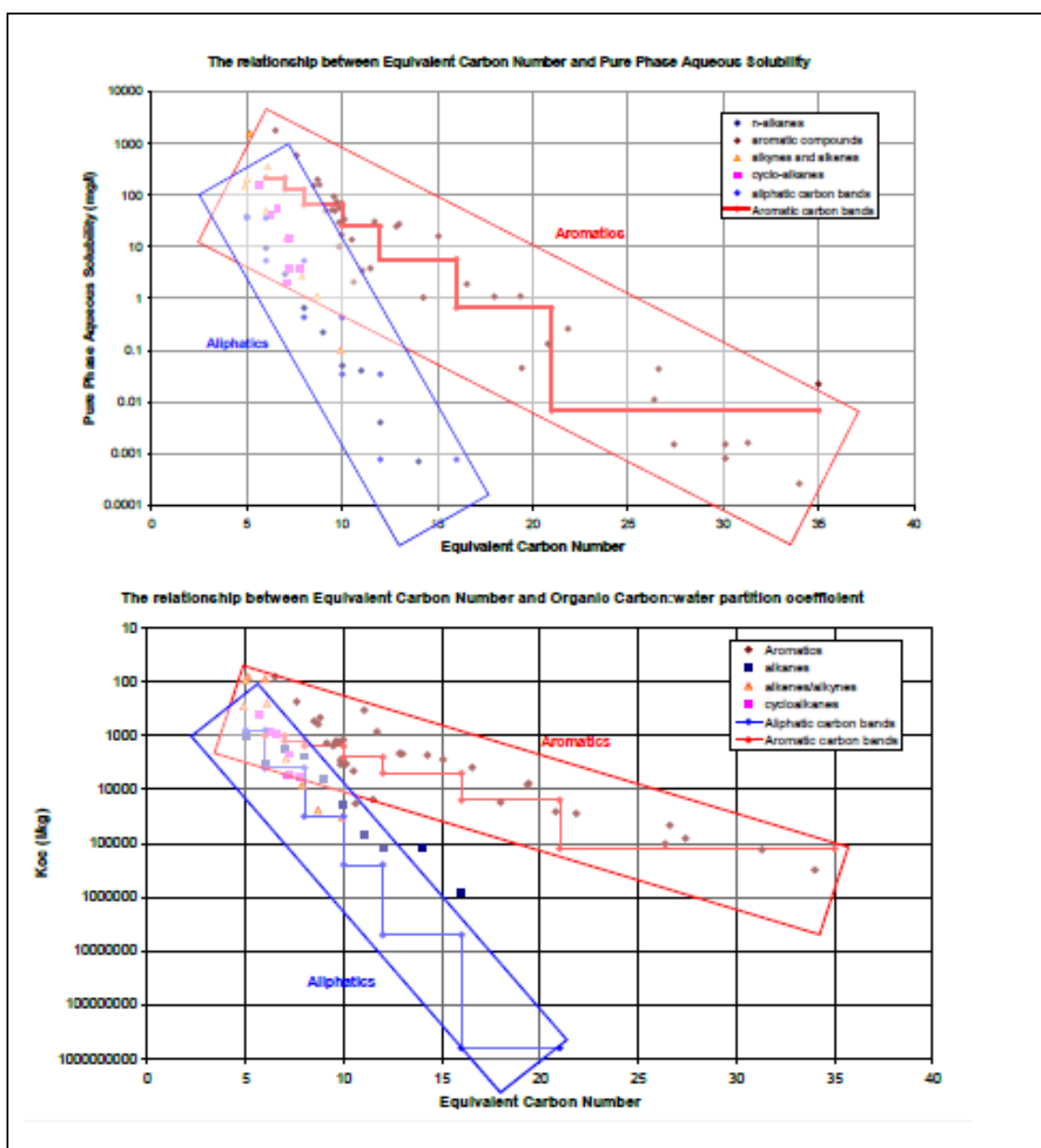
¹⁵ The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) related the boiling point of particular compounds to the boiling point of an equivalent n-alkane (Equivalent Carbon Number) and used this concept to group compounds into aliphatic and aromatic hydrocarbon fractions - see the TPHCWG Series of Publications, 1997. Amherst Scientific Publishers, Volumes 1 to 5

as input parameters for risk assessment modelling. Each carbon band was assigned average values for molecular weight, boiling point, solubility, vapour pressure, organic carbon to water partition coefficient (K_{oc}) and water to air partition coefficient (Henry's Law Constant). The TPHCWG defined 13 carbon bands, 6 for aliphatic hydrocarbons and 7 for aromatic hydrocarbons, based on Equivalent Carbon Numbers (ECN), as follows:

- Aliphatics: EC5-6, >6-8, >8-10, >10-12, >12-16, >16-21;
- Aromatics: EC5-7, >7-8, >8-10, >10-12, >12-16, >16-21, >21-35.

Hydrocarbons with fewer than 5 carbon atoms are gases, such as the simplest hydrocarbon, methane (CH_4), and so are not significant for risks to the water environment, although these can pose a risk to human health, mainly because they are explosive. Most hydrocarbons are liquids (less dense than water) at normal temperature and pressures, but some are solids, especially those with more than 40 carbon atoms, such as those that form bitumen, asphalt and pitch.

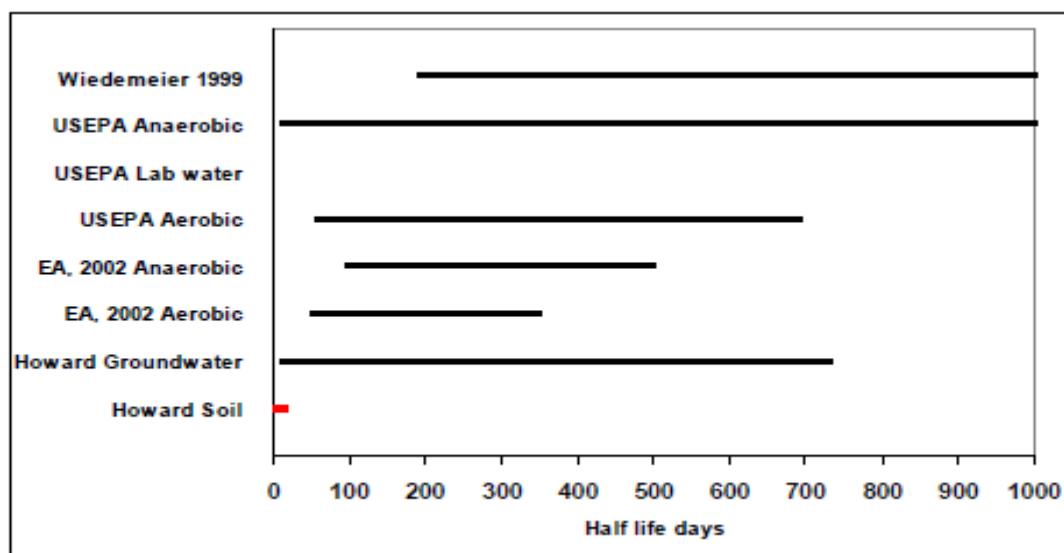
Box 5: Relationship between ECN & key physical properties



Most petroleum hydrocarbon releases originate as mixtures of compounds in free phase form. Raoult's Law states that the effective solubilities of hydrocarbon mixture components are proportional to their mole fractions and may be substantially lower than for their pure phases. Components with higher effective solubility are preferentially dissolved; the effective solubility of remaining components could therefore increase with time. Predicting the long-term variation in hydrocarbon concentrations dissolving from non-aqueous phase source zones can present a significant challenge for risk assessment modelling.

Degradation is one of the principal mechanisms that act to reduce hydrocarbon mass in groundwater and is a key contributing factor in determining why hydrocarbon plumes are typically <100m in length. Degradation processes are generally biogenic and occur primarily under aerobic conditions. Where a mixture of hydrocarbons is present, degradation can be competitive. The potential for and efficacy of degradation processes is therefore highly site-specific. Hydrogeological risk assessment models are often sensitive to degradation parameters, e.g. rates. It is therefore important that degradation processes are well understood and quantified through multiple lines of evidence. Ideally degradation rates should be determined from monitoring data and/or microcosm studies but often this level of assessment is beyond the scope and timescales of most risk assessments. Published degradation rates (often first-order half-lives) can provide a reasonable alternative but can be highly variable, reflecting the influence of the site conditions for which they were determined. The variability of first-order benzene degradation rates (half –lives) cited in some common literature sources is illustrated in Box 6 below.

Box 6: Variability in first-order benzene degradation rates



Risk assessment modellers should justify the selection of literature degradation parameters with consideration to site geology, hydrogeology and geochemistry.

2.4.2 Modelling Case Study

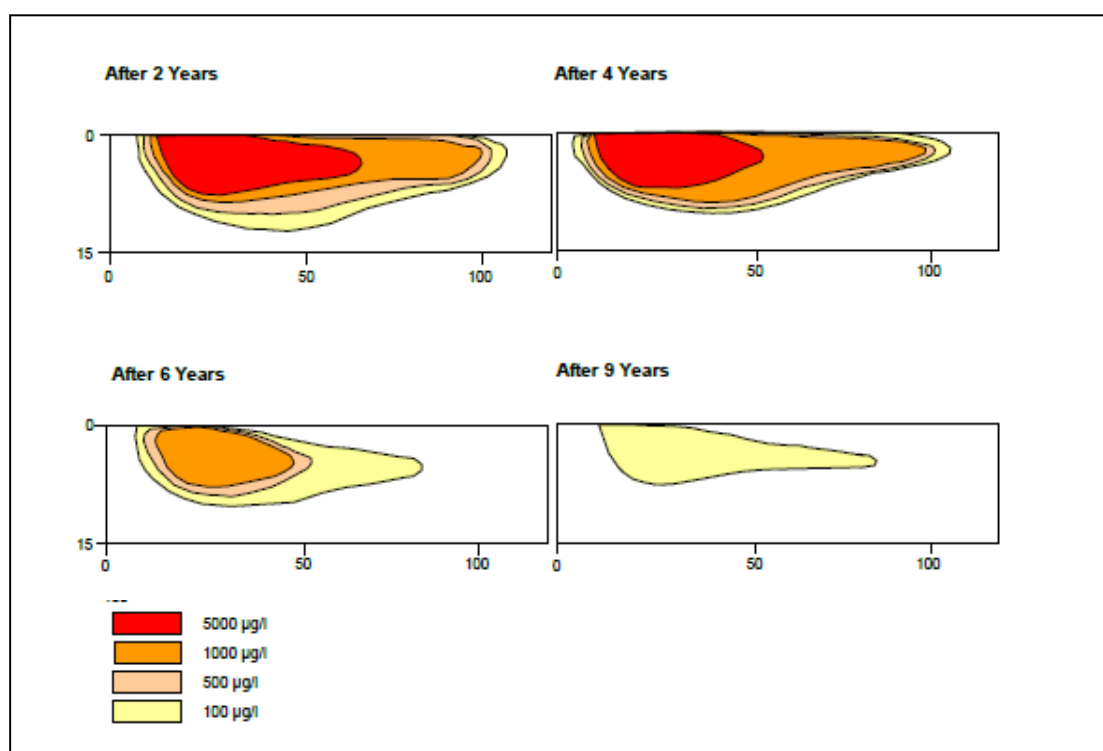
Mike went on to present a case study to demonstrate the level of data collection and assessment that may be required to conceptualise and model petroleum hydrocarbon plumes in groundwater.

The study concerned an accidental loss of 50,000 litres of petroleum from an underground storage tank that resulted in pollution of a chalk aquifer.

Groundwater monitoring data were collected over a 10-year period and culminated in the development of a quantitative model to predict hydrocarbon concentrations and the life of the plume down-gradient of the source.

Competitive dissolution of the non-aqueous phase source including: benzene, toluene, ethyl benzene, xylenes (BTEX), methyl tertiary butyl ether (MTBE) and other simple aromatic components, had resulted in a localised impact to the underlying aquifer. The case study focussed on benzene as the principal risk driver. The benzene dissolved phase plume expanded to a length of around 100m within two years with concentrations in the plume core in excess of 5,000µg/litre. The plume achieved stable condition within four years and was shrinking after six years (Box 7).

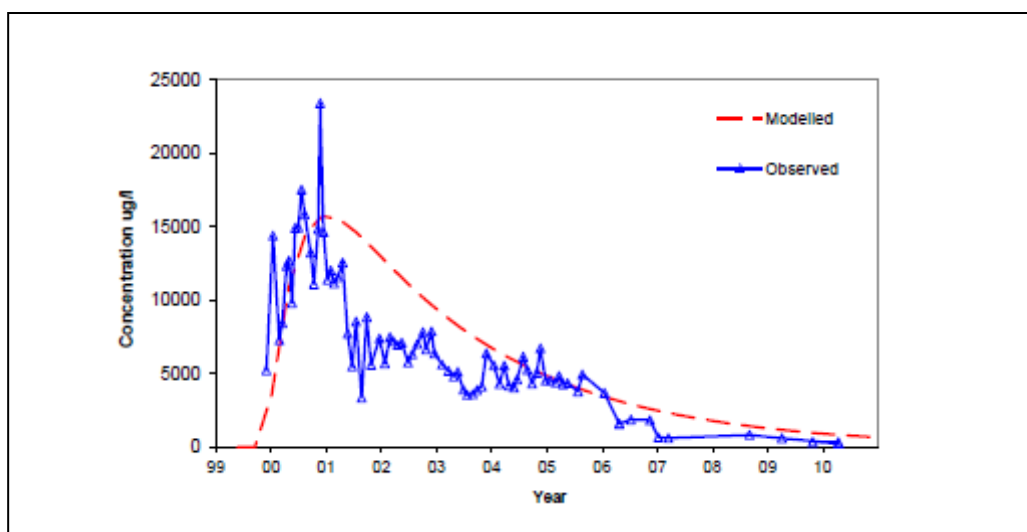
Box 7: Condition of a benzene plume over time



Degradation of hydrocarbons and the depletion of electron acceptors (dissolved oxygen, nitrate, sulphate) was apparent with time. Benzene was notably more persistent than most of the other components (ethyl benzene, toluene and xylenes). The rate of benzene degradation was more rapid in the plume fringes (half-life <100 days) where dissolved oxygen, nitrate and sulphate were available at higher concentrations and could sustain degradation reactions. The plume core was more depleted of electron acceptors, causing benzene degradation to proceed more slowly (half-life ~300 days). The depletion of the source term was inferred from the recovery of electron acceptor concentrations at the tail of the plume.

A model of the conceptualised benzene plume was fitted to monitoring data and used to better understand potential risks at a down-gradient point of compliance. The model highlighted the significance of seasonal changes in plume direction on concentrations at the point of compliance (Box 8).

Box 8: Comparison between modelled & monitored concentrations



2.4.3 Key Issues for Risk Assessment

Hydrocarbon impacts to groundwater present unique challenges to risk assessors:

- Mixtures - common hydrocarbons are present as mixtures. It is not possible to identify every compound nor is it practical to incorporate all compounds into risk assessments.
- Choice of Analysis - risk assessment requires detailed laboratory analysis. Some laboratory data will be unsuitable for risk assessment. Laboratory methods must be well understood to avoid double-counting and data gaps.
- Multiple Phases – hydrocarbons will occur and transfer rapidly between phases (vapour, dissolved, sorbed, non-aqueous phase (mobile and residual)). Most industry standard risk assessment models are not capable of representing all hydrocarbon phases.
- Identification of Risk Drivers – in hydrocarbon mixtures comprising a wide range of compounds, risk driving compounds (e.g. benzene) may represent a very small fraction and may not be representative of the total hydrocarbon mass.
- Contaminant properties – can be highly variable and site-specific, especially for degradation. Degradation parameters and rates have not been published for the TPHCWG aliphatic and aromatic fractions.

2.4.4 Approach to Overcome Issues for Risk Assessment

The Environment Agency's Remedial Targets Methodology¹⁶ and supplementary guidance on petroleum hydrocarbons in groundwater¹⁷ outline the UK approach to groundwater risk assessment.

Risk assessors must develop a robust conceptual model and establish if there are any potential pollutant linkages and contaminants of concern. The contaminants of concern are the risk driving compounds or fractions that will be subjected to

¹⁶ Environment Agency. 2006. Remedial targets methodology. Hydrogeological risk assessment for land contamination

¹⁷ Environment Agency. 2009. Petroleum hydrocarbons in groundwater: Supplementary guidance for hydrogeological risk assessment

more rigorous assessment. For lighter fuels, such as petrol, risk assessment is usually based on the individual components, e.g. the BTEX compounds. For heavier fuels, where there are too many compounds to consider individual components, the assessment is based on hydrocarbon fractions as defined in TPHCWG¹⁸. Some assessment of the mobility of non-aqueous phase sources (if present) should be completed.

The compliance point¹⁹ should be located down-gradient of the source area with consideration of the nature of the contaminant and aquifer setting:

- for Hazardous Substances, the compliance point should generally not exceed 50m in a Principal Aquifer; and
- for Non-Hazardous Substances, the compliance point should generally not exceed 50m in a Principal Aquifer and 250m in a Secondary Aquifer.

Quantitative risk assessment can be performed using analytical fate and transport models such as the Remedial Targets Worksheet or commercially available equivalent. The risk assessor must select the appropriate model to suit the conceptual model. Predicted concentrations can be compared with water quality standards to estimate risk. The model output should be reality checked using the conceptual model to complete risk evaluation and identify the requirement for remediation, should this be considered beneficial.

2.4.5 Summary

Petroleum hydrocarbons present unique challenges to risk assessment. Hydrocarbons may exist as complex mixtures, in multiple-phases with variable properties and behaviour. Risk assessment requires appropriate detailed analysis, identification of risk drivers, qualitative and quantitative assessment including the choice of suitable models/tools. The key is the collection of good quality data and robust conceptual understanding.

2.5 Assessment of the Vapour Risk from Groundwater

Robert Ettinger of Geosyntec Consultants presented the current methods being used by practitioners in the United States to evaluate vapour intrusion of petroleum hydrocarbons from groundwater. He started with a discussion of the reasons why 'multiple lines of evidence' investigations have been unsuccessful in evaluating the indoor air pathway at petroleum release sites. He then went onto discuss the use of modelling and empirical evidence that captures natural vadose-zone biodegradation as a way of evaluating vapour intrusion of petroleum hydrocarbons from groundwater. He also discussed the criteria being developed within the US to screen out petroleum hydrocarbon release sites that present only low risks to human health.

2.5.1 Introduction

Subsurface migration of petroleum hydrocarbon vapours and vapour intrusion into indoor air is often identified as a potential exposure pathway for human occupants of buildings over or near contaminated soils and groundwater. However, site investigations rarely demonstrate the presence of a complete exposure pathway and rarely are unacceptable risks to human health identified.

¹⁸ Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). 1997. Selection of representative TPH fractions based on fate and transport considerations, Volume 3

¹⁹ A point along a source-pathway-receptor linkage at which a target concentration is set in order to protect a receptor from exposure that could lead to unacceptable risk - Environment Agency, GP3 - see Reference 6

Within the US, multiple lines of evidence investigations have often been used to assess the vapour to indoor air pathway. Typical investigations involve a combination of source characterisation through the collection of soil, groundwater and soil vapour samples, vapour intrusion modelling and indoor air evaluation.

Multiple lines of evidence investigation methods often provide challenges in the assessment of petroleum hydrocarbon sites. Source characterisation is often problematic due to the temporal and spatial variability that can occur in groundwater, vapour and soil concentrations and distribution across sites.

Vapour intrusion modelling can also be challenging as models typically rely on default parameters for soil, building and other characteristics with few measured or calibrated site specific data. This invariably results in model outcomes that are often not a true representation of site conditions. Furthermore, numerical vapour intrusion models, such as Johnson and Ettinger, are known to over-estimate petroleum hydrocarbon vapour intrusion by several orders of magnitude²⁰.

Indoor air evaluation at petroleum hydrocarbon release site also has significant challenges. In occupied buildings, human activities, such as opening windows and the use of heating, can influence indoor air monitoring results. In residential properties, indoor air monitoring may cause disruption and upset to residents. Temporal and spatial variation in vapour concentrations may not be captured when undertaking indoor air evaluation. Furthermore, indoor air monitoring is limited to sites where buildings are already present and can only be used in the assessment of current site use; it cannot be used for redevelopment sites where no buildings are present or sites where the building type might change.

One of the greatest challenges with indoor air evaluation in the US is that quantifying the concentration of contaminants indoors can be difficult due to the significant contribution of background sources within buildings. Often measured background concentrations of contaminants will be greater than risk based screening levels with measurements taken indoors often greater than those measured outdoors even if the vapour intrusion pathway is not complete. This means it is often difficult to distinguish indoor air results from background when measured soil gas concentrations are near screening assessment criteria.

The challenges associated with the evaluation of the vapour intrusion pathway have lead to a consideration of alternative methods of assessing risks at petroleum release sites. Recent developments include the use of modelling and empirical evidence that capture natural vadose-zone biodegradation to improve the risk assessment screening process.

2.5.2 The Petroleum Vapour Intrusion Conceptual Model

Vapour intrusion occurs when hydrocarbon vapours from contaminated soil or groundwater migrate upwards toward the ground surface and into overlying buildings through gaps and cracks in foundation slabs or basement walls.

The migration of hydrocarbon vapours throughout most of the subsurface is thought to be primarily the result of diffusive transport processes where, over time, there will be a net chemical movement from zones of high concentration to those of lower concentration. Near buildings or other enclosed spaces, significant advective transport processes may exist due to the pressure differences associated with a building, as compared to the subsoil, that result from the operation of indoor appliances, such as heating, ventilation and air conditioning, and temperature differences and building-wind interaction.

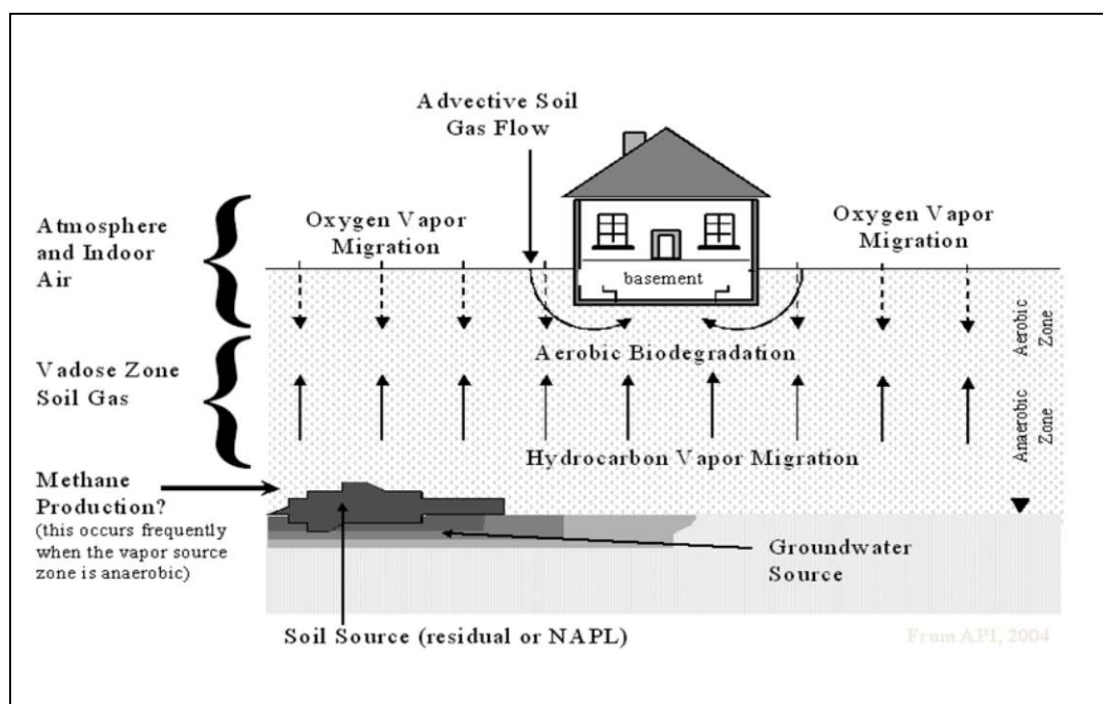
²⁰ Abreu, L.D.V. & P.C. Johnson. 2006. Simulating the effect of aerobic biodegradation on soil vapour intrusion into buildings: Influence of degradation rate, source concentration and depth. *Environmental Science and Technology* 40, no.7, pp2304-2315

The processes that cause hydrocarbon vapour transport into buildings can also bring oxygen from the atmosphere to the subsurface. Where sufficient oxygen is present, micro-organisms can use this oxygen to metabolise hydrocarbon vapours by aerobic biodegradation, which results in the production of carbon dioxide (CO₂).

Microbiological degradation can also occur in the absence of O₂, producing methane (CH₄) by a process called anaerobic biodegradation. The CH₄ will subsequently diffuse upward within the subsurface and be degraded aerobically along with other hydrocarbons at shallower depths where O₂ concentrations are (typically) higher.

The petroleum vapour intrusion conceptual model is illustrated in Box 9:

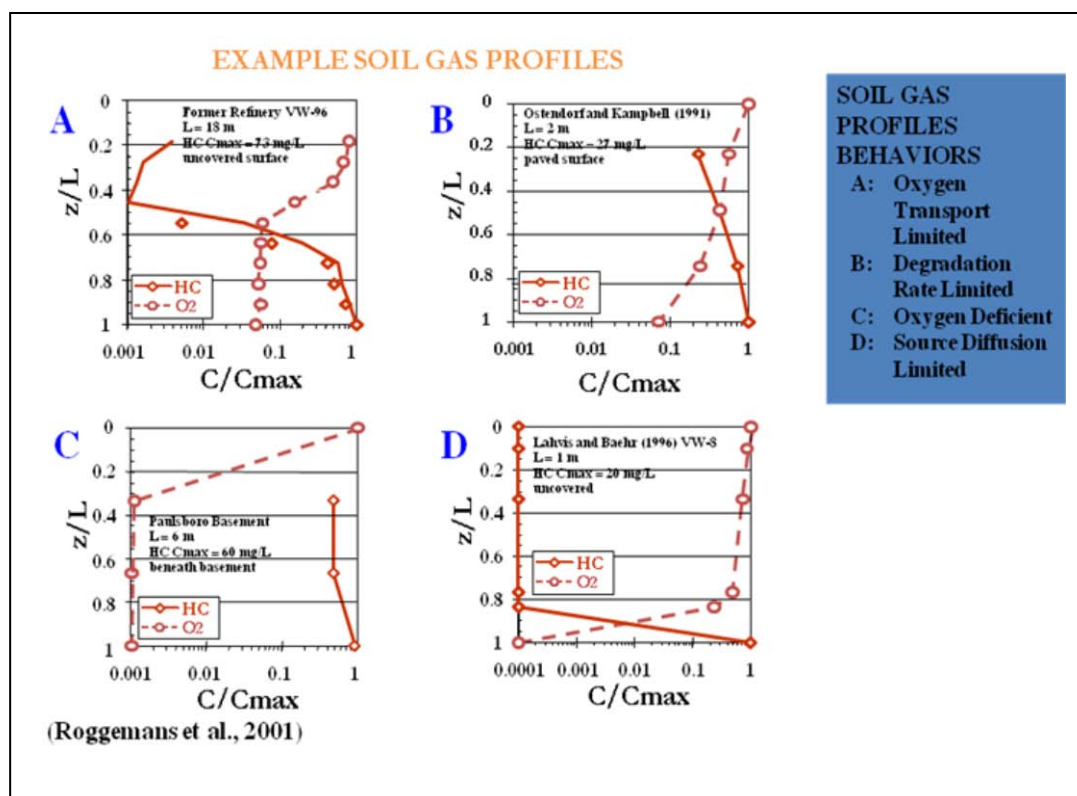
Box 9: Petroleum vapour intrusion conceptual model²¹



A substantial reduction in the vapour concentration of petroleum hydrocarbons via aerobic biodegradation has been observed by several researchers in natural settings. Roggemans *et al*²² evaluated the aerobic biodegradation of petroleum hydrocarbons in the subsurface using data collected from a number of petroleum hydrocarbon release sites. He identified four behavioural categories (A to D) of petroleum hydrocarbon vapours as they migrate through the unsaturated zone. The four categories are illustrated in Box 10 and summarised below:

- ²¹ American Petroleum Institute (API). 2005. Collecting and interpreting soil gas samples from the vadose zone. A practical strategy for assessing the subsurface vapor-to-indoor air migration pathway at petroleum hydrocarbon sites. Publication Number 4741
- ²² Roggemans, S., Bruce, C. L., Johnson, P. L. & Johnson, R. L. 2001. Vadose zone natural attenuation of hydrocarbon vapours: An empirical assessment of soil gas vertical profile data. API Bulletin 15, American Petroleum Institute, Washington DC, USA

Box 10: Example soil gas profiles



Note:

z is the distance measured down from the upper surface (ground surface or basement foundation); L is the distance from the upper surface of the VOC source to the upper boundary; z/L_{source} represents the normalised depth profile

Soil gas profile - behaviour A (oxygen transport limited)

Hydrocarbon vapour concentrations decrease with increasing distance above the source more rapidly than what would be expected by diffusion transport processes alone. Concentrations decrease in three distinct zones.

The first zone is from the source to a depth where active aerobic biodegradation occurs. This zone is anoxic and diffusion is the primary transport mechanism. Petroleum hydrocarbon vapour concentrations decrease marginally with little or no evidence of aerobic degradation.

The second portion of the profile represents the active zone of aerobic biodegradation, with a dramatic reduction of hydrocarbon concentrations and consumption of O_2 .

In the third zone hydrocarbon concentrations are typically very low or not detectable and O_2 concentrations usually approach atmospheric conditions at ground surface.

Soil gas profile - behaviour B (degradation rate limited)

Hydrocarbon vapour concentrations attenuate as O_2 concentrations increase from above the source to the ground surface due to aerobic biodegradation. This category might be expected at sites with a thin unsaturated zone where biodegradation is slow relative to oxygen diffusion or where the vapour source is at a low concentration compared with atmospheric oxygen concentrations.

Soil gas profile - behaviour C (oxygen deficient)

Hydrocarbon vapour concentrations are persistent and O₂ is depleted throughout the vertical profile. Volatile petroleum hydrocarbons migrate by diffusion from the source to the shallow subsurface. This may be observed in the presence of surface covers (i.e. pavement), structures, or elevated moisture content in the soils, which would limit O₂ transport.

Soil gas profile - behaviour D (source diffusion limited)

Hydrocarbon vapour concentrations show rapid attenuation located directly above the vapour source and O₂ concentrations rapidly increase. This may occur where the source is located in a zone that has a lower diffusion rate than the overlying soils, for example where the source is within or below a thick capillary fringe.

Studies such as that carried out by Roggemans *et al* illustrate the significance of the effect of aerobic biodegradation on petroleum hydrocarbon vapour concentrations in the subsurface and hence vapour intrusion into buildings.

2.5.3 Biodegradation Modelling

A variety of models have been developed by the US market to simulate biodegradation in the unsaturated zone. These include:

- Screening Bio-Model (Lahvis, 2006²³). This models biodegradation throughout the vadose zone.
- Dominant Layer Model (Johnson et al, 1999²⁴). This models biodegradation in user-defined degradation zone.
- Oxygen Limited Model (DeVaull, 2007²⁵). This models biodegradation in zones of sufficient oxygen.
- Three Dimensional Model (Abreu & Johnson, 2005²⁶). This is a numerical code that calculates VOC and oxygen fate and transport.

These models require additional parameters to those used within traditional vapour intrusion models and therefore have a greater level of associated uncertainty. The models are typically used in the US to assess significance and sensitivity of biodegradation on vapour intrusion pathways rather than for site-specific risk estimation.

2.5.4 Modelling Studies

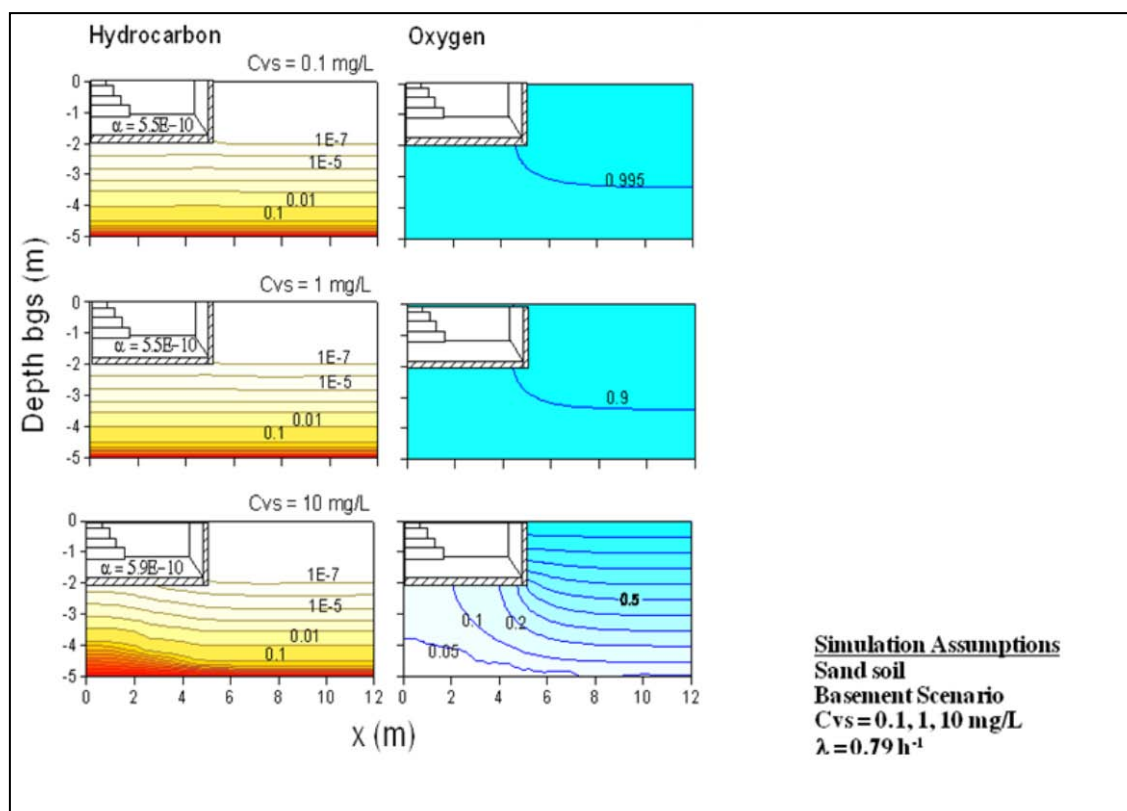
The Johnson and Abreu Three Dimensional Model²⁶ was used in a study by Abreu in 2009²⁷ to calculate vapour intrusion attenuation factors for groundwater

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- ²³ Lahvis, M. 2006. Alternative model-based approach for assessing vapor intrusion at petroleum hydrocarbon sites. Geological Society of America Abstracts with Programs, 38 (7), the Geological Society of America, Colorado, USA, p373
- ²⁴ Johnson, P.C, Kemblowski, M.W. & Johnson, R.L. 1999. Assessing the significance of contaminants vapour migration to enclosed spaces: Site-specific alternatives to generic estimates. Journal of Soil Contamination 8, no. 3, pp389-421
- ²⁵ Devaull, G.E. 2007. Indoor vapor intrusion with oxygen-limited biodegradation for a subsurface gasoline source. Environmental Science & Technology, 41, American Chemical Society, Washington, USA, pp3241-3248
- ²⁶ Abreu, L.D.V. & P.C. Johnson. 2005. Effect of vapor source – building separation and building construction on soil vapor intrusion as studied with a three-dimensional numerical model. Environmental Science & Technology, 39, American Chemical Society, Washington, USA, pp 4550-4561
- ²⁷ Abreu, L.D.V., Ettinger, R. & McAlary, T. 2009. Simulated soil vapour intrusion attenuation factors including biodegradation for petroleum hydrocarbons. Groundwater Monitoring & Remediation, Volume 29, Issue 1, pp105-117

sources. The aim of the study was to improve understanding of the effect of biodegradation conditions on vapour intrusion and to develop a methodology for screening out low source concentration (e.g. dissolved phase) petroleum hydrocarbon sites.

The Abreu 2009 study established that source concentration influences the soil vapour concentration within the subsoil and the indoor air concentrations of petroleum hydrocarbons. Box 11 presents the simulated effect of the source concentration on soil vapour concentration distributions for hydrocarbons and oxygen during aerobic biodegradation for a building with a basement. As the vapours diffuse upward, they are attenuated as shown by the “iso-attenuation contours.” The source vapour concentrations simulated in each figure are 0.1, 1 and 10 mg/litre.

Box 11: Effect of vapour source concentration



Note: Johnson and Ettinger (1991) defined a parameter to relate the vapour concentration of a chemical inside the building to its vapour concentration at the subsurface source and called it the “vapour intrusion attenuation factor,” or “alpha” (α). It is defined as the concentration in indoor air divided by the concentration of soil gas at the source.

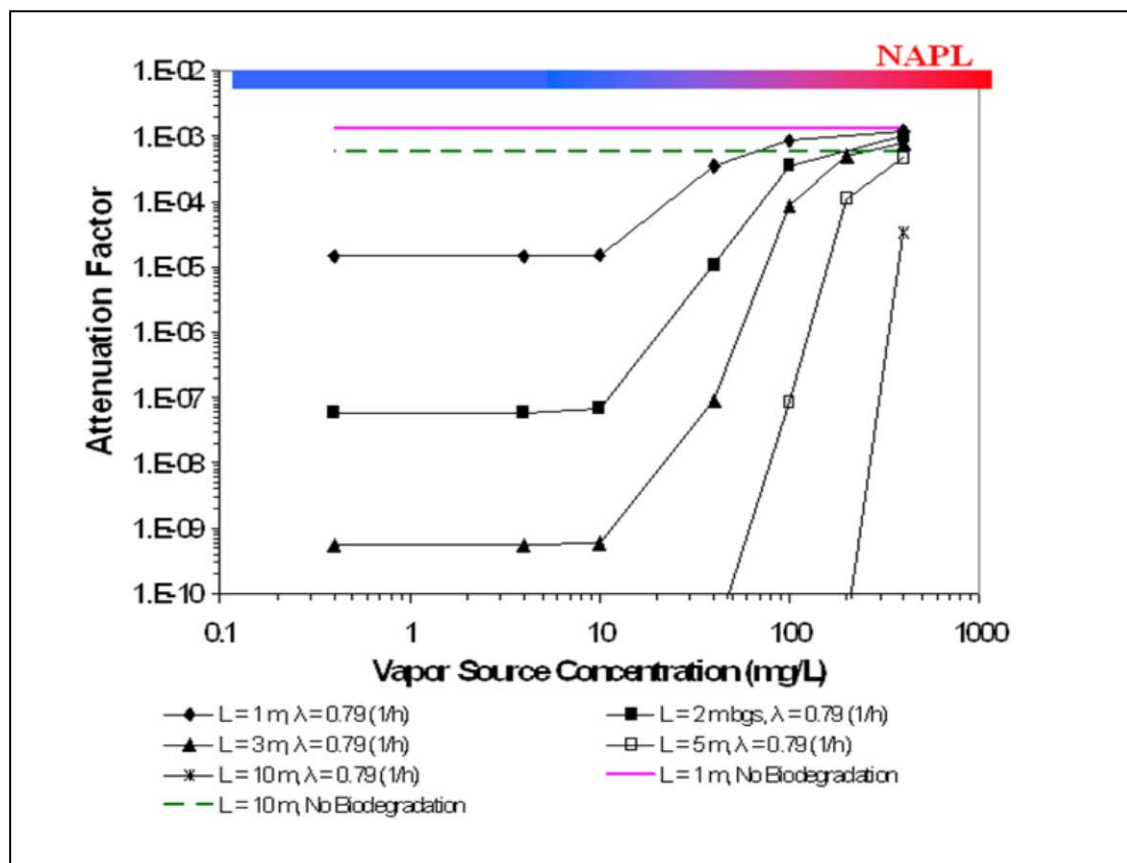
$$\alpha = \frac{C_{\text{indoors}}}{C_{\text{soil gas}}}$$

The simulations in Box 11 show that vapour transport beneath the basement is completely attenuated by biodegradation, even for the highest source concentration of 10 mg/litre. As the source concentration increases from 0.1 mg/litre to 10 mg/litre, oxygen utilisation and biodegradation also increase

resulting in increased attenuation. At lower source concentrations (0.1 mg/litre and 1 mg/litre) vapour transport attenuation is the same, demonstrating that attenuation depends very little on source concentration at lower values.

Box 12 from Abreu *et al* 2009²⁷ is a plot of the hydrocarbon attenuation factor in the unsaturated zone versus source vapour concentration for a range of vertical separation distances between the source and the building foundations. Plots are presented for five source depths, 1, 2, 3, 5 and 10 m below ground surface. The plots show biodegradation is likely to have a significant effect on indoor air concentration for dissolved phase groundwater sources and these effects increase with source depth. For NAPL sources, attenuation increases with increasing source vapour concentration, until they reach oxygen depletion at which point biodegradation beneath the foundation of the building ceases. Therefore, where NAPL is present the effect of biodegradation on the indoor vapour concentration may be minimal due to oxygen depletion.

Box 12: Impact of biodegradation on petroleum hydrocarbon vapour intrusion



Note: *L* is source – foundation distance; Modelling assumptions: Atmospheric O_2 source at ground level; Benzene source; No additional hydrocarbon sinks; Sand soil; Basement scenario; $\lambda = 0.79 \text{ h}^{-1}$

The findings of the study by Abreu 2009 demonstrated that vapours associated with low dissolved phase source strengths beneath buildings are attenuated within a few metres of clean overlying soil. This study supports the development of criteria for petroleum hydrocarbon contaminated sites that can quickly screen out sites with a low likelihood of being of concern.

2.5.5 Petroleum Empirical Databases to Support the Development of Screening Values

The Environmental Protection Agency Office of Underground Storage Tanks has developed a database of field information focused on petroleum hydrocarbon sites. The database contains enough high-quality data to determine the thickness of clean overlying soil necessary to fully attenuate vapours from their respective dissolved source strengths. The database has been used to support the development of screening criteria to be used to exclude sites that have a low likelihood of being of concern. The proposed vapour intrusion screening values developed in a number of different studies are presented in Table 2.

Table 2: Proposed petroleum vapour intrusion screening criteria

Reference	Soil gas threshold ($\mu\text{g}/\text{m}^3$)	Depth to source screening criteria	
		Dissolved plume	NAPL plume
Davis (2009) ²⁸	No detection	5 ft (1.5 m)	30 ft (10 m)
Wright (2011) ²⁹	50	5-10 ft (1.5 – 3 m)	30 ft (10 m)
Lahvis (2011) ³⁰	30, 50 and 100	0 ft (0 m)	13 ft (4 m)

The studies showed that vapours associated with dissolved phase plumes are attenuated within 1.5m of clean overlying soil and that NAPL plumes, where sufficient oxygen is present, are attenuated within 10m of clean overlying soil.

2.5.6 Regulatory Application of Screening Values

The screening depths discussed above are being directly applied by some US states. For example, the California EPA Water Board in its document 'Policy for Low Threat Closure Sites Applicable to Petroleum UST Sites'³¹ has provided guidance on low-threat vapour intrusion criteria.

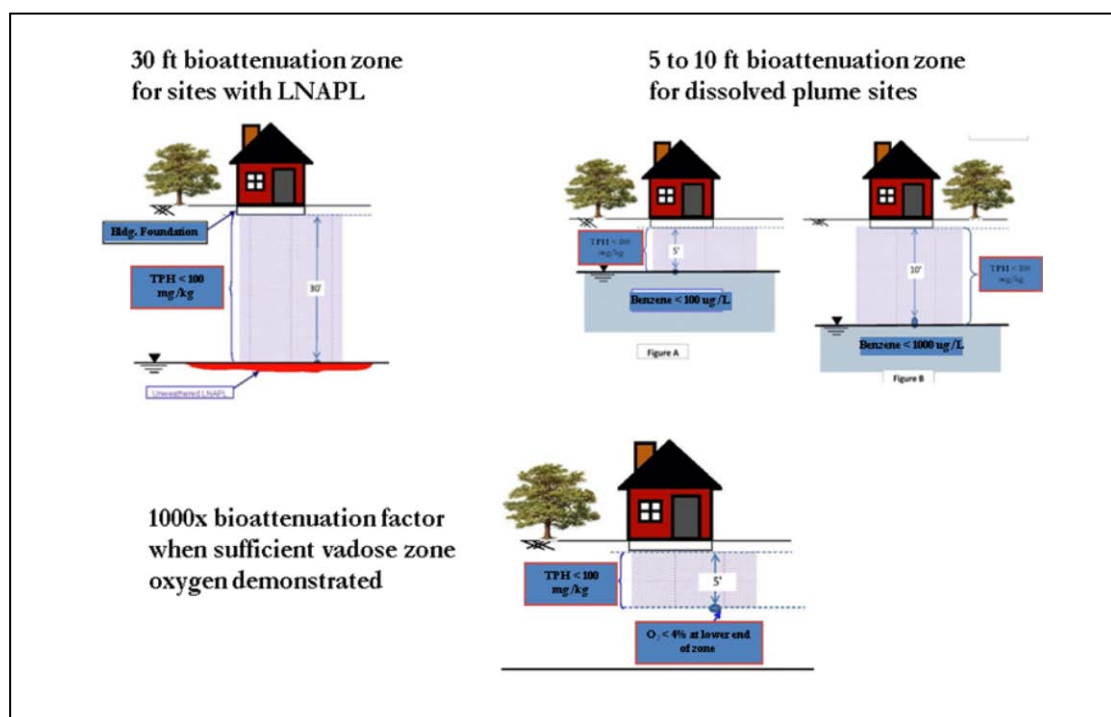
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- ²⁸ Davis, R. 2009. Bioattenuation of petroleum hydrocarbon vapors in the subsurface: Update on recent studies and proposed screening criteria for the vapor intrusion pathway. L.U.S.T. Line Bulletin 61 (May), pp11–14
- ²⁹ Wright, J. 2011. Establishing exclusion criteria from empirical data for assessing petroleum hydrocarbon vapour intrusion, Program and Proceedings of the 4th International Contaminated Site Remediation Conference 2011, CleanUP, Adelaide, South Australia, September 11 – 15, 2011, pp.142-143
- ³⁰ Lahvis, M.A. 2011. Significance of biodegradation at petroleum hydrocarbon sites: Implications for vapor intrusion guidance. Presentation at 23rd Annual US EPA National Tanks Conference and Expo, St Louis, Missouri, March 19-21
- ³¹ California EPA State Water Resource Control Board. 2012. Policy for low threat closure sites applicable to petroleum UST sites

These are applicable to sites on or adjacent to land where a release of petroleum hydrocarbons has occurred in the context of two scenarios:

- in existing buildings which are occupied or may be reasonably expected to be occupied in the future; and
- where buildings for human occupancy are reasonably expected to be constructed in the future.

Box 13 illustrates the four potential exposure scenarios and describes the characteristics and criteria associated with each scenario used by the California EPA Water Board. Each scenario is also described below:

Box 13: Example regulatory application California EPA Water Board



Scenario 1 – NAPL plume

The recommended bioattenuation zone is a continuous zone that provides a separation of at least 30 feet (10m) vertically between the LNAPL in groundwater and the foundation of existing or potential buildings. The total petroleum hydrocarbon (TPH) concentration should also be less than 100 mg/kg throughout the entire depth of the bioattenuation zone.

Scenario 2a- benzene <100 µg/litre

The recommended bioattenuation zone is a continuous zone that provides a separation of at least 5 feet (1.5m) vertically between the dissolved phase benzene and the foundation of existing or potential buildings. The TPH concentration should also be less than 100 mg/kg throughout the entire depth of the bioattenuation zone.

Scenario 2b - benzene >100 µg/litre but <1000 µg/litre

Where benzene concentrations are equal to or greater than 100 µg/litre but less than 1000 µg/litre, the recommended bioattenuation zone is a continuous zone

that provides a separation of at least 10 feet (3m) vertically between the dissolved phase benzene and the foundation of existing or potential buildings. The TPH concentration should also be less than 100 mg/kg throughout the entire depth of the bioattenuation zone.

Scenario 3 – benzene <1000 µg/litre, oxygen ≥ 4%

Where benzene concentrations are less than 1,000 µg/litre and oxygen in the bioattenuation zone is known to be equal to or greater than 4%, the bioattenuation zone is a continuous zone that provides a separation of least 5 feet (1.5m) vertically between the dissolved phase benzene and the foundation of existing or potential buildings. The TPH concentration should also be less than 100 mg/kg throughout the entire depth of the bioattenuation zone.

The screening criteria described above are not applicable for all sites. For example they may not be suitable in assessing large petroleum release sites such as refineries and depots. They also may not be suitable for sites with large areas of impermeable surface covers as this may inhibit oxygen from migrating into the subsurface and hence hinder biodegradation processes. The screening criteria are also not suitable for sites where residual hydrocarbons are present in soil over the plume. Furthermore the screening criteria are unsuitable for chlorinated solvent contaminated sites.

2.5.7 Conclusions

The overall conclusions were summarised as follows:

- Bioattenuation significantly affects the potential vapour intrusion of petroleum hydrocarbons and should be considered in the decision-making process.
- Traditional multiple lines of evidence approach will lead to many false-positive determinations.
- Modelling and empirical data support the use of simple exclusionary criteria to screen out low risk sites.

3 SITE INVESTIGATION AND SAMPLING

3.1 Introduction

The site investigation and sampling workshop was facilitated by Jon Parry (SLR Consulting) and Ed Stutt (WCA Environment). The rapporteur was Charles Bacon (University of Bristol/Golder Associates (UK) Ltd.).

The group members introduced themselves and chose the topics that would be discussed in the available timeframe.

Four key issues were addressed:

- groundwater sampling and analysis;
- field testing;
- well development; and
- NAPLs.

3.2 Key Issues

3.2.1 Groundwater Sampling and Analysis

The group noted that the design of the sampling approach needs to be founded on clear data objectives and within budget, such that sufficient good quality data are gathered for qualitative and quantitative risk assessments^{32,33,34}. There are many different sampling tools and techniques available and these need to be carefully considered.

The group agreed that in most cases low flow sampling is becoming a preferred option for representative and repeatable results combined with providing simultaneous field data³⁵. Although this is not the most economic or fastest method and is limited by suction head, there is the advantage of limiting the volume of wastewater that may need special disposal. Another key advantage of low flow sampling is the precision in depth sampling, which is critical for cases of plume characterisation. Other techniques, such as bailers, cannot give this resolution, although they may be useful for rapid or initial assessments.

Turbid (unfiltered) samples are often related to inertia pumping and poorly developed or constructed wells. A paper by Zemo (2009)³⁶ was brought to the group's attention as it contains evaluations of different sampling methods and their effects on results. When reviewing sampling results, sample deviations from the expected contaminant concentrations estimated by the CM (for example in comparison to effective solubility calculations) need to be assessed in the context of the sampling approach.

³² CL:AIRE. 2008. Principles and practice for the collection of representative groundwater samples. Technical Bulletin TB03

³³ International Standards Organisation. ISO 5667-1. 2006. Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques

³⁴ International Standards Organisation. ISO 5667-11. 2009. Water quality — Sampling — Part 11: Guidance on sampling of groundwaters

³⁵ Puls, R.W. & Barcelona, M.J. 1996. Low-flow (minimal drawdown) groundwater sampling procedures. U.S. EPA, Ground Water Issue, Publication Number EPA/540/S-95/504

³⁶ Zemo, D.A. 2009. Suggested methods to mitigate bias from non-dissolved petroleum in ground water samples collected from the smear zone. Ground Water Monitoring & Remediation 29, no. 3, pp77–83

The method of sampling is often not reported by practitioners. This can have a significant impact on any assessment of the reliability of the results. Regulators present at the workshop stressed the need for sampling methods to be fully reported so that their acceptability can be assessed. In addition, the rationale for the choice of a particular sampling method(s) needs to be reported. For continuity and auditing purposes, therefore, it should be common practice to document the methods used (as separate metadata). It was highlighted that whilst laboratory testing of water samples will have UKAS/MCERT accreditation, this cannot make up for poor sampling methods during the site investigation.

In addition, laboratory results are also influenced by specific preparation methods that can each be UKAS/MCERT accredited whilst producing different results. It was considered helpful therefore for preparation methods to be documented and their implications understood and taken into account.

The risk of cross contamination during sampling was highlighted. There is a cost benefit to be gained by submitting blank, trip and duplicate samples for analysis as this can prevent false positives, which can skew the direction of an investigation or remediation strategy. Submitting these samples is not standard practice, generally due to cost implications. However, the potential future benefits need to be considered and communicated to clients.

Low-cost rapid initial site investigations using cheaper sampling methods (i.e. bailers) can produce data that may result in much uncertainty or inaccuracy. This may lead to more expensive follow-up work or delays. The limitations of basic initial scoping studies should be made clear to clients, as well as possibly being a false economy in the longer term.

There is good groundwater sampling guidance available but workshop members agreed that it would be beneficial to promote the existing key documents as set out in the references given in this report.

3.2.2 Field Testing

The group discussed the use of field testing methods as a means of providing complementary lines of evidence, and as a way of quickly indicating trends and variations across a site. An additional advantage is the large quantity of data that can be generated.

The correct selection and use of field tools is imperative, especially as it is difficult to determine performance standards equivalent to UKAS or MCERTS accreditation for field testing results. In line with the recommended transparency in recording site investigation meta data, field testing reports should include the rationale for the chosen tool, specific methods used, on-site calibration, the type and manufacturer of the instrument as well as serial numbers and dates of service calibration. YSI multi-meter kits, in particular, were praised for their reliability.

PID/FID equipment is considered to be standard kit for hydrocarbon investigations although the data obtained (and methods used) are often not presented in reports. The equipment can also be used in different ways and this may lead to inconsistent results. The data may be useful as a guide for further sampling and as a way of producing contrasts in relative measures. The importance of good calibration was stressed.

It was noted that Pelister equipment has different detection limits for total organics and can show evidence for methanogenesis.

Geophysical techniques were discussed and considered to be excellent tools in providing good resolution of data, especially at sites with heterogeneous geology and chlorinated solvent contamination³⁷.

Vapour screening was also considered to be highly useful for hydrocarbon contaminated sites and can play a valuable role in guiding the positioning of monitoring wells and in delineating source distribution.

In general, field testing techniques were considered to be excellent tools for developing 'lines of evidence' in site investigations and petroleum hydrocarbon contamination delineation projects.

3.2.3 Well Installation

The group noted that publicly available data should be collected before any site investigation begins. Resources including online BGS borehole logs and geological maps can be used to plan well design. The anticipated groundwater elevation and regional hydrogeology can be estimated from these types of information sources, in line with best practice in developing the conceptual model. It is important that work proceeds on a staged basis and that the conceptual model is revised continuously. The group felt that there is a need for some reliable published guidance stating the relative merits of different drilling techniques.

For detailed sampling resolution, it was considered best practice to keep the length of well screens to a minimum and based on actual site geology. Heterogeneity within geological units, or characteristics such as fining upwards sequences, should dictate screen length and position. If possible, boreholes should be core-drilled and the core used as the basis for the design. This also allows field testing of core samples, i.e. PID data that can guide the installation design. The major disadvantage of auger-drilled boreholes is that arisings are mixed, samples are from unknown depths and water strikes are difficult to report. In general, it was considered that it is often better to be conservative, and install multiple wells with shorter screens across different sections of what may be mapped or published as a single geological unit. For fractured geology, cored boreholes are useful for providing crucial information about fracture distribution and characteristics.

It was emphasised that care must be taken to ensure that monitoring wells do not act as new pathways for contaminant migration. Screens must never cross different formations or 'puncture' any important aquitards or aquicludes that may be present. If wells are damaged or destroyed then they may act as contaminant pathways. The well head design should prevent contaminants entering the subsurface down the well, and should be able to cope with any future developments at a site (i.e. if the site is to be subsequently disturbed by excavations).

Well development was considered important for the quality of samples and the stability of field measurements. Removal of three well volumes should not be used as a generic rule and is unlikely to be sufficient in most cases. Surge blocks are often found to perform well, especially as the gravel pack is being installed. Consideration of the design of gravel packs is essential, especially for wells designed to have long life spans. Properly developed wells may need extra gravel emplaced as the gravel consolidates properly during development (as per the case study example discussed in the expert presentation).

³⁷ CL:AIRE. 2007. The use of geophysical investigation techniques in the assessment of contaminated land and groundwater. Technical Bulletin TB05

The use of well socks was discussed as they are almost universally used in installations, often as a cheap alternative to proper well installation. However, the group felt that their use should be subject to specific consideration; for example in cases where hydrocarbons are present well socks can act as a sorbent and may become a long-term source. For optimum results and performance, the gravel pack should be based on the particle size distribution of the formation in which the well sits, and for high budget installations this should always be considered. This is much more common in the USA than the UK. Well tests in wells constructed with less robust development techniques are far less reliable because of the greater well skin effects. Sampling results are significantly affected by turbidity which may be related to well development and surging. Methods (such as turbidity cones and tubes) exist for assessing turbidity during purging. The results should be recorded along with all the other installation details, including the number of bags of gravel used during installation. This information can be useful when interpreting anomalous data that may be related to poor installation design and construction.

Bentonite pellets were also mentioned as past experience has shown that once buried these often do not hydrate, compact and seal properly and therefore are highly ineffective. If this is likely to be an issue, clean water should be poured down the well annulus or consideration should be given to preparing a bentonite grout (bentonite powder/cement/water mix) before installation which can then be pumped into the well.

3.2.4 NAPL

The group discussed the possible merits of sampling groundwater below any NAPL present. There are rarely good reasons to undertake such sampling and there are serious limitations on the reliability of data obtained using conventional sampling methods. The source of the NAPL should be considered as should the pathways by which it is migrating. Multiple level wells are a possible option for NAPL sources if used cautiously and provided a high standard of installation is achieved. Some innovative methods have been reported for sampling groundwater below LNAPL³⁸ but these are not standard practice and it is not known whether the methods have been critically evaluated. It was considered satisfactory (qualitatively) to consider the groundwater beneath product to be at saturation with respect to the NAPL phases.

Interface probes can be useful for measuring NAPL thickness, but it was noted that they could be a source of cross contamination and erroneous results. To obtain reliable data, therefore, interface probes must be used by trained personnel and be regularly cleaned and maintained.

3.3 Conclusions

The group concluded the workshop with the following observations:

- Attention needs to be given to best practice and to the recommended guidance currently available.
- Whilst it was acknowledged that budget constraints and other factors such as project scope and timeframes might be relevant, practitioners should aspire to follow best practice. In addition, site investigations should always be designed on a site-by-site basis, rather than using an 'off the shelf' standard scoping method.

³⁸ Schaffner, I. R., Wieck, J. M., Asselin, M. B. & Lamb, S. R. 2012. Collection of groundwater samples from beneath an LNAPL: An ice-coating method. GZA GeoEnvironmental Inc.

- Research has been undertaken on the errors and uncertainties of different sampling methods and the impact of different approaches on overall results. The selection of sampling technique can have a significant influence on the quality of the sample collected. However, provided the limitations and constraints of a chosen technique are clearly understood and communicated, the full range of available techniques is valid. One key factor is the continuity of methodology on a site by site basis, with robust documentation and transparent reporting of the methods used considered essential. This is especially important for long-term or baseline studies where different consultants may be involved over time.
- The site investigation is founded on the conceptual model. This needs to be well-grounded and open to reconsideration as more data become available. Given that sites are always different and investigation strategies can be complex, there is a responsibility on experienced senior staff to not just pass on their knowledge and skills to junior staff, but also to inspect sites for themselves.
- An awareness of the different available investigation options and the basis for their use is essential. Complementary datasets from different investigation methods can supply multiple lines of evidence, not just for contaminant concentrations and distribution, but also in the context of providing possible supplementary evidence, such as oxygen concentrations and the potential for biodegradation. Eliminating cross contamination and false positives is essential and cost cutting in this area can be a false economy.
- Well design is key for the quality of the data produced. We should aspire for high quality well installations and ensure that the rationale for the design and the methodology used in site investigations are clearly reported.
- Water sampling is a professional activity and standards do exist. It was noted that auditing is not often carried out on the water sampling aspects of projects, particularly compared to the level of auditing of laboratory testing, even though field sampling can cause as much if not more variance in results. Auditing templates are available, such as BSI 8550 2010³⁹.

3.4 Recommendations

The group agreed that the key issue associated with the site investigation and sampling of petroleum hydrocarbons in groundwater was not a shortage of guidance but rather that best practice documentation needs to be more strongly promoted and, then adhered to, during site investigation work.

³⁹ British Standards Institution. BS 8550:2010. Guide for the auditing of water quality sampling

4 LABORATORY ANALYSIS AND ENVIRONMENTAL FORENSICS

4.1 Introduction

This workshop was designed to encourage a discussion of the main issues associated with the laboratory analysis of petroleum hydrocarbons and environmental forensics.

The workshop was to be facilitated by Hazel Davidson (Derwentside Environmental Testing) and Ken Scally (Jones Environmental Forensics). Unfortunately Ken was unable to attend the meeting and therefore the session was facilitated by Hazel Davidson and focused more on the laboratory analysis of petroleum hydrocarbons.

The rapporteur was David Megson of the University of Plymouth.

Prior to the day, the following references were circulated to familiarise delegates with the topics to be discussed:

- Method for the determination of volatile petroleum hydrocarbons (MADEP, 2004)⁴⁰
- Method for the determination of extractable petroleum hydrocarbons (MADEP, 2004)⁴¹
- PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition (Yunker, 2001)⁴²
- Technical Note – Forensic Approaches and Considerations in Identifying PAH Background (Costa and Sauer, 2005)⁴³
- Journal of Environmental Forensics Volume 3, Issue 3-4, (2002)⁴⁴
- The UK Approach for Evaluating Human Health Risks from Petroleum Hydrocarbons in Soils (Environment Agency, 2005)⁴⁵

All delegates were asked to pick three key issues associated with the laboratory analysis of petroleum hydrocarbons that represent accepted scientific understanding of and/or good practice, and also to identify areas that will require further work to improve and clarify current knowledge and practice.

4.2 Key Issues

Through an open discussion the delegates presented many ideas on what they believed were the key issues. There was much overlap between ideas but the following key issues were identified.

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- ⁴⁰ Massachusetts Department of Environmental Protection (MADEP) 2004. Method for the determination of volatile petroleum hydrocarbons, MADEP-VPH-04-1.1
- ⁴¹ MADEP. 2004. Method for the determination of extractable petroleum hydrocarbons, MADEP-EPH-04
- ⁴² Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D. & Sylvestre, S. 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* 33, pp489-515
- ⁴³ Costa, H.J., & Sauer, T.C. 2005. Technical Note – Forensic approaches and considerations in identifying PAH background. *Environmental Forensics* 6, pp9-16
- ⁴⁴ *Environmental Forensics*, 2002. Volume 3, Issue 3-4. <http://www.tandfonline.com/doi/abs/10.1080/716100406>
- ⁴⁵ Environment Agency. 2005. The UK approach for evaluating human health risks from petroleum hydrocarbons in soils, Science Report P5-080/TR3

Variations between analytical laboratories

- differences in nomenclature and terminology
- differences in methodologies
- differences in analytical limits of detection

Scheduling issues

- what sample preparation is required?
- what analytical methodology is required?
- what sample clean-up is required?
- what suite of hydrocarbons should be analysed?

Understanding the uncertainty in analytical data and how this is monitored

- understanding surrogate recovery
- what daily QC checks do (or should) laboratories perform?
- understanding precision and bias
- understanding Proficiency Testing (PT) data

Taking duplicate samples

- why should duplicates be taken?
- what can duplicates be used for?

Environmental forensics

- how is contamination age-dated?
- how is a spill source identified?
- which chemicals should be analysed

The key issues discussed by the group were as follows.

4.2.1 Variations Between Analytical Laboratories

Delegates reported large variations in a number of areas when dealing with different laboratories. Laboratories use different terminologies and there is often a lack of consistency in how relevant terms are used. This can lead to uncertainty in ensuring the scheduling of appropriate laboratory analysis.

Different laboratories are free to use different analytical methodologies to undertake analysis of the same group of petroleum hydrocarbon compounds. For example, extraction can be performed using liquid or solid phase extraction techniques. The laboratory is also free to choose the type of solvent they wish to use for the extraction. Different methodologies have different merits and limitations; however the laboratory should state what technique has been used and regularly record and monitor the performance of the technique. If the analysis is accredited to ISO 17025 or MCERTS then this quality control monitoring will be routine.

The use of different techniques can result in varying data quality and different analytical limits of detection. When comparing data sets produced from different laboratories, the data analyst should be aware that these differences could be significant. If they are not considered then the analyst may wrongly attribute any statistical differences in the data to site processes, rather than the effect of using different analytical techniques. Particular problems can arise when dealing with historical datasets and when combining historical and recent data. The

implications of combining such data should be explored and the advice of the laboratory should be sought where necessary.

4.2.2 Scheduling Issues

Issues associated with scheduling samples for analysis tended to be due either to confusions in nomenclature or a lack of understanding on the part of the scheduler about which of the many available tests is most appropriate for their particular scenario.

This appeared to be an area where an improvement in communication between the scheduler and the laboratory would address many problems. If laboratories are made aware of the details of specific projects/sites, and the rationale for testing, it should be possible for them to recommend the most appropriate type of analysis and to point out any limitations of any proposed test methods.

The group called for more guidance on available methods of analysis and the circumstances under which they should be used since it was clear that no single test method is appropriate in all cases. Table 3 sets out guidance on preparative sample handling techniques for different applications. Table 4 summarises some of the most common hydrocarbon analysis suites.

Hydrocarbons exist in water in several forms:

- surface skim or product layer;
- colloidal suspension (tiny droplets suspended in water);
- truly dissolved in the water phase;
- attached to sediment sampled with the water.

Preparative procedures allow these different phases to be analysed.

It was noted that different results could sometimes be reported for the same analytes in any particular sample. This commonly occurs when BTEX compounds are analysed as part of a petroleum hydrocarbons suite and also as part of a VOC suite. Deciding which data to use involves checking the analytical methodology. Usually BTEX compounds quantified in a petroleum hydrocarbons suite will have been analysed using Gas Chromatography Mass Spectroscopy (GC MS) and the BTEX in the VOC suite by Gas Chromatography Flame Ionisation Detector (GC FID). GC MS is a more accurate and sensitive instrument than GC FID and so any data obtained by GC MS should be used preferentially.

Table 3: Guidance on sample preparation techniques

Fraction	Description	What it should be used for
Total hydrocarbons	The whole sample, including any sediment, is shaken in a separating funnel with the solvent, and then allowed to settle prior to removal of the solvent layer for analysis.	This analysis is common for effluent monitoring where the total hydrocarbon loading passing into a drainage system is required.
Total aqueous hydrocarbons (after GFC filtration)	Filtration is the process used to remove particulate matter (sediment) from the sample, and a glass fibre (GFC) filter is used. This type of filter will not remove significant amounts of free product, dissolved or colloidal hydrocarbons.	To calculate the amount of hydrocarbons that may be 'mobile' in the groundwater and therefore possibly pose a risk to controlled waters or human health.
Total aqueous hydrocarbons (after sedimentation)	Sedimentation is an alternative technique used when analysing the aqueous phase. The sample is left so that sediments settle out and the liquid is removed for analysis. The liquid will include free product, colloidal and dissolved hydrocarbons. It is possible for minor amounts of fine sediment to also be included.	To calculate the amount of hydrocarbons that may be 'mobile' in the groundwater and therefore possibly pose a risk to controlled waters or human health.
Truly dissolved hydrocarbons (after filtration)	The filter for this analysis is cellulose 0.45 micron filter, which will allow adsorption of hydrocarbons onto the filter paper from the solution, and therefore only the truly dissolved hydrocarbons will be measured.	The dissolved phase represents the portion of a compound that is truly dissolved in the groundwater. The amount of a compound that can be dissolved in water is limited and depends on the solubility of the compound, the properties of the solution and environmental factors. This limit is usually referred to as the saturation limit, and is generally quite low for most organic compounds.
Cleaned up EPH	Sample clean up is a process that removes interfering polar compounds to ensure a more accurate analysis of the target hydrocarbons. The clean up involves passing the solvent extract through a silica based column and then eluting with an aromatic based solvent. This will then include the aliphatics and aromatics, but leave the polar NSO compounds (usually indigenous) on the column.	This procedure removes biogenic or 'natural' background organics, such as humic acids, which often make up a large portion of the 'natural' background hydrocarbons.

Table 4: Guidance on different types of petroleum hydrocarbon analysis

Analysis	Description	Uses
Free phase product, or Whole Oil Analysis or Non Aqueous Phase Liquid (DNAPLs or LNAPLs)	Provides a chromatographic fingerprint of the product, allowing identification and an estimate of the degree of weathering.	Characterising a spill material and the source of contamination. Assessing risks to controlled waters or human health.
*VPH (Volatile Petroleum Hydrocarbons), also known as GRO or PRO (gasoline or petrol range organics)	VPH are a group of hydrocarbons with a boiling point range between 36°C and 220°C. They include the aliphatic hydrocarbons that elute on a GC chromatogram within C ₅ through C ₁₂ and aromatic hydrocarbons quantitated within C ₆ through C ₁₂ .	Assessments where the risk driving contaminants have been found to be in this range. For example petrol, white spirits and certain petroleum naphthas. VPH also include BTEX and MTBE. However, following Environment Agency guidance, ⁴⁵ analysis from selected carbon number bands as per the TPHCWG advice would be recommended.
*EPH (Extractable Petroleum Hydrocarbons)	EPH are a group of hydrocarbons with a boiling point range between approximately 150°C and 265°C. They include the aliphatic hydrocarbons that elute on a GC chromatogram within C ₁₀ through C ₃₅ and aromatic hydrocarbons quantitated within C ₁₁ through C ₃₅ .	Assessments where the risk driving contaminants have been found to be in this range. For example diesel fuel, jet fuel and certain fuel oils and lubricating oils. However, following Environment Agency guidance, ⁴⁵ analysis from selected carbon number bands as per the TPHCWG advice would be recommended.
*DRO (Diesel Range Organics)	DRO is a term applied to hydrocarbons that are commonly found in mid-range fuels such as diesel. The method covers petroleum hydrocarbons that elute on a GC chromatogram within C ₁₂ through C ₂₈ .	Assessments where the risk driving contaminants have been found to be in this range. However, following Environment Agency guidance, ⁴⁵ analysis for selected carbon number banding as per the TPHCWG advice would be recommended.
*LORO (Lube Oil Range Organics)	LORO is a term applied to hydrocarbons that are commonly found in lubricating or engine oils. The method covers petroleum hydrocarbons that elute on a GC chromatogram within C ₂₆ through C ₃₅ .	Assessments where the risk driving contaminants have been found to be in this range. However, following Environment Agency guidance, ⁴⁵ analysis for selected carbon number banding as per the TPHCWG advice would be recommended.

Table 4: Guidance on different types of petroleum hydrocarbon analysis...cont.

Analysis	Description	Uses
Banded EPH	The EPH range can be quantified into various carbon bands, such as C ₁₀ – C ₁₆ , C ₁₆ – C ₂₁ , C ₂₁ – C ₂₈ , C ₂₈ – C ₃₅	This can be helpful in risk assessment, as it provides data on the hydrocarbon split.
TPHCWG (Total Petroleum Hydrocarbons Criteria Working Group)	TPHCWG refers to 13 fractions of aliphatic and aromatic petroleum hydrocarbons within EC ₅ through EC ₃₅ .	Essential for quantitative risk assessment, and ideally investigations should include analysis of this full suite to initially characterise the contamination. This can be used to identify the likely risk driving compounds and focus future testing if necessary. Future testing can then be undertaken on specific TPHCWG bands.

Notes to table:

**These terms are not consistent between laboratories; different labs will use different techniques, which will result in different results. Analysis using the TPHCWG split would be recommended in place of these techniques.*

There was also a request by representatives of laboratories that schedulers should include more detail on the chain of custody forms. With petroleum hydrocarbon samples there should be comments identifying samples expected to contain high concentrations of hydrocarbons or free product - this information will warn laboratory staff that:

- further dilution of the sample may be required as concentrations may exceed the calibration data and could damage the instrument;
- samples should be carefully ordered and checked to ensure there is no 'carry over' from a highly contaminated sample onto the subsequent sample - this will also help to reduce instrument downtime and could avoid the need to re-analyse samples.

4.2.3 Understanding the Uncertainty in Analytical Data and How this is Monitored

There was a long discussion around the uncertainty in analytical data and how this is monitored and can be accounted for. When analytical results are received from the laboratory, reported results should not be assumed to exactly represent the concentrations in the sample, let alone the site. Sampling error was discussed by the site investigation and sampling group (section 3); however one source of error that is not always considered is the error in the analysis itself.

This error is one of the more easily quantifiable errors and is recognised within the wider scientific community and in academia; however it is not commonly considered by the contaminated land industry. A justification for this is provided in Environment Agency guidance⁴⁵ which states that the errors involved in sample collection are likely to be far more significant. Whilst this is likely to be the case, the risk assessor should be aware that their laboratory results are not always 100% accurate and there may be some significant errors associated with the reported value. Laboratories will know the uncertainty associated with their methods, as this is determined during the method development and validation procedures. In addition, surrogate compounds are added to monitor the efficiency of the extraction process for each sample.

Extraction of petroleum hydrocarbons from a sample is not 100% efficient. The extraction process and sample preparation can introduce a degree of uncertainty into the reported result. As a general rough rule of thumb, a good extraction efficiency is in the region of 85% to 115%, whereas 70% to 130% is generally considered to be acceptable. Extraction efficiencies can be highly variable and large differences can be reported in different sample matrixes. Extraction efficiency from water samples is usually fairly good; however high concentrations of particulate matter can increase variability in efficiency. The extraction efficiency is measured by the laboratory through the use of a surrogate compound. The surrogate is a compound that is chemically similar to the analyte of interest, but is unlikely to be present in the sample. For petroleum hydrocarbon analysis, chloro-octadecane and 2,5-dibromotoluene are often used. The surrogate is added to the sample in a known concentration prior to sample extraction and clean-up. The concentration of the surrogate is then measured along with the analytes of interest to assess the efficiency of the analytical technique. This surrogate recovery should be reported as a percentage along with the other analytes in the results section. However, it is often unclear which surrogate is used and which surrogate applies to which analyte. In some instances the surrogate recovery is not included with the analytical results.

The constant monitoring of analytical performance and the recording of this information is essential for a laboratory to gain ISO and MCERTS certification. This information is very rarely reported with the analytical results; however it should be made available on request. The following list includes some standard Quality

Control (QC) procedures that a laboratory should take to ensure they are maintaining appropriate levels of performance:

- Measuring accuracy: This involves the analysis of a solution containing the analytes of interest in a known concentration. This is performed by analysing a known standard, which can be either a calibration standard or preferably a certified reference material (CRM). This should be analysed once every 24 hours and ideally with every batch of 10 – 20 samples. This is undertaken to measure the accuracy of the analytical instrument, or how close the calculated value is to the 'true value'.
- Measuring precision: This involves the repeated analysis of a solution containing the analytes of interest in a known concentration. This is performed by analysing the same standard reference material that is used to measure accuracy. The standard deviation of the results of several replicate analyses is a measure of precision, or how reproducible the results are.
- Measuring background contamination: This involves the analysis of a method blank. The method blank should be treated in the same way as a sample. It should be subject to the full extraction and clean up method and be spiked with all standards. The blank is analysed to ensure there is no background contamination that could affect the results.
- Measuring instrument resolution: This involves the analysis of a standard that contains two similar compounds. To check the instrument is working to appropriate levels of resolution the two compounds should be 'adequately resolved' on the chromatogram. Adequate resolution of the target analytes should also be demonstrated through analysis of the calibration standard.
- Proficiency Testing (PT) data: Accredited laboratories are signed up to PT programmes where they receive 'blind samples' every month. The laboratory will analyse the sample and report results back to the programme organiser. The results from the laboratory are compared with the median value of the dataset and results reported back to the laboratory. The report includes a 'Z score': if this score is less than 2 then the laboratory performance is good; if it is greater than 3 then the laboratory should take action to improve their procedures.

If any of these QC checks result in a failure of the acceptable levels set by the laboratory, then the source of the failure should be identified and resolved before any further analysis can commence. The QC performance results are recorded daily on a graph. Monthly graphs showing the recorded performance of each technique can be made available by the laboratory on request. Acquisition of these QC results should not be a major concern for anyone receiving laboratory results. For the majority of investigations the surrogate recovery should be the only QC that needs to be considered.

4.2.4 Taking Duplicate Samples

The group discussed the benefits of analysing duplicate samples.

The collection and analysis of duplicate samples can be undertaken for two reasons:

- to estimate the heterogeneity of the material being sampled; and
- to assess the precision that the laboratory is able to achieve.

This first involves the collection of two samples in the field whereas the second involves the analysis of the same sample twice. The group agreed that the

collection and sampling of duplicate samples was important and analysis of samples at a frequency of 1 in 10 samples seemed reasonable. It was noted that for small / preliminary investigations involving the collection of 2 or 3 samples the analysis of a duplicate is not always required. Analysis of the same sample twice was deemed unnecessary as results for precision can be obtained from the laboratory on request.

The importance of taking duplicate samples on site was emphasised, especially when submitting a sample for analysis of volatile hydrocarbons. The laboratory may have to re-analyse a sample if the concentration recorded is outside the calibration limits of the instrument or if background contamination is found in the analytical blank. In these situations the integrity of the original sample may be compromised through the loss of volatile compounds as the container will have been opened and the sample warmed slightly. In these circumstances it is preferable to analyse the sample from an unopened container that has been kept at a low temperature. This has implications for the collection of samples in the field. When collecting a sample, containers should not be filled sequentially, instead each container should be filled 'bit by bit' until all containers are full.

More guidance on the collection of duplicate samples and quantification of error is presented in a review produced by Ramsey⁴⁶.

4.2.5 Environmental Forensics

Due to the absence of Ken Scally (Jones Forensics) there was only limited debate on environmental forensics techniques.

It was noted that the standard analytical suite normally used to characterise petroleum hydrocarbons was not appropriate for undertaking forensic investigations. The TPHCWG fractions and EPA priority 16 PAHs are selected for analysis based on their risks to health and the environment, and have a limited diagnostic power. The analysis of compounds such as steranes, terpanes and other biomarkers yields much more useful information.

Forensic analysis should only be undertaken by an experienced analyst with the ability to interpret chromatograms and identify the key compounds useful for any specific forensic investigation. Forensic investigations are carried out by obtaining several 'lines of evidence' to allow an assessment based on probability - reliable conclusions cannot be drawn through the creation of only one double ratio plot.

Environmental forensics is an emerging discipline in the UK. However, forensic techniques have been used extensively for over 30 years in the United States. Further information is available from References^{47, 48, 49, 50, 51}.

⁴⁶ Ramsey, M.H. 1998. Sampling as a source of measurement uncertainty: techniques for quantification and comparison with analytical sources, *Journal of Analytical Atomic Spectroscopy*, 13, pp97-104

⁴⁷ Wang, Z. & Stout, S. A. 2007. *Oil Spill Environmental Forensics Fingerprinting and Source Identification*, Academic Press, ISBN 13: 978-0-12-369523-9

⁴⁸ Morrison, R.D. & Murphy, B.L. 2006. *Environmental Forensics Contaminant Specific Guide*, Academic Press, ISBN 13: 978-0-12-507751-4

⁴⁹ International Network of Environmental Forensics (INEF) – an international interest group available to join at no cost through the RSC (<http://my.rsc.org/groups/home/349>)

⁵⁰ Jones Forensics web page (<http://jones-forensics.com/forensics/>)

⁵¹ Exponent web page (http://www.exponent.com/environmental_forensics/#tab_overview)

4.3 Conclusions

The group agreed that many of the laboratory analysis problems discussed during the workshop could be addressed through better communication between the parties involved in both scheduling, and delivering, laboratory analysis data.

4.4 Recommendations

The group made the following recommendations on ways in which the current relationship between the relevant parties could potentially be improved:

1. **Site Staff.** The person responsible for scheduling samples for analysis should include more information on the chain of custody documentation relating to samples that could pose a risk to laboratory staff and those expected to contain unusually high concentrations of a particular analyte.

Where possible all samples should be taken in duplicate. If a limited volume of sample is available, priority should be given to samples intended for the analysis of volatiles (glass vials). It was recommended that approximately 1 in 10 samples collected should be analysed in duplicate so that assessor can improve their understanding of the heterogeneity of sample concentrations at their site.

2. **Risk Assessors.** If in doubt, risk assessors should contact the laboratory to ensure that the correct analysis is undertaken for their specific scenario - note that Tables 3 and 4 provide only a general guide.

If forensic interpretation is required, assessors should seek advice from a specialist. There are thousands of different petroleum hydrocarbons and the compounds analysed for risk assessment purposes are often of limited diagnostic value.

3. **Laboratory Analysts.** The laboratory should aim to provide clearer information. Surrogate recovery data should be included with the analytical results together with clear advice about which compounds the surrogate is applicable to. Further QC data would not normally be required; however it should be made easily and quickly available on request.

To improve understanding of the source of contamination, the group decided that it would be advantageous to have a GC chromatogram included with each analysis. If the risk assessor does not understand what a chromatogram shows, they are encouraged to undertake some training as the chromatogram can add information of much value to the interpretation of analytical data.

5 GROUNDWATER RISK ASSESSMENT MODELLING & THE DEVELOPMENT OF GUIDANCE

5.1 Introduction

The groundwater risk assessment modelling and development of guidance workshop was facilitated by Mike Carey of AMEC. The rapporteur was James Rayner of Geosyntec Consultants.

The expert presentations on groundwater policy and risk assessment modelling for petroleum hydrocarbons engendered discussion of three key issues:

- water quality standards and risk evaluation guidelines;
- biodegradation rates and modelling; and
- modelling soil and non-aqueous phase source zones.

The workshop group considered these issues as follows.

5.2 Key Issues

5.2.1 Water Quality Standards (WQS) for Risk Assessment

The most widely used measure for identifying potential risks to controlled waters is the exceedance of water quality criteria (concentrations) such as Drinking Water Standards (DWS) and Environmental Quality Standards (EQS). Water quality criteria are available for some risk-driving hydrocarbons, e.g. benzene; however, equivalent values for petroleum hydrocarbon fractions have not yet been published in the UK. However, the Environment Agency has developed Predicted No Effect Concentrations (PNEC) for protection of aquatic life (i.e. EQS) for 3 aliphatic and 7 aromatic fractions of the TPHCWG carbon bands, although this is currently still a draft report⁵². Until publication this presents a problem for the assessment of complex mixtures of hydrocarbons where risk-driving compounds may represent only a small fraction of the contaminant flux and consideration of the broader hydrocarbon mass is often warranted.

The former DWS for hydrocarbons/mineral oils of 10 µg/L was withdrawn in 2000. Similarly, the former Bathing Water “no visible film” parameter for mineral oils was withdrawn in 2008. However, some qualitative parameters for petroleum hydrocarbons (e.g. no visible film, no taste to fish, no harm to fish) remain in UK legislation⁵³, it is difficult to incorporate these criteria into quantitative risk assessment.

Therefore risk assessors have been forced to resort to alternatives, including:

- using laboratory detection limits;
- adopting standards for surrogate/indicator compounds; or
- deriving quasi DWS and/or EQS in-house.

Members of the workshop group suggested that the absence of published standards has led to inconsistency in the assessment and regulation of hydrocarbon impacts to groundwater and they stressed the need for publication of such values. The use of detection limits and/or surrogate criteria is largely

⁵² Environment Agency. 2010. Petroleum Hydrocarbons – Proposals for thresholds for the protection of aquatic life (unpublished draft)

⁵³ Water Quality (Water Supply) Regulations SI/2000/3184; Bathing Water Regulations SI/2008/1097; Surface Waters (Fishlife) (Classification) Regulations SI/1997/1331 as amended by SI 2003/1053

subjective and members highlighted problems in identifying risk-driving indicator compounds for the various hydrocarbon fractions.

There are several methods in circulation for the derivation of drinking water and environmental quality standards, the use and parameterisation of which could require expert judgement. The methods set out below were discussed during the workshop or distributed for comment afterwards.

The World Health Organisation (WHO) Guidelines for Drinking Water Quality⁵⁴ provide one method for deriving potable water standards (C , mg/litre), based on the fraction (f , [-]) of the tolerable daily intake (TDI, mg/kg body weight/day) attributed to drinking water, mean adult bodyweight and water consumption rate (IR, litres/day), as follows:

$$C = \frac{f \cdot TDI \cdot BW}{IR}$$

Regulatory endorsement of such a method coupled with development of relevant guidance would provide a useful alternative for risk assessors for hydrocarbons and other substances for which potable water standards have not yet been published. The workshop group agreed that methods to derive toxicity-based drinking water standards should also consider taste, odour and solubility limits.

The Massachusetts Department of Environmental Protection (MADEP) has published risk-based criteria that are protective of aquatic receptors⁵⁵ (BATELLE, 2007). The approach used involved estimating the acute and chronic toxicity of hydrocarbon fractions to aquatic organisms based on equilibrium partitioning theory.

The theory states that the toxicity of hydrocarbons in sediments to benthic organisms is caused by partitioning from sediment particles into pore water and from pore water into the tissues of sediment-dwelling organisms. Toxicity data (LC_{50} (mg/litre)) for aquatic species (fish, shellfish, crustaceans, insects etc.) exposed to hydrocarbon compounds were reported to be proportional to $\log K_{ow}$. Linear regression of this relationship was used to predict concentrations in pore water and sediment that would be toxic to aquatic organisms. Criteria in pore water and sediment were derived for eight groupings (fractions) of petroleum hydrocarbons based on similar toxicological and chemical properties set out in Table 5 (based on Table 6 of Reference⁵⁵).

⁵⁴ World Health Organisation. 2011. Guidelines for drinking water quality, 4th Edition

⁵⁵ BATELLE. 2007. Sediment toxicity of petroleum hydrocarbon fractions. Report prepared for Massachusetts Department of Environmental Protection, Office of Research and Standards, 1 Winter Street, 8th Floor, Boston, MA 02108. Prepared by BATELLE, 397 Washington Street, Duxbury, MA 02332

Table 5: Petroleum hydrocarbon toxicity criteria for aquatic organisms

Hydrocarbon Fraction	Toxicity-based Pore Water Criteria (µg/litre)	Toxicity-based Sediment Criteria (mg/kg organic carbon)
Aliphatics C5-C8	218	1,591
Aliphatics C9-C12	6.3	2,722
Aliphatics C13-C18	0.05*	5,543
Aliphatics C19-C36	0.0001*	9,883
Aromatics C6-C8	1,191	531
Aromatics C9-C12	46.2	228
Aromatics C13-C15	5.2	125
Aromatics C16-C24	0.12*	40

**Note: The fraction is not likely to be toxic, toxicology-based pore water concentration exceeds mean aqueous solubility*

BATELLE demonstrated that this methodology could also be adapted to derive criteria for different groupings (fractions) of hydrocarbons, such as those commonly reported by UK laboratories. The method could therefore be of some interest to UK groundwater modellers/risk assessors in providing an alternative to current options for selecting assessment criteria. The review and possible use of the methodology presented in the BATELLE and similar studies could outline the way forward for hydrocarbon fraction EQSs.

Most decisions regarding contaminated groundwater are driven by measured or predicted contaminant concentrations, which may appear to be relatively stable or to show notable changes with time. However, concentration data alone cannot answer all questions critical to assessment of the risks associated with contaminant plumes. Consideration of plume dynamics, in part indicated by mass flux, can improve risk evaluation⁵⁶. It was apparent that the use of mass flux in risk assessment was not a widely applied concept amongst members of the workshop group. Potential barriers to its use could include the absence of published quantitative guidelines on the use of mass flux and that flux estimates are not directly output from groundwater risk assessment model software in common use in the UK. Workshop group members with experience in applying mass flux to risk assessment commented that this had been semi-quantitative and subjective but that it had added significant value to the risk evaluation process and had met with regulatory approval.

The Significant Possibility of Significant Pollution of Controlled Waters (SPoSPoCW) will be determined using the new Category 1-4 system outlined in the revised Part 2A Statutory Guidance⁷. It is envisaged that existing/future water quality standards could be used as Category 4 criteria. An Environment Agency project is proposed to develop supplementary guidance on significant pollution. The expectation is that Category 2/3 will be determined through quantitative risk assessment; Category 2 being identified where concentrations are considered

⁵⁶ Interstate Technology & Regulatory Council (ITRC). 2010. Use and measurement of mass flux and mass discharge. MASSFLUX-1. Washington, D.C.: Interstate Technology & Regulatory Council, Integrated DNAPL Site Strategy Team. www.itrcweb.org

'significant' subject to cost/benefit considerations. There was general agreement that measured or predicted concentrations exceeding compliance values at designated compliance points alone would not indicate Category 2 'SPoSPoCW', highlighting the disconnect between the raw results of risk assessment modelling and identifying actual risk.

The use of 'plume length' as a possible additional criterion for identifying Category 2 was discussed. Contaminant plumes containing 'significant' concentrations at points of compliance and that were larger than 'normal' might be considered Category 2. The length of a stable plume provides some indication of natural attenuation capacity. Larger than 'normal' length plumes could therefore suggest lower attenuation capacity and greater potential for actual risk to receptors. Were such a metric to be adopted, the following requirements for developing these criteria were identified:

- contaminant specificity;
- determination of threshold plume length per contaminant; and
- plume stability and lifetime to be considered.

Hydrocarbon plume length was the subject of several US studies in the 1990s, e.g. Rice *et al*⁵⁷, Mace *et al*⁵⁸ and Newell *et al*⁵⁹ which determined that approximately 90% of the US hydrocarbon plumes studied were less than ~100m in length⁶⁰. Similar studies of UK aquifers would be required to establish 'normal' plume lengths and lifetimes for common groundwater contaminants, including petroleum hydrocarbons. Such an effort would almost certainly require support and data from industry.

Cost/benefit factors are a consideration in identifying Category 2 SPoSPoCW and feature in other current guidance including CLR 11⁶¹ and the Environment Agency's Remedial Targets Methodology¹⁶. The workshop group suggested that, to date, cost/benefit analysis for soil and groundwater remediation had been largely qualitative and subjective. The robustness of such assessments when used to disprove Category 2 SPoSPoCW could come under scrutiny and warrant more rigorous analysis. It was acknowledged that high level cost/benefit analysis (performed by economists) could be overkill for most contaminated site assessments and that some intermediate level approach would be more suitable. The need for better guidance on how cost/benefit factors could be evaluated and what threshold level would indicate that regulatory intervention was necessary and viable (i.e. determination of a Category 2 SPoSPoCW case) was identified. Such guidance should tie in with existing and emerging practices regarding sustainability (e.g. CL:AIRE⁶²), and should include procedures for communicating cost/benefit analysis findings to stakeholders.

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- ⁵⁷ Rice, D.W., Grose, R.D., Michaelson, J.C., Dooher, B.P., MacQueen, D.H., Cullen, S.J., Kastenburger, W.E., Everett L.G. & Marino, M.A. 1995. California Leaking Underground Fuel Tank (LUFT) Historical Case Analysis. CA Environmental Protection Dept.
- ⁵⁸ Mace, R.E., Fisher, R.S., Welch, D.M. & Parra S.P. 1997. Extent, mass and duration of hydrocarbon plumes from leaking petroleum storage tank sites in Texas. Bureau of Economic Geology, University of Texas at Austin, Texas, Geologic Circular 97-1
- ⁵⁹ Newell, C.J., Hopkins, L.P. & Bedient, P.B. 1989. A hydrogeologic database for ground-water modeling. Ground Water, Volume 28, No. 5, pp703-714
- ⁶⁰ American Petroleum Institute (API). 1998. Characteristics of dissolved petroleum hydrocarbon plumes - results from four studies. API Soil/Groundwater Technical Task Force
- ⁶¹ Environment Agency. 2004. Model procedures for the management of land contamination, Contaminated Land Report 11
- ⁶² CL:AIRE & Sustainable Remediation Forum (SURF) UK. 2010. A framework for assessing the sustainability of soil and groundwater remediation

5.2.2 Modelling Hydrocarbon Degradation in Groundwater

The key process governing petroleum hydrocarbon fate in groundwater is biodegradation. Groundwater risk assessment models in common use in the UK represent contaminant biodegradation using a first-order decay model. First-order biodegradation rates (half-lives) have been published by the Environment Agency for common risk-driving hydrocarbons including BTEX, chlorinated solvents, phenol etc.⁶³ but not for petroleum hydrocarbon fractions. Where site-specific biodegradation rates cannot or have not been determined, common practice has been to adopt published rates for surrogate/indicator compounds and/or make professional judgements. The simulated outputs of groundwater risk assessment models are generally sensitive to biodegradation rate values; the current approach has led to inconsistency in risk assessment of complex hydrocarbon mixtures that rely on fraction-based fate and transport modelling.

CoronaScreen⁶⁴, a spreadsheet based natural attenuation screening tool, provides an alternative to the first-order decay model used by other software. Biodegradation is modelled as the mixing of electron acceptors across the plume fringes (influenced by vertical and transverse dispersion) and their depletion consistent with electron donor reaction stoichiometry. Two members of the workshop group had used this model in risk assessment of hydrocarbon plumes. The key advantage of CoronaScreen is that it is capable of more meaningfully accounting for competitive biodegradation in mixed hydrocarbon plumes than other analytical groundwater models routinely used. The main disadvantage is the amount of site-specific data needed and the requirement for the installation and sampling of multi-level monitoring wells. The cost and complexity of data acquisition could therefore preclude the use of CoronaScreen in most early iteration/basic risk assessments.

Members of the workshop group agreed that publication of biodegradation rates for petroleum hydrocarbon fractions would benefit early iteration/basic risk assessments (that often mainly rely upon literature values in preference to developing site-specific parameters) and should help to reduce inconsistency.

The development of generic biodegradation rates would require appraisal of the fate of petroleum hydrocarbon fractions in UK aquifers and the influence of different biogeochemical conditions, in a manner similar to the advice provided in Reference⁶³. The focus of scientific journal papers has often been on the fate of individual hydrocarbon compounds rather than complex mixtures represented as fractions. Consideration of the effects of compositional differences between fractions derived from different sources of hydrocarbon contamination (e.g. coal tars, diesel etc.) on reaction kinetics could therefore present significant challenges to the development of generic rates. It is likely that use of hydrocarbon fraction data could be a simpler approach but this would almost certainly require some level of input from the industry to provide sufficient, good quality data.

The Remedial Targets Methodology¹⁶ assumes that only organic compounds that are in the dissolved phase are biodegraded. Members of the workshop group stated that this was overly conservative and that degradation reactions of adsorbed contaminants should also be considered in groundwater risk assessment modelling. Some clarification of relative significance of biodegradation of adsorbed versus dissolved phase contaminants is perhaps warranted.

⁶³ Environment Agency. 2002. The effects of concentration on the potential for natural attenuation. R&D Technical Report P2-228/TR

⁶⁴ Wilson, R.D., Thornton, S.F., Hüttmann, A., Gutierrez-Neri, M. & Slenders, H. 2005. CoronaScreen: Process-based models for natural attenuation assessment. Guidance for the application of NA assessment screening models

5.2.3 Modelling Soil and Non-Aqueous Phase Source Zones

Soil and non-aqueous phase source zones were identified as being challenging for groundwater risk assessment, in particular where modelling relies upon conservative pore water partitioning estimates. While laboratory leaching tests were in some cases useful, reported 'dissolved phase' data could indicate non-aqueous phase contaminants were entrained in the supernatant during the test procedure leading to over-estimates of leaching potential and mobility. Direct measurement of groundwater concentrations immediately down-gradient of the source zone were considered to be a better means of estimating dissolved phase source strength.

Remedial targets in soil for low carbon number hydrocarbons generated from pore water partitioning calculations are often very low and not achievable using sustainable remedial technologies. It was suggested that remedial targets for problem compounds/fractions should be collated and compared with typical remediation technology capabilities to better understand what is realistic and practical.

5.3 Conclusions

The workshop group debated three key problem areas for the risk assessment of petroleum hydrocarbons in groundwater. These were linked to:

- compliance and risk estimation/evaluation;
- biodegradation; and
- source zone modelling.

Consensus was reached on several elements of these topics. However, the group identified the need for the development of guidance in four areas (see recommendations below) to address its main concerns that were:

- the lack of consistency in the performance and regulation of risk assessment of petroleum hydrocarbons in groundwater: and
- the implementation of the new Statutory Guidance for Part 2A Category 1-4 system⁷.

5.4 Recommendations

The group made the following recommendations:

4. Groundwater/surface water standards protective of human health (drinking water) and ecological/environmental receptors for petroleum hydrocarbon fractions (Table 2.1 of Reference¹⁷) should be published. Supplementary outputs from this process could include standardised methodologies for deriving potable water and environmental water quality standards and aggregating individual compound standards into fractions/groupings that could have wider application. This work should consider solubility constraints of certain fractions (e.g. Aliphatic C₁₆-C₂₁, Aliphatic C₂₁-C₃₅) and whether water quality standards are required.
5. Biodegradation rates for petroleum hydrocarbon fractions (Table 2.1 of Reference¹⁷) for use in common UK groundwater risk assessment models should be derived. The work should consider the effects of compositional differences of fractions derived from different sources of hydrocarbon contamination (e.g. coal tars, diesel etc.) and the hydrogeology of key UK aquifers and their effects on biodegradation kinetics. It is likely that significant input from the industry will be required to provide sufficient, suitable data to complete such a study.

6. Technical guidelines to provide a means of distinguishing between Category 2 (SPoSPoCW) and Category 3 (not SPoSPoCW) cases of water pollution under Part 2A should be developed. The workshop group agreed that concentrations exceeding water quality criteria alone would not indicate SPoSPoCW and that other metrics should be developed to facilitate this (e.g. plume dynamics, cost benefit analysis (CBA)).
7. Supplementary guidelines on conducting CBA for contaminated site assessments should be produced. The guidance should adapt quantitative analyses to complement existing risk assessment and sustainability practices, provide criteria to support the use of CBA in line with UK contaminated land policies and legislation, and outline strategies for communicating the outcome of CBA to stakeholders.

The Group believed that poor dissemination of some previous guidelines/reports has led to a degree of esotericism in the risk assessment community.

Effective promulgation of new guidelines was thought to be important to their success and therefore should be considered as part of the above recommendations.

6 ASSESSMENT OF THE VAPOUR RISK FROM GROUNDWATER

6.1 Introduction

This workshop was intended to look at the key issues associated with the assessment of risks from vapours. Simon Clennell Jones of WSP Environmental facilitated the workshop and the rapporteur was Natasha Glynn of Atkins.

Prior to the day, the following reference materials were circulated for consideration by the participating delegates:

- CIRIA C682⁶⁵
- Environment Agency R&D Technical Report P5-018/TR⁶⁶
- Environment Agency SR3⁶⁷
- USEPA 2004⁶⁸
- Wilson 2008⁶⁹

6.2 Key Issues

The key issues identified by the group are presented and discussed below:

6.2.1 Current Approaches to Site Investigation and Monitoring

Soil gas investigations

The group discussed site investigation methodologies commonly used by the UK contaminated land industry for assessing the significance of the subsurface-vapour-to-indoor-air exposure pathway. The use of dedicated soil gas monitoring points versus the collection of data from other environmental media, such as soils and groundwater, was debated.

It was agreed that to assess the subsurface-vapour-to-indoor-air pathway, an initial screen of soil and groundwater data was warranted. Where a potential subsurface-vapour-to-indoor-air exposure pathway was identified, further site-specific investigation, focusing on soil gas should be undertaken. The use of groundwater monitoring wells to collect soil gas samples was agreed to be unsuitable as the gathered data do not provide information on soil gas concentrations within the unsaturated zone and do not capture the effect of biodegradation on hydrocarbon vapour concentrations. There was consensus across the group that soil gas investigations should consist of the collection of samples from dedicated soil gas monitoring points consisting of narrow diameter wells installed above the capillary fringe. Leak testing of soil gas monitoring wells was also briefly discussed and it was acknowledged that raised awareness of such testing was needed in the industry.

The collection and use of soil gas data to evaluate the subsurface-vapour-to-indoor-air exposure pathway were identified as representing a relatively new

⁶⁵ CIRIA. 2009. The VOCs Handbook. Investigating, assessing and managing risks from inhalation of VOCs at land affected by contamination, CIRIA Report C682

⁶⁶ Environment Agency. 2002. Vapour transfer of soil contaminants, R&D Technical Report P5-018/TR

⁶⁷ Environment Agency. 2009. Updated Technical background to the CLEA Model, Science Report SC50021/SR3 (Chapter 10)

⁶⁸ USEPA. 2004. Users guide for evaluating subsurface vapor intrusion into buildings, EPA Contract No.68-W-02-33

⁶⁹ Wilson, S. 2008. Modular approach to analysing vapour migration into buildings in the UK, Land Contamination and Reclamation, 16 (3), pp223-236

approach in the UK. It was agreed that although guidance is available on best practice techniques for soil gas site investigations (e.g. CIRIA's VOC Handbook and API 4741⁷¹) this was not always being put into practice.

The group discussed the soon to be published British Standard on Investigations for Ground Gas⁷⁰ and agreed that this should raise the profile of soil gas investigation within the industry.

Soil gas and indoor air sampling methodologies

The group considered sampling techniques frequently used in the UK. Commonly used methods were identified as active sampling techniques such as: soil gas/air drawn into analytical devices such as PIDs; soil gas/air drawn into a sample container such as a tedlar bag or summa canister; or soil gas/air passed through a sorbent tube. A passive technique often used comprises of a diffusion tube that is left in a sample location for a known period of time.

Active vapour sampling, using either gas analysers for bulk gases or canisters for volatile organic contaminants were recognised as being the most commonly used techniques by the group. Passive sampling using diffusion tubes was a less commonly used method, although it was agreed that the method did have benefits as it was the only technique which may capture temporal variations in soil gas concentrations. The semi-quantitative nature of passive monitoring was noted.

The group concluded that the UK contaminated land industry would benefit from further guidance on passive and active sampling techniques and a consistent industry approach to sampling and analysis should be developed.

Multiple lines of evidence investigations

The group discussed use of multiple lines of evidence investigations to provide more than one reasoned line of evidence as to why the vapour intrusion pathway is considered inactive or unlikely. Group members considered that where a vapour source is present or suspected, a multiple lines of evidence investigation could potentially consist of the following decision-making process:

- initially, collect soil and groundwater samples to decide whether the vapour intrusion pathway is likely to be active at the site - if the answer is 'yes', then;
- collect soil gas samples from dedicated monitoring points, assess the soil gas concentrations and compare with the soil and groundwater data. Do the soil gas concentrations make sense in comparison with the soil and groundwater results or could there be another source present?
- model the vapour intrusion pathway using the various lines of evidence - is there a potential risk?
- where buildings may already be present, collect indoor air samples and consider whether the results are consistent with the model findings.

6.2.2 Quantitative Risk Assessment Approaches

Lateral vapour migration through the unsaturated zone

The group discussed conceptual models for the vapour intrusion pathway.

Lateral soil gas migration through the unsaturated zone, moving independently of a groundwater source, was identified as a pathway that is often not considered in

⁷⁰ British Standards Institute. 2012. BS 8576, Investigations for ground gas (in consultation).

conceptual models. One of the reasons for this may be because current risk assessment models used in the UK do not consider lateral soil gas migration as a separate pathway. It was agreed the development of a soil gas migration model would benefit the UK industry and help raise awareness of this pathway.

The lateral distances soil gases may migrate through the unsaturated zone, away from the source, were then discussed. It was noted that in the US some states have adopted an 'exclusion distance' of circa 30m between the source/plume and receptor for halogenated hydrocarbons and an 'exclusion distance' of between 5–10m for the petroleum hydrocarbons. The group considered whether a similar 'rule of thumb' could be adopted in the UK. It was agreed that further work on the appropriateness of adopting such exclusion criteria for UK sites was needed, but such criteria could be developed in the future. The group also agreed that if 'exclusion criteria' were developed for the UK, they would need to be accompanied by guidance to ensure they were used correctly.

UK specific building type model

Software models used by the UK contaminated land industry for assessing the significance of the subsurface-vapour-to-indoor-air exposure pathway were discussed. It was noted that many of the software models available on the market, including the Johnson and Ettinger model used in CLEA v1.06, over-estimate vapour migration into UK buildings as they do not consider UK specific foundation types. This means that factors such as dilution of petroleum hydrocarbon vapours within sub-floor voids is often not considered.

The Wilson modular approach⁶⁹ to analysing vapour migration into buildings in the UK was briefly discussed. The group agreed that the suggestions in the paper with regards to UK specific foundations should be investigated further. It was agreed by the group that a UK specific model with the options to select different foundations types, common to UK buildings, should be developed. It was noted that any new model would need to be calibrated with UK field studies prior to use to ensure it was protective.

Consideration of biodegradation in the unsaturated zone

The group briefly discussed biodegradation of petroleum hydrocarbon vapours within the unsaturated zone. Questions were raised as to whether the screening criteria being used by some US states, as identified in the presentation given by Robert Ettinger, could be used within the UK.

It was noted that there are limited data available on the biodegradation of petroleum hydrocarbon in the unsaturated zone for UK sites. It was agreed therefore that it is currently uncertain whether the US screening criteria could be relied on for UK soils. The group suggested that further research on biodegradation of petroleum hydrocarbons in the unsaturated zone should be carried out within the UK.

Development of screening criteria

Methods to produce UK criteria to screen out sites that present a low subsurface-vapour-to-indoor-air risk were discussed. It was agreed that developing screening criteria would help to raise the profile of the subsurface-vapour-to-indoor-air pathway within the UK contaminated land industry and would therefore be beneficial.

The group discussed the development of generic assessment criteria for groundwater vapour concentrations (GACGV) currently being undertaken by the SoBRA vapour subgroup. The assumed depth to groundwater to be used in the development of the GACGV, and the matrix type, were debated. It was agreed that a shallow depth to groundwater and conservative matrix type should be

assumed to ensure the GACGV were protective. Concerns were then raised as to whether this would make the GACGV overly conservative, which may result in many sites not being screened out at an early stage. The group agreed that it was important that the derived GACGV were transparent and that users of the GACGV understood the parameters used in their development so they were not used incorrectly. It was suggested that a sensitivity analysis should be carried out prior to the GACGV being published; this could be made available to users of the GACGV.

6.3 Conclusions

The main conclusions from the discussion group are presented below:

- The group agreed upon the importance of appropriate site investigation design in assessing the significance of the subsurface-vapour-to-indoor-air exposure pathway at petroleum hydrocarbon release sites. It is considered to be important to consider 'multiple lines of evidence investigations' for the assessment of petroleum hydrocarbon release sites.
- The group agreed that the current risk assessment models being used by the UK contaminated land industry for assessing the subsurface-vapour-to-indoor-air exposure pathway were conservative and often not directly applicable to the UK buildings.
- The group agreed that as an industry, awareness of the potential risks associated with subsurface-vapour-to-indoor-air exposure pathway needed to be raised.

6.4 Recommendations

The recommendations from the discussion group are presented below:

1. Further UK guidance and training on soil gas site investigation and monitoring should be produced within the UK contaminated land community to increase awareness of best practice techniques.
2. Further UK guidance and training on conceptual models for vapour intrusion pathways should be conducted to raise awareness of potential risks from lateral vapour migration pathways.
3. A consistent UK approach to 'multiple lines of evidence' investigations should be developed.
4. A UK specific database could be initiated and maintained for collating site derived evidence of the effect of biodegradation in the unsaturated zone on hydrocarbon vapour concentrations and lateral distances for vapour migration. UK specific field data should also be collected and used to calibrate software models.
5. Further research is needed within the UK to develop methods to screen out low risk sites.
6. Consideration should be given to developing a vapour intrusion model applicable to the UK; this could include modelling of the lateral soil gas migration pathways, the inclusion of UK specific building and foundation types and biodegradation in the unsaturated zone.

7 CONCLUDING REMARKS

7.1 Key Issues and Recommendations

The SoBRA Summer Workshop 2012 identified a number of key issues pertinent to assessing the risks associated with petroleum hydrocarbons in groundwater.

Several of the issues identified by the workshop groups are universally important for achieving good quality risk assessment in land contamination applications. For example:

- the critical role played by both the initial and refined CMs in informing the design and implementation of site investigation work;
- the need to understand and use the most appropriate tools and techniques - whether these are based in the field, in the laboratory or at a desk (e.g. fate and transport models); and
- the need to recognise and make allowance for uncertainties when evaluating risk assessment findings.

However, many of the key issues identified by the groups are specific to the risk assessment of petroleum hydrocarbons in groundwater and stem directly from the complexity of both the chemistry of the compounds and their behaviour in the subsurface environment once an uncontrolled release has taken place.

These issues are reflected in the conclusions and recommendations put forward by each of the workshop groups as detailed in the relevant sections of this report.

Key issues and recommendations were as follows.

Site investigation and sampling

The main conclusion reached by this group was that while the investigation and sampling of groundwater contamination involving petroleum hydrocarbons present particular challenges (for example, in relation to the positioning, design and development of groundwater monitoring wells, and to the use of specific sampling techniques such as low flow sampling), there is no shortage of good practice guidance in this area.

This group felt that the key barrier to effective delivery of good practice site investigation and sampling is that existing guidance is too often ignored for practical or budgetary reasons. This group felt that existing guidance should be given more prominence, and be more vigorously promoted and observed.

Laboratory analysis and environmental forensics

This workshop group acknowledged that the laboratory analysis of petroleum hydrocarbons can be difficult and subject to uncertainty due mainly to: the complex chemistry; confusion over nomenclature; the number/variety of different preparation and analytical techniques potentially available; and a lack of good communication between those scheduling laboratory testing and those supplying laboratory services.

However, the group felt that many of the existing problems could be addressed by better communication between the parties. Several recommendations were made on how this could be achieved including: involving laboratories at an early stage in the scheduling process and in cases of doubt; providing more detailed information to laboratories on 'chain of custody' documentation about the likely nature/level of contamination of samples being submitted for analysis; greater use of duplicate samples; and more feedback and support from laboratories on

matters such as QA/QC performance and the implications this might have for the evaluation of laboratory data.

The group also recognised the very specialist nature of forensic investigations and assessment, and the fact that particular techniques and skills would be necessary where a project requires some form of forensic input.

Groundwater risk assessment modelling and the development of guidance

This group identified three key areas of interest: water quality standards and risk evaluation guidelines; biodegradation rates and modelling; and modelling soil and non-aqueous phase source zones.

The group considered that further research and/or the development and publication of guidelines would do much to improve groundwater risk assessment involving petroleum hydrocarbons. The group called for:

- groundwater/surface water standards protective of human health (drinking water) and ecological/environmental receptors for petroleum hydrocarbon fractions;
- biodegradation rates for petroleum hydrocarbon fractions for use in common UK groundwater risk assessment models;
- technical measures for distinguishing between Category 2 (SPoSPoCW) and Category 3 (not SPoSPoCW) cases of water pollution under Part 2A, bearing in mind that simple exceedance of water quality criteria should not be sufficient, and that other metrics, such as plume dynamics and CBA, should play a role.
- guidance on the conduct of CBA for contaminated land applications.

The group also felt that any such guidelines/guidance should be actively and effectively promoted to ensure good dissemination and take-up amongst practitioners and other stakeholders.

Assessment of the vapour risk from groundwater

In addition to recognising the role of good design in the investigation of the subsurface-vapour-to indoor-air exposure pathway in cases involving petroleum hydrocarbons and groundwater, this group felt that it was important to consider a 'multiple lines of evidence' approach to investigation and assessment. Members felt that current UK models for this exposure pathway were too conservative and that current awareness of this exposure pathway in the UK is low.

The group put forward several proposals to address these issues that included:

- further guidance and training on soil gas site investigation and monitoring and on the conceptualisation of the vapour intrusion pathway;
- a more consistent approach to 'multiple lines of evidence' investigations;
- the development of an empirical UK specific database on biodegradation rates in the unsaturated zone and in relation to the lateral movement of gases;
- the development of methods to screen out 'low risk' sites; and
- the further development of UK models for predicting vapour intrusion which take into account UK data on factors such as biodegradation, lateral movement and UK specific building types.

7.2 Delivering the Recommendations

In common with previous events, SoBRA's 2012 Summer Workshop produced a number of recommendations that members believe would improve UK risk assessment practice both in general and in relation to petroleum hydrocarbons in groundwater.

Some of the recommendations potentially involve further research and the development of guidance; others are more concerned with promoting existing good practice guidance and ensuring that it is actually followed.

Through its working groups, SoBRA has already demonstrated a capability for developing technical initiatives and delivering consensus-based solutions. Several of the recommendations outlined in this report may be amenable to this type of approach. Any member who wishes to take forward any recommendation using the 'SoBRA working group' mechanism is urged to contact the SoBRA Executive Committee.

As for recommendations on the need for greater compliance with existing good practice guidance, by publishing this report SoBRA is signalling its strong commitment to upholding the highest possible standards of risk assessment practice in the UK. It does so in the reasonable expectation that this will lend much needed support to practitioners, regulators and others who share the same, important objective.

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APPENDIX 1 - WORKSHOP GROUPS

WORKSHOP 1: Site Investigation and Sampling

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APPENDIX 2 - ABBREVIATIONS

API	American Petroleum Institute
AST	Aboveground Storage Tank
BGS	British Geological Society
BSI	British Standards Institution
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
BW	Body Weight
CBA	Cost Benefit Analysis
CLEA model	Contaminated Land Exposure Assessment model
CM	Conceptual Model
CRM	Certified Reference Material
DNAPL	Dense Non Aqueous Phase Liquid
DRO	Diesel Range Organics
DWS	Drinking Water Standard
ECN	Equivalent Carbon Number
EDR 2009	Environmental Damage (Prevention and Remediation) Regulations
EPA 1990	Environmental Protection Act 1990 c.43
EPH	Extractable Petroleum Hydrocarbons
EPR 2010	Environmental Permitting Regulations SI/2010/675
EQS	Environmental Quality Standard
FID	Flame Ionization Detector
GAC	Generic Assessment Criterion
GACGV	Generic Assessment Criterion for Groundwater Vapour
GC FID	Gas Chromatography Flame Ionisation Detector
GC MS	Gas Chromatography Mass Spectroscopy
GRO	Gasoline Range Organics
IED	Industrial Emissions Directive 2010/75/EU
INEF	International Network of Environmental Forensics
IPPC 1996	Integrated Pollution Prevention and Control Directive 96/82/EC
IR	Ingestion Rate
ISO	International Standards Organisation
ITRC	Interstate Technology & Regulatory Council
K _{oc}	Organic Carbon to Water Partition Co-efficient
LIF	Laser Induced Fluorescence

LNAPL	Light Non Aqueous Phase Liquid
LORO	Lube Oil Range Organics
MADEP	Massachusetts Department of Environmental Protection
MCERTS	Monitoring Certification Scheme
MIP	Membrane Interface Probe
MTBE	Methyl Tertiary Butyl Ether
NAPL	Non Aqueous Phase Liquid
NPPF	National Planning Policy Framework 2012
NSOs	Nitrogen, Sulphur, Oxygen containing compounds
PAH	Polycyclic Aromatic Hydrocarbon
Part 2a	Part 2A of the Environmental Protection Act 1990
PID	Photoionization Detector
PPS	Planning Policy Statement
PT	Proficiency Testing
QA/QC	Quality Assurance/Quality Control
SCR	Site Condition Report
SPoSPoCW	Significant Possibility of Significant Pollution of Controlled Waters
TDI	Tolerable Daily Intake
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbons Criteria Working Group
UCM	Unresolved Complex Mixture
USEPA	United States Environmental Protection Agency
UST	Underground Storage Tank
VOC	Volatile Organic Compound
VPH	Volatile Petroleum Hydrocarbons
WHO	World Health Organization