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# Petroleum Hydrocarbons in Groundwater:

Guidance on assessing petroleum hydrocarbons using existing hydrogeological risk assessment methodologies

CL:AIRE

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## Version Control Sheet

<b>Version number</b>	<b>Version Date</b>	<b>Description of Changes</b>
1	31 January 2017	
1.1	29 March 2017	<p>p18. Reference changed from Feenstra and Cherry (1998) to Mercer and Cohen (1990).</p> <p>p25. Amended footnote “e” to read that the xylene EQS is an Environment Agency “operational” target and is not listed in the 2015 Directions.</p> <p>p25. Amended Table 5.3 and footnote “g” to indicate that benzo(a)pyrene can be considered as a marker for the other PAHs, hence only benzo(a)pyrene needs to be monitored</p>

# Executive Summary

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This document provides guidance on assessing the risks to groundwater and surface water from petroleum hydrocarbon compounds. It complements the Environment Agency's guidance given in the Remedial Targets Methodology (Environment Agency, 2006<sup>a,b</sup>) and should be read alongside that report and Groundwater Protection: Principles and Practice (GP3, Environment Agency, 2013). The objective of this guidance is to establish an effective, reliable and consistent approach to petroleum hydrocarbon assessment within hydrogeological risk assessments. This document aims to provide advice on how to:

- Evaluate the risk from hydrocarbon mixtures;
- Consider analytical techniques available;
- Estimate the implications of non-aqueous phase liquid (NAPL) for dissolved phase groundwater risk assessments; and
- Promote a lines of evidence approach to evaluate the importance of biodegradation of other natural attenuation processes.

Incorporating petroleum hydrocarbon compounds into existing hydrogeological risk assessment methodologies presents a number of challenges. Fortunately, detailed research and guidance has been published in recent years, which help assessors evaluate these potential risks robustly. In particular:

Petroleum hydrocarbon and light non-aqueous phase liquid (LNAPL) conceptual site models, and fate and behaviour:

- CL:AIRE LNAPL Handbook (CL:AIRE, 2014)
- American Petroleum Institute (API) Interactive LNAPL Guide (API, 2006)

Selecting constituents of potential concern (CoPC) for petroleum hydrocarbon releases:

- Bowers and Smith (2014)
- Total Petroleum Hydrocarbon (TPH) Criteria Working Group series (TPHCWG, 1997<sup>a,b</sup>, 1998<sup>a,b</sup>, 1999)

Simulating long-term transient source behaviour of LNAPL sources:

- Thornton *et al.* (2013)

Evaluating the mobility of LNAPLs in the subsurface using LNAPL transmissivity:

- ASTM International Standard E2856 on LNAPL transmissivity (ASTM, 2013)

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# 1. Introduction

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The document provides guidance on assessing the risks to groundwater from petroleum hydrocarbon compounds and is a supplementary report to the Environment Agency's *Remedial Targets Methodology: Hydrogeological Risk Assessment for Land Contamination* (Environment Agency 2006<sup>a,b</sup>). However, the guidance may also be pertinent to other risk assessment methodologies.

The large number of hydrocarbon compounds present in crude oil and crude oil-derived products, such as fuels, lubricants and bitumens, and other similar substances, coupled with the wide choice of analytical techniques for determining and characterising these, has led to inconsistencies in the approaches used for incorporating them into hydrogeological risk assessments.

This document identifies particular issues with assessing the risks from petroleum hydrocarbon compounds to controlled waters, but should be read in conjunction with relevant Environment Agency advice and good practice guidance. For this reason, readers should satisfy themselves that they understand what petroleum hydrocarbons are and how they behave in the subsurface environment. They should also be familiar with the risk assessment process and existing Environment Agency advice. A list of useful references is given in Section 1.4.

The objective of this guidance is to establish an effective, reliable and consistent approach to petroleum hydrocarbon assessment within hydrogeological risk assessments. Specific aims of the guidance include advice on how to:

- Evaluate the risk from hydrocarbon mixtures;
- Select and interpret the data from available analytical techniques;
- Estimate the implications of non-aqueous phase liquid (NAPL) for dissolved phase groundwater risk assessments; and
- Promote a lines-of-evidence approach to support the consideration of natural attenuation processes (principally biodegradation) in site-specific risk assessment of petroleum hydrocarbons.

The document also provides advice on selecting appropriate water quality targets for petroleum hydrocarbon compounds.

Other aspects of risk assessment such as risks to human health are dealt with elsewhere (for example, Environment Agency, 2005). Migration of petroleum hydrocarbon compounds in the subsurface is a potential pathway to human receptors, including via vapour intrusion into buildings. If in the course of undertaking a hydrogeological risk assessment, a potential pathway via transport with groundwater and subsequent vapour migration is identified, then the risks to human health and other relevant receptors should be considered. Vapour intrusion is also an area where science has evolved, for example by considering the attenuation of petroleum hydrocarbons vapours in the unsaturated zone by aerobic biodegradation:

- United States Environmental Protection Agency (USEPA) Vapor intrusion web resource (USEPA, 2016)
- Lahvis *et al.* (2013)

This guidance does not explicitly cover organic compounds of a non-crude oil origin which may be present as additives in a fuel or lubricant, or have become mixed with hydrocarbons in the environment. These compounds can generally be dealt with as

single contaminants by following the Remedial Targets Methodology (Environment Agency, 2006<sup>a,b</sup>) or other risk assessment approaches.

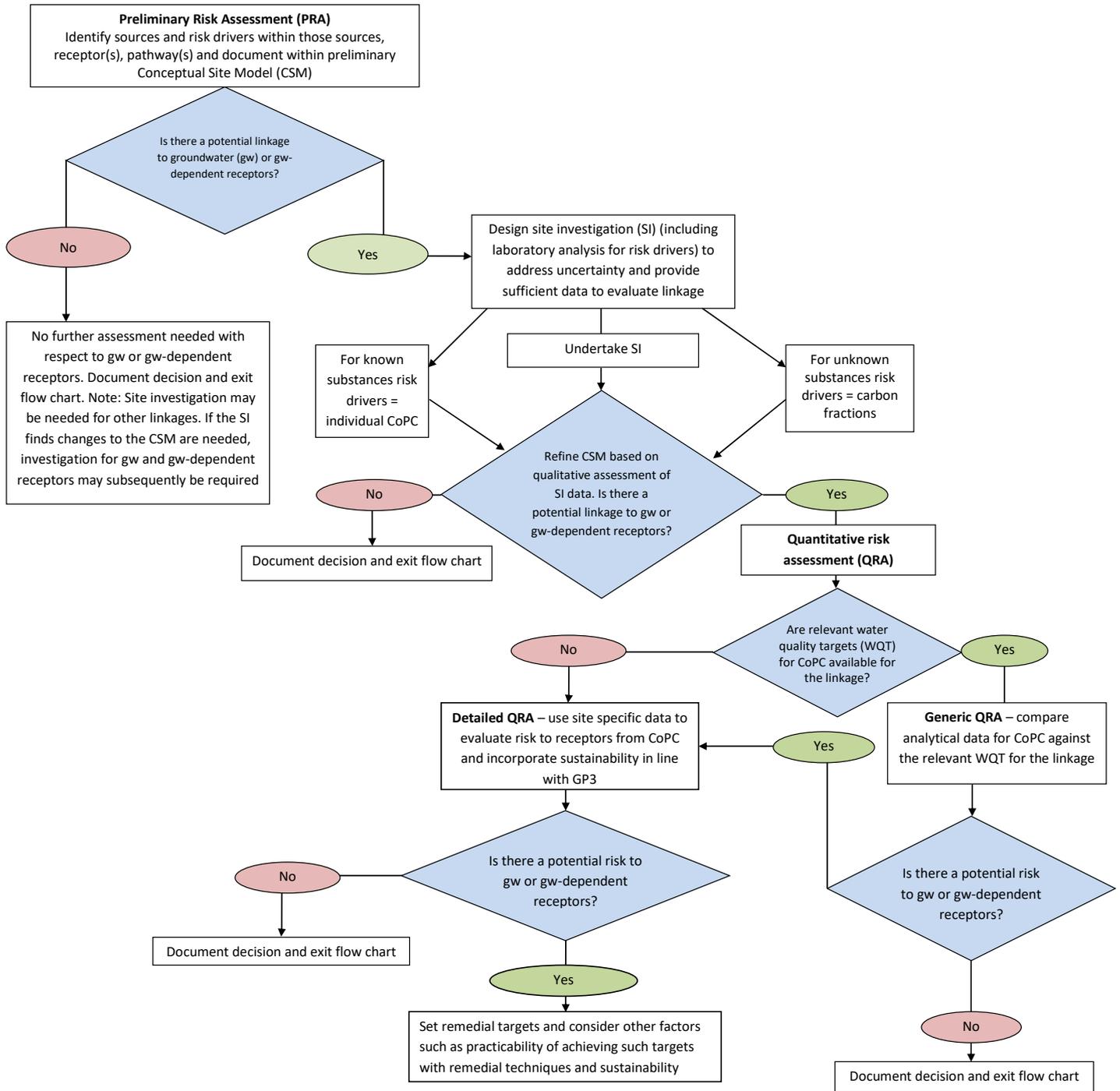
## **1.1 Risk assessment framework**

An overall framework for the management of land contamination is described in *Model Procedures for the Management of Land Contamination* (CLR11, Environment Agency 2004). The first step in the land management process is risk assessment which commences with development of a conceptual model. The conceptual model presents the level of site understanding at any one time during the land management process. The conceptual model informs future work and is refined as more information is gained through site investigation, risk assessment and then as appropriate through remediation trials/pilots, remediation operation and subsequent verification.

A risk assessment can have both qualitative and quantitative elements. Typically, more site-specific information is gained and uncertainty reduces as the risk assessment develops from qualitative to quantitative assessment. The aim of the qualitative assessment is to eliminate low risk sites and/or to determine the scope of the quantitative assessment.

The risk assessment should be relevant, sufficient, and reliable, and the decision-making process transparent. In particular, any areas of uncertainty, and the implications of uncertainty on the risk assessment, should be documented. To aid reporting, reference should be made to the aims and objectives for the protection, management and remediation of groundwater of the relevant United Kingdom (UK) environmental regulator. Any relevant guidance or regulatory processes should be followed.

The risk assessment process for petroleum hydrocarbons is summarised in Figure 1.1.



**Figure 1.1. Flow diagram for hydrocarbon risk assessment**

The risks to controlled waters from petroleum hydrocarbons arise in two ways:

- **Groundwater as a receptor:**
  - downward movement of NAPL giving the potential for free phase hydrocarbons to reach the water table;
  - leaching of petroleum hydrocarbons from soils and downward flow of dissolved-phase hydrocarbons through the unsaturated zone to the water table;
  - indirect discharge of hydrocarbon impacted water ('run-off') entering soak-aways, or leaking from drains or oil-water separators, and moving down to the water table;
  - indirect and direct discharge to soil / groundwater under permitted conditions;
  - direct discharge to groundwater via leakage from infrastructure, such as tanks or drainage systems at or below the groundwater elevation;
  - vapour from a subsurface source dissolving in pore water and migrating down to the water table.
- **Groundwater as a pathway (groundwater - dependent receptors):**
  - hydrocarbons that have already reached the water table developing into a dissolved phase plume that reaches a receptor, such as a:
    - water supply well or borehole;
    - statutory drinking water source protection zone (SPZ);
    - spring;
    - groundwater-dependant surface water body;
    - groundwater-dependant terrestrial ecosystem;
    - regulatory compliance point located within the aquifer
      - Environment Agency guidance of 250m default for non-hazardous pollutants and 50m for hazardous substances (GP3, Environment Agency, 2013)
  - mobile NAPL migrating laterally directly to a receptor. This should be considered separately within the risk assessment process. Further guidance on assessing the mobility of light NAPL (LNAPL) is given in API (2002) and CL:AIRE (2014). Dense NAPLs (DNAPLs) are described in Environment Agency (2003<sup>a</sup>). The Remedial Targets Methodology spreadsheet and most other common groundwater risk assessment tools only assess the movement of dissolved substances. In these risk assessment tools, any NAPL source is assumed to be stationary.

Volatilising and dissolving hydrocarbon compounds from NAPL can form a source of vapour that could migrate upwards into buildings or laterally as a dissolved groundwater plume. These may present a potential human health risk, which should be appropriately assessed; references to assist in this regard are provided in Section 1.4. Similarly, hazardous permanent ground gases (particularly methane and carbon dioxide) can be generated as a consequence of biodegradation of petroleum hydrocarbons, and particularly from readily biodegradable biofuel components such as

ethanol (Morgan *et al.*, 2014). These potential risks should be considered in line with BS8576 (BSI, 2013) and other applicable guidance.

The overall risk assessment methodology for groundwater is set out in *Remedial Targets Methodology: Hydrogeological Risk Assessment for Land Contamination* (Environment Agency, 2006<sup>a</sup>). The risks to groundwater and groundwater-dependent receptors need assessing with the use of a conceptual site model (CSM). From this all plausible source - pathway - receptor (S-P-R) linkages between hydrocarbon impacted soils or groundwater and receptors should be identified. The risk assessment process determines whether hydrocarbons present in soils and groundwater pose an unacceptable risk to human health, the environment or other relevant receptors.

Following identification and characterisation of the S-P-R linkages, water quality criteria, termed Remedial Target Concentrations (RTCs) in the Remedial Targets Methodology (see Section 5.2), are derived for the receptors. The analytical data representative of the source are assessed by comparison against the target concentration as part of the assessment to determine whether a quantitative hydrogeological risk assessment is required. Where appropriate, a detailed quantitative risk assessment (DQRA) is then undertaken.

If an unacceptable risk is identified, then remedial objectives / targets are derived against which remediation or other risk-management options can be evaluated and implemented. In line with relevant guidance (Environment Agency, 2006<sup>a</sup>), sustainability should be considered, in particular the balance of environmental, social and economic impacts caused by the shortlisted remediation options, versus the environmental, social and economic benefit generated by undertaking that remediation, i.e. does remediation provide net-benefit? SuRF-UK provides a framework for sustainability assessment (CL:AIRE 2010; 2011; Bardos *et al.*, 2012; 2016). It is also important to consider the technical feasibility of achieving such targets.

Recommended approaches for DQRA for hydrocarbons are described in this document; their use depends on the type of hydrocarbons present and the information available. The preferred approach is based on assessing the risks from individual hydrocarbon compounds identified within a mixture and should be followed where data exist to support its use. The second approach assesses the risks from hydrocarbon compounds in the form of petroleum hydrocarbon fractions. This approach should be used where characterisation of individual hydrocarbon compounds does not readily facilitate a robust risk assessment.

## 1.2 Incorporating hydrocarbons in hydrogeological risk assessment

Incorporating hydrocarbons into existing hydrogeological risk assessment methodologies presents a number of challenges:

- **Mixtures.** Hydrocarbon compounds are frequently found as complex mixtures of a large number of compounds. It is not always possible to identify every compound present within such a mixture. Even if it were, it is difficult to incorporate all of them within a hydrogeological risk assessment.
- **Choice of analysis.** There are a number of analytical techniques available for the determination of hydrocarbons and choosing the most appropriate technique, along with subsequent data interpretation, needs careful consideration.
- **Phases.** Hydrocarbons exist in a number of phases in the subsurface environment (potentially as vapour, mobile NAPL, residual NAPL, sorbed to solid material and dissolved in the aqueous phase) and can move readily

between phases. Existing hydrogeological risk assessment methodologies generally assume that contaminants exist in one of two phases – either in aqueous solution or sorbed to solids.

Multiple phases present a number of challenges:

- obtaining representative samples can be difficult; and
- the relative distribution of hydrocarbons within the phases may change over time.

Where NAPL is present in the subsurface, it may form a long-term source of groundwater contamination through dissolution and migration either through the unsaturated zone or directly into groundwater. This is particularly the case where water levels vary seasonally or are tidally influenced and residual NAPL is present.

NAPL can also present a direct risk when mobile. The potential for free phase migration therefore requires assessment, including consideration of NAPL viscosity and NAPL head. Section 4.2 discusses the risks from NAPL migration but does not provide guidance on methods for assessing the risk of migration. References listed in Section 1.4 should be consulted on this matter.

- **Identification of risk drivers.** Risk drivers are constituents of potential concern (CoPC) that present the greatest risk to health or the environment. By managing the risk-driving CoPC any potential risks associated with other components in the mixture are also managed. The results of chemical analysis can be difficult to interpret in terms of identifying which compounds or groups of compounds present the greatest risk to controlled waters, and necessitate consideration of the product chemistry and potential exposure scenarios.
- **Degradation.** Hydrocarbons can undergo biodegradation in the subsurface environment. This may reduce their concentration and/or toxicity in groundwater and may help to reduce the risk that they pose to groundwater receptors. It is therefore important that consideration of degradation is included in the risk assessment to ensure that the risks are not overstated where there is evidence that degradation is occurring. A lines-of-evidence approach is recommended to determine the role of natural attenuation processes (Environment Agency, 2000).

Guidance on dealing with these challenges is set out in Sections 2 to 7.

### **1.3 Use of the term ‘total petroleum hydrocarbons’**

Total petroleum hydrocarbons (TPH) is a widely used – and often misused – term for mixtures of hydrocarbons when they are subject to environmental analysis. TPH is an analytical method-defined measurement. The term TPH is not used in this document except where necessary for consistency with earlier publications. This is because analytical techniques will not quantify all hydrocarbons present; reported values are rarely, if ever, a ‘total’; and will include measurement of hydrocarbons that are not derived from oil.

There is also ambiguity associated with the term ‘mineral oil’ and other broad banded analytical groupings such as Gasoline Range Organics (GRO) and Diesel Range Organics (DRO). Therefore these terms will only be used when referring to a specific analytical method.

## 1.4 Useful guidance and key references

This document is designed to supplement existing guidance. The following documents in particular offer useful advice for undertaking hydrogeological risk assessment and/or information on hydrocarbon properties and behaviour:

- *Remedial Targets Methodology: Hydrogeological Risk Assessment for Land Contamination* (Remedial Targets Methodology) (Environment Agency, 2006<sup>a</sup>);
- *Remedial Targets Methodology: Hydrogeological Risk Assessment Spreadsheet model v3.2* (Environment Agency, 2006<sup>b</sup>);
- *Groundwater Protection: Principles and Practice (GP3). Version 1.1* (Environment Agency, 2013);
- *An Illustrated Handbook of LNAPL Transport and Fate in the Subsurface* (CL:AIRE, 2014);
- *The UK Approach for Evaluating Human Health Risk Assessment from Petroleum Hydrocarbons in Soils* (Environment Agency, 2005);
- *Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater* (Environment Agency, 2000);
- ConSim – software developed by Golder Associates for the Environment Agency (Environment Agency, 2003<sup>b</sup>);
- *Model Procedures for the Management of Land Contamination (CLR11)* (Environment Agency, 2004);
- Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG) Series:
  - *Volume 1: Analysis of Petroleum Hydrocarbons in Environmental Media* (TPHCWG, 1998<sup>a</sup>);
  - *Volume 2: Composition of Petroleum Mixtures* (TPHCWG, 1998<sup>b</sup>);
  - *Volume 3: Selection of Representative TPH Fractions Based on Fate and Transport Considerations* (TPHCWG, 1997<sup>a</sup>);
  - *Volume 4: Development of Fraction Specific Reference Doses and Reference Concentrations for Total Hydrocarbons* (TPHCWG, 1997<sup>b</sup>);
  - *Volume 5: Human Health Risk-based Evaluation of Petroleum Release Sites: Implementing the Working Group Approach* (TPHCWG, 1999).
- *An Illustrated Handbook of DNAPL Transport and Fate in the Subsurface* (Environment Agency, 2003<sup>a</sup>);
- *Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Magnitude* (API, 2002); and
- *Constituents of potential concern for human health risk assessment of petroleum fuel releases* (Bowers and Smith, 2014).

This document draws extensively on the information and guidance given in the five volumes of the TPH Criteria Working Group (TPHCWG) series. These are referred to as TPHCWG throughout the text.

Full references are given in Section 8.

## **1.5 How to use this guidance**

The issues identified in Section 1.2 are addressed in this guidance as follows:

- Section 2 considers the approach to dealing with hydrocarbon mixtures;
- Section 3 considers the choice of analysis for hydrocarbons;
- Section 4 describes the approach to dealing with separate phases;
- Section 5 considers the identification of risk drivers and setting water quality targets;
- Section 6 considers degradation of hydrocarbons;
- Section 7 describes the overall risk assessment approach; and
- Section 8 provides lists of key references and further reading.

## 2. Petroleum hydrocarbons as mixtures

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### 2.1 Introduction

Common hydrocarbon mixtures such as fuels (petrol, diesel, kerosene) and lubricating oils are highly complex mixtures of compounds. It is almost impossible and certainly impractical to identify and quantify every single component within a hydrocarbon product. Furthermore, it may not be necessary, practicable or cost-effective to undertake a DQRA for each of them.

The difficult challenges that hydrocarbon mixtures pose to the hydrogeological risk assessment process are:

- Describing and characterising hydrocarbon mixtures;
- Obtaining analysis that is meaningful; and
- Assessing the risks when there are large numbers of compounds present, especially identifying which compounds or groups of compounds present the greatest risk. This issue is dealt with in Section 5.

The recommended approach is to identify key risk-driving compounds and/or hydrocarbon fractions, whose assessment and, if required, management or remediation will also ensure appropriate management of other lower priority CoPC.

### 2.2 Characterising hydrocarbon mixtures

Most analyses of environmental samples (for example, determination of the benzene concentration in a soil sample) produce a concentration value for the substance specifically targeted by the analysis. Using this approach for complex hydrocarbon mixtures provides concentration values only for a limited number of targeted compounds. The approach does not provide information on compounds that have not been specifically targeted.

Analysis of individual compounds is a robust approach for fuels if the chemistry of the original material is well known and CoPC have been derived for all of the potential risk-driving components. For petrol, diesel and aviation fuel (kerosene), recommended CoPC are presented in Bowers and Smith (2014).

### 2.3 Carbon banding and aromatic/aliphatic split

An approach developed for the analysis and assessment of hydrocarbons involves separating hydrocarbons into aromatic and aliphatic fractions, then subdividing these into carbon bands. This approach has been widely accepted for use in human health risk assessment (for example, TPHCWG, Volumes 1 to 5 and Environment Agency (2005<sup>a</sup>) and is useful when considering the risks to controlled waters since the fractions can be assigned representative fate and transport properties.

The division into carbon bands is based around the concept of 'equivalent' carbon (EC) number (see Box 2.1). Using the EC number concept allows compounds with similar boiling points to be grouped into specific carbon bands. Using simple partition models, this then enables the likely behaviour of compounds to be approximately predicted where published information on these compounds is limited. A full explanation of the approach is given in TPHCWG Volume 3 (TPHCWG, 1997<sup>a</sup>).

### Box 2.1. Equivalent carbon number

The carbon number is the number of carbon atoms contained within a particular molecule (for example, hexane and heptane contain six and seven carbon atoms respectively and therefore possess a carbon number of 6 and 7 respectively). For *n*-alkanes, the carbon number and the EC number are the same.

The EC number is based on the retention time of the gas chromatographic separation based on column material that separates hydrocarbon compounds according to their boiling points. For example, benzene with a boiling point of 80°C exhibits a retention time approximately midway between those of *n*-hexane (carbon number of 6 and boiling point of 69°C) and *n*-heptane (carbon number of 7 and boiling point of 98°C). Therefore, benzene has an EC number of approximately 6.5.

However, there are marked differences in the chemical properties between aliphatic and aromatic compounds within equivalent carbon bands, for example, benzene (EC 6.5) has an aqueous solubility of 1,780 mg/l but hexane (EC 6) has a solubility of 9.5 mg/l (both at 15°C).

TPHCWG identified a number of carbon band ranges (Table 2.1) to which it assigned properties related to their environmental fate. Similar carbon band ranges have been proposed by the Environment Agency for human health risk assessment (Environment Agency, 2005). A full range of TPH fraction properties is provided in TPHCWG Volume 3 (TPHCWG, 1997<sup>a</sup>).

**Table 2.1. TPHCWG and Environment Agency carbon bands**

TPHCWG	Environment Agency <sup>†</sup>		
Aliphatic carbon bands	Aromatic carbon bands	Aliphatic carbon bands	Aromatic carbon bands
EC5–EC6	EC5–EC7(benzene)	EC5–EC6	EC5–EC7 (benzene)
>EC6–EC8	>EC7–EC8(toluene)	>EC6–EC8	>EC7–EC8 (toluene)
>EC8–EC10	>EC8–EC10	>EC8–EC10	>EC8–EC10
>EC10–EC12	>EC10–EC12	>EC10–EC12	>EC10–EC12
>EC12–EC16	>EC12–EC16	>EC12–EC16	>EC12–EC16
>EC16–EC35	>EC16–EC21	>EC16–EC35	>EC16–EC21
	>EC21–EC35	>EC35–EC44	>EC21–EC35
			>EC35–EC44
		>EC44–EC70	

Note: Care needs to be exercised in reporting ranges. The carbon band range should be precisely and clearly defined to avoid under- or over-reporting.

<sup>†</sup> After: Environment Agency, 2005

There are some minor differences between the carbon band ranges listed by TPHCWG and those proposed for use by the Environment Agency (2005<sup>a</sup>) for assessment of risks to human health. However, these do not significantly affect the understanding of risk to groundwater as they relate to the higher carbon number bands, which contain compounds that have very low water solubility and mobility in the subsurface environment, and hence present a low risk to the aquatic environment.

As the carbon number increases, the number of compounds within each carbon band also increases. For example, the aromatic carbon band ranges >EC5–EC7 and >EC7–EC8 contain only benzene and toluene respectively, aromatic >EC8–EC10 includes ethylbenzene and the xylene isomers (amongst others), whereas the aromatic carbon band range >EC12–EC16 contains many aromatic substances, including some polycyclic aromatic hydrocarbons (PAHs).

In summary, the use of carbon banding with aliphatic/aromatic fractionation provides information on the distribution of hydrocarbons within a mixture in terms of their molecular weight and their chemistry. This can be used to characterise a hydrocarbon mixture of unknown origin and aids in the identification of the likely product, or mixture of products. The analysis can also be used in an assessment of the risks posed to controlled waters.

Advice on the use of carbon band ranges in risk assessment is given in Section 7.

# 3. Analysis of petroleum hydrocarbons

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## 3.1 Analytical considerations

Analysis of environmental samples (soil, groundwater and LNAPL) for petroleum hydrocarbons is required to support a hydrogeological risk assessment. Analysis will help to determine the concentration of hydrocarbons in a mixture and hence its composition.

Samples containing hydrocarbons typically include large numbers of individual compounds, not all of which are readily identified by conventional analysis. To overcome this challenge, a range of analytical methods have been developed or adapted for use. For example, the methods described by the Standing Committee of Analysts (SCA) which are published as 'blue books' on the Environment Agency website (Environment Agency, 2016). In addition, some individual hydrocarbon compounds can be identified by commonly available analytical techniques.

The varying properties of the constituents of hydrocarbon mixtures mean that a suite of analyses will often be required to provide sufficient information for use in hydrogeological risk assessment. Care is needed in specifying analyses in order to avoid:

- Under-reporting: where some of the hydrocarbons are not determined; and
- Over-reporting: where double accounting may occur in situations where hydrocarbons are reported by more than one method.

The selection of analytical method(s) will depend on:

- Product source of the hydrocarbon mixture (where this is known);
- Its phase (sorbed, NAPL, aqueous); and
- The matrix requiring analysis (product, soil or water).

An important aspect in the planning and commissioning of analysis is communication with the analytical laboratory. Laboratory staff should be able to advise whether:

- A particular method is suitable for an intended purpose; and
- The performance of the method is adequate in terms of its bias, precision and limit of detection.

However, laboratories can only offer suitable advice if they are provided with all relevant information.

Laboratory analysis for use in hydrogeological risk assessment also needs to report results at concentrations that have value within the risk assessment context. Notably, the laboratory reporting limit should be below the relevant water quality criteria, although this is sometimes difficult to implement. For example, some PAH environmental quality standards (EQS) are lower than the practicable analytical reporting limits for groundwater/surface water samples (Section 5.2).

Analysis of a number of other determinands may also be required to support a hydrogeological risk assessment for hydrocarbons, particularly determinands that provide information on the redox conditions in groundwater and the concentration of

electron acceptors (dissolved oxygen, nitrate, sulphate, etc.). This information is generally required for assessment of the biodegradation of hydrocarbons (Environment Agency, 2000).

### 3.1.1 Analytical methods

The analytical methods available for use in hydrogeological risk assessment of controlled waters form two categories:

- **Screening analysis** – includes any method that provides a single figure (or limited carbon banding) for hydrocarbon concentration, including both laboratory and field (field test kit) methods; and
- **Detailed analysis** – provides information on the concentration of individual compounds and/or discrete carbon bands, and aliphatic/aromatic fractionation.

An investigation strategy may adopt both, or if the nature of hydrocarbon is understood, may choose to use only detailed analysis of appropriate CoPC.

### 3.1.2 Screening analysis

Measurements that provide limited information on hydrocarbon concentrations are typically not generally suitable for hydrogeological risk assessments. However, screening analysis may be useful in:

- Identifying the presence of hydrocarbons, i.e. whether they are present or not;
- Determining the likely type of hydrocarbons (whether it is diesel, petrol, etc.) when limited carbon banding is available. Caution should be taken when assigning hydrocarbon type. Mixtures that fall within particular ranges (e.g. GRO, DRO) may not be the expected product. Consult the CSM to inform the decision;
- Determining the likely phases present (based on concentration);
- Delineating the extent of contamination (including during remediation);
- Indicating an approximate hydrocarbon concentration;
- Understanding the total carbon load that a remediation system must be capable of treating; and
- Tracking remediation progress over time (i.e. to identify trends in total hydrocarbon concentration reduction).

### 3.1.3 Detailed analysis

Detailed analysis to determine the concentration of individual compounds or of discrete carbon band ranges (i.e. TPHCWG analysis or equivalent) is **always** required to support a quantitative hydrogeological risk assessment. Table 3.1 lists analytical methods applicable to soil and groundwater.

Other techniques are available to characterise the heavier hydrocarbon fractions, which may be present in products such as bitumen, lubricating oils, waxes, tars and greases. The heavier fractions (compounds >20 carbon atoms) are very unlikely to contain hydrocarbon compounds with appreciable aqueous solubility. These compounds are therefore unlikely to be of interest in a hydrogeological risk assessment, except in certain geological environments such as karst, where suspended solid and/or LNAPL may potentially be transported over significant distances. These risks should be considered on a site-specific basis, although research (Schwarz *et al.*, 2011) suggests

the likelihood that karstic transport of high molecular weight components, such as PAHs, causing an unacceptable impact on groundwater is low.

Detailed results from the analysis of volatile organic compounds and semi-volatile hydrocarbon compounds are reported as a concentration for a specified compound. Most laboratories have developed their own target lists for these compounds based on standard methodologies. It is possible to adapt target lists for particular groups of contaminants or to develop project-specific target lists. Target lists are typically available for:

- **Volatile organic compounds (VOCs) analysis** – includes a range of low molecular weight aromatic hydrocarbons and selected aliphatic hydrocarbons up to EC12;
- **BTEX analysis** – a variant on VOC analysis which specifically targets benzene, toluene, ethylbenzene and the three xylene isomers; and
- **Semi-volatile organic compounds (SVOCs) analysis** – targets compounds in the range EC12 to EC40. Analysis for PAHs is a variant of SVOC analysis targeted at a specific group of PAHs. This is usually the US Environmental Protection Agency (USEPA) 16 PAHs (USEPA list of priority pollutants specified in the Clean Water Act of 1977, also referred to as 16 USEPA or 16-PAH).

Concentrations of physico-chemically similar but non-targeted compounds are either not reported or reported as tentatively identified compounds (TICs). Discuss any elevated concentrations of TICs with the laboratory in order to assess their significance and the level of confidence in their identification and concentration. Further analysis to provide quantitative information may be required where TICs have been identified.

**Table 3.1. Analytical methods for use in hydrocarbon hydrogeological risk assessment (detailed analysis)**

Name	Variants	Main advantages	Main disadvantages
VOCs/BTEX	BTEX only EPA method 8260 (BTEX, naphthalene, trimethylbenzenes)	<ul style="list-style-type: none"> <li>• Provides quantitative analysis of key determinands often quantified to low detection levels.</li> </ul>	<ul style="list-style-type: none"> <li>• Only identifies compounds on target list (unless TICs are specified).</li> </ul>
SVOCs (speciated)	PAHs only	<ul style="list-style-type: none"> <li>• Provides quantitative analysis of key determinands often quantified to low detection levels.</li> </ul>	<ul style="list-style-type: none"> <li>• Only identifies compounds on target list (unless TICs are specified).</li> </ul>
Carbon banding with aromatic/aliphatic fractionation	<ul style="list-style-type: none"> <li>• Different carbon band ranges can be specified.</li> <li>• Calibration may be against a particular hydrocarbon product.</li> </ul>	<ul style="list-style-type: none"> <li>• Provides values for carbon band ranges rather than individual compounds.</li> <li>• Provides detail of hydrocarbon composition based on the specific carbon range defined.</li> </ul>	<ul style="list-style-type: none"> <li>• Does not detect heavy hydrocarbons &gt;C40</li> </ul>

### 3.1.4 Accreditation

Analysis should only be commissioned from a competent laboratory, such as one holding appropriate quality assurance accreditation, e.g. United Kingdom Accreditation Service (UKAS) or the Environment Agency's Monitoring Certification Scheme (MCERTS).

The Environment Agency requires that any soil results submitted to them in support of a hydrogeological risk assessment for regulatory purposes should comply with the requirements of the MCERTS performance standard for laboratories undertaking chemical testing of soil.

## 3.2 Data quality assessment

Laboratories usually report analytical results as a concentration, typically in mass/mass or mass/volume units (for example, mg/kg or mg/l respectively). Reports should contain relevant quality assurance and quality control (QA/QC) information, including chain-of-custody information and identification of non-conforming samples. Results of gas chromatography (GC) with flame ionisation detection (FID) or mass spectroscopy (MS) analysis should include chromatograms.

In addition to standard checks, check laboratory results against the following key hydrocarbon-specific criteria:

- The results should make sense when compared with field descriptions (visual and olfactory observations);
- VOC concentrations should agree with reported odorous material and/or photo ionisation detector (PID) readings;
- The presence of hydrocarbons in water samples at concentrations in excess of the aqueous solubility can occur. This may indicate the presence of suspended solids or NAPL in the sample. (see Section 4.4);
  - Any samples showing concentrations in excess of aqueous solubility should be flagged and used with caution in risk assessment.
  - It is appropriate for dissolved organic carbon (DOC) to form part of the standard analytical suite when petroleum hydrocarbons are measured.
- Carbon banding (Table 2.1) results should be consistent with the anticipated hydrocarbon source, although some allowance for weathering should be made; and
- Analysis may not have identified and quantified all of the hydrocarbon mass present. This unresolved mass and the implications of this uncertainty should be flagged in any subsequent report.

The range of analyses selected should quantify all hydrocarbons present in a sample up to EC35 (a narrower range of analyses may be warranted if it is established that the contamination is composed of entirely lighter-end hydrocarbons). Examine chromatograms and compare them with those for both fresh and weathered products to provide information if possible on the degree of weathering as for example, loss of volatile components. Any unusual features should be identified and explanations sought. Consideration should be given to the circumstances of the project. Comparison of fresh and weathered products may be difficult to interpret on a site with an extensive history of industrial use and a multitude of source types mixed together.

The wide range of analytical methods available means that selecting an appropriate analysis may be a significant source of confusion: if uncertain, talk to a laboratory

analyst. Communicate your project requirements, such as the purpose of the analysis and the environmental criteria to which the results will be compared. It is also pertinent to make available to the laboratory all field observation logs, pictures, CSMs and other information that would assist in selecting the most appropriate analysis.

Table 5.1 provides a guide to CoPC to select for common hydrocarbon products. The analysis can be tailored for particular hydrocarbon products. Where unusual products are the source, discuss the most appropriate method with the laboratory. Screening analyses, such as SVOC, may be an efficient way to determine the content of an unknown mixture, but if you already know what is in the mixture, specific analysis of individual CoPC or other components may provide data with lower detection limits.

### **3.3 Analysis of free phase product**

The analysis of free product and very highly contaminated samples may be problematical for laboratories that specialise in environmental analysis as these may overload laboratory instruments or cause cross-contamination. Where possible, samples that are known (or suspected) to contain free product should be identified to the laboratory so that they can be dealt with appropriately.

# 4. Hydrocarbons as free phase contaminants

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## 4.1 Key considerations

Many petroleum hydrocarbon products are liquids that are immiscible with water. Spills or leaks of these products can result in liquid phase hydrocarbons entering the subsurface.

The presence of separate phase hydrocarbons can complicate sampling, particularly where NAPL is present in groundwater boreholes. Under these conditions, it is difficult to obtain a representative sample of groundwater as the process of sampling can result in mixing of NAPL and groundwater.

Where separate phases are present, analysis of each phase is required to support a quantitative hydrogeological risk assessment.

## 4.2 Non-Aqueous Phase Liquids

Where the source of contamination is a NAPL that is present on or below the water table as either mobile or residual LNAPL or as DNAPL, the Environment Agency considers that 'the contamination has already entered controlled waters' (see GP3, Environment Agency, 2013) and is therefore not a continuing input for the purposes of Part 2A of the Environmental Protection Act 1990 and/or Part 3 of the Waste and Contaminated Land (Northern Ireland) Order 1997 (pending). This is also the case for Natural Resources Wales. Therefore, the key regulatory objectives that apply in England, Wales and Northern Ireland in this situation are to:

- Minimise further input of pollutants to groundwater from the overlying unsaturated zone;
- Mitigate the impact on soil and groundwater if receptors are at risk, to manage those unacceptable risks; and
- Minimise expansion of any contaminant plume within groundwater to prevent further pollution of the aquifer and any dependent receptors.

Mobile NAPL may represent a direct risk to receptors via its movement through the unsaturated and saturated zones. NAPL also represents a potential secondary source giving rise to dissolution of constituent compounds into groundwater, and their subsequent transport in the dissolved phase to a receptor. Consequently, the management of this on-going secondary source of contamination needs careful consideration. Where NAPL is present, the risk assessment should consider:

- Whether the NAPL is expanding, steady or declining;
- Likelihood and causes of movement of mobile NAPL;
- Significance and likely longevity of dissolved-phase contamination arising from mobile and / or residual NAPL;
- Potential for VOC emissions from NAPL;
- Potential for depletion of the LNAPL source over time, leading to a declining source concentration (e.g. Thornton *et al.*, 2013);
- Technical feasibility of NAPL remediation, including;

- residual NAPL saturation in local geology;
  - theoretical NAPL removal efficiency;
  - theoretical mass removal achievable.
- Sustainability criteria – for example, the balance of environmental, social and economic impacts caused by attempts to remediate a NAPL source, versus the environmental, social and economic benefit of undertaking that remediation. SuRF-UK provides a framework for sustainability assessment (CL:AIRE, 2010; 2011; Bardos *et al.*, 2012; 2016)

### 4.3 Identification of free phase product

The presence of NAPL can be identified by:

- Observation in soil samples and open excavations;
- Measurements in monitoring boreholes (for example, using an interface probe). Where NAPL is present or suspected, boreholes should be constructed such that the screened section permits entry of the mobile NAPL into the borehole. Guidance on monitoring borehole design is provided in Environment Agency (2006<sup>c</sup>). The thickness of LNAPL in a monitoring well typically exceeds the thickness of the mobile LNAPL in the subsurface by a factor estimated to range between 2 and 10. Due to this difference, the LNAPL thickness measured in a monitoring well is commonly referred to as the "apparent thickness" and is not an accurate measurement of the LNAPL thickness in the subsurface Marinelli and Durnford (1996); and
- Measurements in field investigations, using techniques such as membrane interface probes (MIP) and laser induced fluorescence (LIF) on direct-push equipment.

The presence of NAPL may also be inferred from the detection of elevated concentrations of dissolved hydrocarbons in groundwater. Various 'rules-of-thumb' have been proposed, but a dissolved concentration measured in groundwater greater than 10% of the effective aqueous solubility of the compound is often considered a fair indicator that NAPL is present in the locality (Mercer and Cohen, 1990).

### 4.4 Groundwater sampling

When obtaining and analysing groundwater samples for hydrocarbon hydrogeological risk assessments, give specific consideration to the presence of:

- **Suspended solids** – which may contain sorbed low-solubility hydrocarbons. Solvent extraction of unfiltered samples will normally extract these components, which would then be recorded as components of the dissolved-phase.

Sampling records should therefore identify and describe the type and nature of any suspended solids present in water samples.

Although filtering would remove the influence of suspended solids, it should not be undertaken as most filter papers are made of organic material that can sorb organic substances.

Options to reduce or remove suspended solids within samples include:

- appropriate well design (Nielsen and Nielsen, 2007);

- further well development until the water runs clean (over-vigorous purging may however increase turbidity, cause loss of volatiles and increase aeration);
- minimal agitation during sampling (for example, through the use of low flow sampling equipment).
- **Small globules of free phase product** – which can sometimes go unobserved during sampling. Their presence is likely to result in the more soluble compounds reaching equilibrium between the free and aqueous phases prior to analysis, leading to the aqueous concentration measured being close to the effective solubility.

Take particular care in the field to identify and document the presence of free phase product in water samples and submit only those water samples that do not contain possible free phase for chemical analysis when reliable dissolved-phase concentration data are required.

In the laboratory, only analyse the aqueous phase. Samples containing free phase product may be retained or discarded depending on the circumstance. In some cases free phase analysis may assist with source apportionment. Where aqueous phase analysis is needed, the further samples should be submitted. In both cases the laboratory should contact the client to determine the course of action.

These phenomena illustrate the need for care to avoid results being reported that may lead to incorrect conclusions regarding the risks to groundwater.

## 4.5 Physical properties of free phase product

The measurement of physical properties such as density, viscosity and interfacial tension of free phase may be required to evaluate NAPL movement and remediation. For further guidance see Environment Agency (2003<sup>a</sup>) and CL:AIRE (2014).

## 4.6 Estimation of dissolved phase concentrations in the presence of free phase

The movement of hydrocarbons between phases needs to be understood. In the context of hydrogeological risk assessment, the critical relationships are between:

- Free phase product and water; and
- Water and soil or the aquifer matrix (sorption to organic carbon).

The relationship between product and water can be estimated using Raoult's Law (see Box 4.1).

Partitioning between water and organic carbon can be described by the following equation, which is valid only at low concentrations and if the isotherm is linear (see also CL:AIRE, 2014):

Soil-water partition coefficient,  $K_d = f_{OC} \times K_{OC}$

where:

$K_{OC}$  = organic carbon-to-water partition coefficient (l/kg);

$f_{OC}$  = fraction organic carbon.

Always compare the results of any calculations with analytical data to ensure that they are reasonable. For example, groundwater concentrations downgradient of the source should not exceed the measured/calculated concentration at the source.

Box 4.1 gives a relationship for estimating solubility based on molecular weights and Box 4.2 contains an example calculation to estimate aqueous concentrations in the presence of free product.

Molecular weights are unlikely to be derived from site-specific measurements and the use of literature values is generally required. Example molecular weights are given in Table 4.1. Where molecular weights are not available, consider using a plausible range of values.

**Table 4.1. Representative molecular weights of hydrocarbon sources**

Hydrocarbon product	Approximated molecular weight (g/mole)
Petrol (gasoline)	105
Kerosene	165
Diesel (gas oil)	230

Source: USEPA (2015)

**Box 4.1. Raoult's Law**

The aqueous solubility of the various substances within an ideal hydrocarbon mixture in contact with water depends on their proportion (mole fraction) within the mixture and their pure phase solubility. In an analogy to Raoult's Law, which describes partitioning between gas and liquid phases, the solubility of the hydrocarbon mixture can be estimated according to the relationship:

$$C_i = x_i C_i^0$$

where:

$C_i$  = effective solubility of compound  $i$  (in mixture) at equilibrium (mg/l);

$x_i$  = mole fraction of  $i$  in the mixture;

$C_i^0$  = aqueous solubility concentration of the pure compound (mg/l).

The mole fraction,  $x_i$ , is defined as:

$$x_i = MF_i \times \left( \frac{MW_o}{MW_i} \right)$$

where:

$MF_i$  = mass fraction of compound  $i$  in hydrocarbon mixture;

$MW_i$  = molecular weight of compound  $i$ ; (g/mole);

$MW_o$  = approximated molecular weight of the hydrocarbon mixture (g/mole).

Larger hydrocarbon molecules (naphthalene and above) within a mixture can have a higher effective solubility than predicted by Raoult's Law. This reflects the fact that some compounds in their pure state would be solids at normal environmental temperatures. When a more accurate estimate of their effective solubility is required, a liquid/solid fugacity factor should be included in the above equation (Brown *et al.*, 2006).

**Box 4.2. Example calculation to estimate source term aqueous concentrations in the presence of free product**

Petrol has formed a pool of LNAPL at the water table over an area of 10 × 10 m. The main risk drivers within the petrol in this example are BTEX. The concentration of the various BTEX compounds has been determined by targeted analysis, allowing their effective solubility to be calculated using Raoult's Law.

Taking benzene as an example, the mole fraction of benzene,  $x_{benzene}$ , is derived as follows:

$$\begin{aligned} \text{Mass fraction of benzene in NAPL, } MF_{benzene}, &= 1\% (0.01) \\ \text{Molecular weight of benzene, } MW_{benzene}, &= 78.11 \text{ g/mole} \\ \text{Pure phase aqueous solubility of benzene, } C^0_{benzene} &= 1,780 \text{ mg/l} \\ \text{Approximated molecular weight of petrol, } MW_{petrol}, &= 105 \text{ g/mole (Table 4.1)} \end{aligned}$$

$$x_{benzene} = MF_{benzene} \times (MW_{petrol}/MW_{benzene}) = 0.01 \times (105/78.11) = 0.013$$

Raoult's Law gives the effective solubility,  $C_{benzene}$ , of benzene as:

$$C_{benzene} = x_{benzene} \times C^0_{benzene} = 0.013 \times 1780 = 23.14 \text{ mg/l}$$

The results of this calculation and those for the other BTEX compounds are tabulated below. All the calculations are based on a molecular weight (MW) for petrol of 105 g/mole.

Substance	% weight (by analysis) (mass fraction)	Pure phase solubility, $C^0$ mg/l (literature value)	Molecular weight, MW g/mole	Mole fraction, $x$ (calculated)	Effective solubility, $C_i$ mg/l (calculated)
Benzene	1.0	1,780	78.11	0.013	23.14
Toluene	8.0	590	92.13	0.091	53.79
Ethylbenzene	2.0	152	106.20	0.020	3.01
Xylenes	7.5	200	106.20	0.074	14.83

The effect of dissolution of the most soluble components from a NAPL can be to leave the remaining NAPL relatively depleted in those components. Over time this preferential dissolution (or volatilisation) of the most soluble or volatile compounds results in a decreasing concentration within the NAPL, and reducing effective solubility of the compounds in groundwater. NAPL behaves as a transient source, giving rise to lower concentrations of the more soluble components over time (Thornton *et al.*, 2013). If source zone NAPL chemistry and mass is described adequately in the CSM, transient source behaviour may be used to more accurately simulate the behaviour of a NAPL source zone over time, and the consequent risks to groundwater. Thornton *et al.* (2013) illustrate the approach with a case study.

# 5. Identification of CoPC and water quality targets

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## 5.1 Hydrocarbon characterisation

As part of the risk assessment, characterisation of the hydrocarbon contamination is necessary to identify those compounds or groups of compounds that present the greatest risk to groundwater. These compounds are termed the constituents of potential concern (CoPC) and should include those compounds that are considered the likely risk-drivers for a given product release.

Where possible, the CoPC should be identified as individual substances from targeted detailed analysis (Section 2.3). Where the analysis does not identify individual substances or where the nature of the contamination requires, the CoPC will be identified within carbon bands (Sections 2.3 and 7.3).

The number of CoPC can be reduced by eliminating from consideration those compounds that have very low solubility in water and/or that are poorly mobile in the subsurface environment. These compounds should not normally present a risk to groundwater in the dissolved phase, a conclusion that can be supported through travel time calculations within the DQRA.

Among the hydrocarbon components, CoPC for hydrogeological risk assessment will normally include those compounds or fractions that are:

- Relatively soluble in water;
- Mobile (i.e. show a low soil-water partition coefficient,  $K_d$ ); and
- Present a relatively high hazard (e.g. have low drinking water standards or EQS).

In addition, they are likely to have the following properties:

- Persistent within the subsurface environment;
- Relatively abundant within the source mixture, i.e. they are present in a NAPL at levels that could lead to groundwater concentrations in excess of water quality targets; and
- Require an appropriate criterion for assessment such as a defined water quality criterion (drinking water standard or EQS) or may require site specific derivation if it lacks a standard but is considered a major component of concern.

Where possible, knowing the products that have been historically used on the site is also important as this will provide information on the risk drivers likely to be present, and can help early targeting of analysis to the relevant CoPC.

The more mobile components within a hydrocarbon mixture can be identified by reference to published data on organic carbon partition coefficients ( $K_{oc}$ ) or octanol-water partition coefficients ( $K_{ow}$ ) (e.g. in the TPHCWG series of reports). Table 5.1 summarises the relative mobility of the petroleum hydrocarbon fractions and their associated indicator CoPC.

**Table 5.1. Mobility ranking of petroleum hydrocarbon fractions**

Carbon band range	Recommended petroleum hydrocarbon CoPC indicators and their EC values	Partition coefficient, $K_{oc}$		Aqueous solubility		Overall relative mobility in groundwater
		Value (l/kg)	Potential sorption ranking	Value (mg/l)	Potential mobility ranking	
Aliphatics EC5–EC6	n-hexane (6)	$7.9 \times 10^2$	high	$3.6 \times 10^1$	moderate	high
Aliphatics >EC6–EC8	n-heptane (7)	$4.0 \times 10^3$	moderate	5.4	moderate	moderate
Aliphatics >EC8–EC10	n-octane (8) n-nonane (9)	$3.2 \times 10^4$	low	$4.3 \times 10^{-1}$	low	low
Aliphatics >EC10–EC12		$2.5 \times 10^5$	low	$3.4 \times 10^{-2}$	low	low
Aliphatics >EC12–EC16		$5.0 \times 10^6$	very low	$7.6 \times 10^{-4}$	very low	very low
Aliphatics >EC16–EC21		$6.3 \times 10^8$	very low	$3.0 \times 10^{-6}$	very low	very low
Aromatics EC5–EC7	benzene (6.5)	$7.9 \times 10^1$	high	$1.8 \times 10^3$	high	high
Aromatics >EC7–EC8	toluene (7.6)	$2.5 \times 10^2$	high	$5.9 \times 10^2$	high	high
Aromatics >EC8–EC10	xylenes (8.6-8.8) ethylbenzene (8.5) 1,2,4-trimethylbenzene (9.8)	$1.6 \times 10^3$	moderate	$6.5 \times 10^1$	high	high
Aromatics >EC10–EC12	naphthalene (11.7)	$2.5 \times 10^3$	moderate	$2.5 \times 10^1$	moderate	moderate
Aromatics >EC12–EC16	2-methylnaphthalene (12.8) acenaphthylene (15.1) acenaphthene (15.5)	$5.0 \times 10^3$	moderate	5.8	moderate	moderate
Aromatics >EC16–EC21	fluorene (16.6), anthracene (19.4), phenanthrene (19.4), pyrene (20.8)	$1.6 \times 10^4$	low	$6.5 \times 10^{-1}$	low	low
Aromatics >EC21–EC35	benzo[a]pyrene (31.3) benzo[b]fluoranthene (30.1) benzo[k]fluoranthene (30.1) benzo[ghi]perylene indeno[1,2,3 cd]pyrene (35.0)	$1.3 \times 10^5$	very low	$6.6 \times 10^{-3}$	very low	very low

To aid the qualitative risk assessment process and help prioritise the carbon band ranges that need to be investigated, Table 5.1 gives a relative ranking of likely hazard to groundwater and groundwater-dependent receptors. The ranking is based on the combined rankings of solubility and the organic carbon to water partition coefficient ( $K_{OC}$ ); the higher the overall ranking, the higher the potential for this substance to be mobile in groundwater and to pose a potential risk to groundwater and groundwater-dependent receptors.

Some hydrocarbon mixtures will consist almost entirely of low mobility compounds (compounds with low aqueous solubility and high  $K_d$ ). In these situations, a quantitative risk assessment may not be necessary as a qualitative risk assessment using solubility and mobility data and estimated travel times may indicate that there is a negligible risk to the identified receptors.

A useful check is to compare the concentrations of compounds determined from analysis of groundwater samples with calculations made using Raoult's Law and against experience from elsewhere. Where there is agreement between the groundwater concentrations and theoretical calculations, confidence in the results will be high. Where there are significant differences, these should be noted and explanations sought. For example: Are the calculations correct? Is free product present in the sample?

Table 5.2 shows the most likely risk drivers for a range of common hydrocarbon products. However, it is essential to assess each site on the basis of detailed site-specific analyses of hydrocarbon compounds.

**Table 5.2. Recommended CoPC for hydrogeological risk assessment of common petroleum hydrocarbon products**

Suspected hydrocarbon source	Carbon banding	Recommended petroleum hydrocarbon CoPC	Other substances of potential concern
Petrol (gasoline) <sup>1</sup>	C4–12	BTEX naphthalene n-hexane	Ether oxygenates (MTBE, TAME, ETBE, DIPE) <sup>3</sup> Lead scavengers <sup>4</sup>
Kerosene (jet fuel) <sup>1</sup>	C6–16	BTEX TPHCWG <sup>5</sup>	2-methylnaphthalene <sup>1</sup>
Light lubricating oils	C6–10	TPHCWG <sup>5</sup>	
Diesel/ domestic heating oil <sup>1,2</sup>	C8–21	BTEX TPHCWG <sup>5</sup>	2-methylnaphthalene <sup>1</sup>
Heavy fuel oils	C12+	TPHCWG <sup>5</sup>	
Lubricating oils and greases	C18->34	TPHCWG <sup>5</sup>	

<sup>1</sup> CoPC derived for groundwater receptor and pathway by Bowers and Smith (2014)

<sup>2</sup> Diesel with biofuel component contains fatty acid methyl esters (FAME) which are not considered to be a significant groundwater risk and are not included in the CoPC list (CONCAWE, 2016).

<sup>3</sup> Ether oxygenates (MTBE, ETBE, TAME, DIPE) are common additives in unleaded petrol and need to be considered in hydrogeological risk assessments. Degradation intermediates from these include tert-butyl alcohol (TBA), tert-amyl alcohol (TEA).

<sup>4</sup> 1,2-dichloroethane and 1,2-dibromoethane. **Relevant only for leaded petrol releases.**

<sup>5</sup> TPHCWG – fractionated TPH considered most efficient method to assess risks for complex petroleum hydrocarbon mixtures.

Table 5.2 includes PAHs as CoPC for a small number of products. PAHs are not present in significant concentrations in the light distillates (petrol, kerosene) since the temperature at which those products are distilled is lower than the boiling point of PAH compounds. Bowers and Smith (2014) found that PAH in middle distillates (such as diesel) were only a potential risk to human health where there was potential for exposure via direct contact (i.e. soil to skin); transport dissolved within groundwater is

unlikely to be significant in most instances. Other NAPLs, such as creosote, contain significantly higher PAH concentrations and will likely warrant more detailed consideration.

## 5.2 Water quality assessment criteria

A major step in undertaking a risk assessment is setting an appropriate water quality target concentration at the compliance point. The overall approach to setting such criteria and the location of compliance points is set out in Environment Agency (2006<sup>b</sup>) and GP3 (Environment Agency, 2013).

A list of potentially applicable water quality standards is given in Environment Agency (2006<sup>b</sup>). Table 5.3 and 5.4 summarises currently available water quality standards for petroleum hydrocarbons.

**Table 5.3. Water quality targets for selected petroleum hydrocarbons and related compounds (µg/l)**

Substance	UK Drinking water standard <sup>a</sup>	EU Environmental Quality Standard (EQS) <sup>c,d,e,f</sup>		Other sources
		Freshwater	Saltwater	
Petroleum products (dissolved or emulsified hydrocarbons)	-	petroleum products must not: <ul style="list-style-type: none"> <li>form a visible film on the surface of the water or form coatings on the beds of watercourses and lakes;</li> <li>impart a detectable 'hydrocarbon' taste to fish;</li> <li>produce harmful effects in fish.</li> </ul>		-
Benzene	1.0	1.0x10 <sup>1</sup>	8.0	1.0 <sup>(i)</sup>
Toluene	-	7.4x10 <sup>1 e</sup>	7.4x10 <sup>1 e</sup>	
Ethylbenzene				3x10 <sup>2 (ii)</sup>
Xylenes	-	3.0x10 <sup>1 e</sup>	3.0x10 <sup>1</sup>	5x10 <sup>2 (ii)</sup>
Naphthalene	-	2.0 <sup>e</sup>	2.0 <sup>e</sup>	
Benzo[a]pyrene	1x10 <sup>-2</sup>	1.7x10 <sup>-4 g</sup>	1.7x10 <sup>-4 g</sup>	1x10 <sup>-2 (i)</sup>
Benzo[b]fluoranthene	1x10 <sup>-1 b</sup>			1x10 <sup>-1 (i)</sup>
Benzo[k]fluoranthene				
Benzo[g,h,i]perylene				
Indeno[1,2,3-cd]pyrene				
TPHCWG fractions	-	-	-	See Table 5.4
1,2-dichloroethane	3.0	1x10 <sup>1</sup>	1x10 <sup>1</sup>	
Methyl tert-butyl ether (MTBE)	-	-	-	1.5x10 <sup>1 (iii)</sup> 2.0x10 <sup>1 (iv)</sup>

<sup>a</sup> Statutory Instruments 2016 No. 614. In addition, drinking water is required to be wholesome and therefore any substances that taint water supply (odour or taste) will effectively be set a drinking water standard equivalent to the taste/odour objection threshold. This can be very low, particularly for aromatic compounds.

<sup>b</sup> Sum of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene and indeno[123-cd]pyrene

<sup>c</sup> DIRECTIVE 2008/105/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council

<sup>d</sup> <http://evidence.environment-agency.gov.uk/ChemicalStandards/ChemicalsByName.aspx>

<sup>(i)</sup> Private Water Supplies Regulations Statutory Instruments 2009 No. 3101

<sup>(ii)</sup> World Health Organisation (WHO) guide values

<sup>(iii)</sup> WHO Taste and Odour threshold

<sup>(iv)</sup> Lower end of USEPA guidance of taste and odour threshold at 20 – 40 µg/L. Health and ecotoxicity based criteria for ether oxygenates, including MTBE, are much higher than the T&O thresholds

<sup>e</sup> The Water Framework Directive (Standards and Classification) Directions (England and Wales) 2015. The EQS for these substances are based on a "long term mean" or an "annual average (AA)" EQS. Note that the xylene EQS is an Environment Agency "operational" target and is not listed in the 2015 Directions: <https://www.gov.uk/guidance/surface-water-pollution-risk-assessment-for-your-environmental-permit> (applicable to England, Northern Ireland and Wales).

<sup>f</sup> The Water Framework Directive (Classification, Priority Substances and Shellfish Waters) Regulations (Northern Ireland) 2015

<sup>g</sup> Benzo(a)pyrene can be considered as a marker for the other PAHs, hence only benzo(a)pyrene needs to be monitored: Freshwaters priority hazardous substances, priority substances and other pollutants - <https://www.gov.uk/guidance/surface-water-pollution-risk-assessment-for-your-environmental-permit>

**Table 5.4. World Health Organization (WHO) guide values for TPHCWG fractions in drinking water**

TPH fraction	Aliphatic fraction (µg/l)	Aromatic fraction (µg/l)
EC5-EC6	1.5x10 <sup>4</sup>	1.0x10 <sup>1</sup> (benzene)
EC>6-EC8	1.5x10 <sup>4</sup>	7.0x10 <sup>2</sup> (toluene)
EC>8-EC10	3.0x10 <sup>2</sup>	3.0x10 <sup>2</sup> (ethylbenzene) 5.0x10 <sup>2</sup> (xylenes)
EC>10-EC12	3.0x10 <sup>2</sup>	9.0x10 <sup>1</sup>
EC>12-EC16	3.0x10 <sup>2</sup>	9.0x10 <sup>1</sup>
EC>16-EC21	-	9.0x10 <sup>1</sup>
EC>21-EC35	-	9.0x10 <sup>1</sup>

Source: WHO, 2008

Soil Guideline Values (SGVs), Category 4 Screening Levels (C4SLs) and Suitable 4 Use Levels (S4ULs) should not be used when undertaking a hydrogeological risk assessment as they were developed to assess risks to human health and may not be protective of groundwater or surface water.

## 6. Biodegradation

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An important consideration when assessing the risks from hydrocarbon compounds to groundwater is whether biodegradation occurs and, if so, the rate at which it occurs. Information on degradation rates should help to assess whether natural attenuation processes provide sufficient protection to the receptors without the need for further intervention.

There are numerous studies (reviewed in USGS, 2006) that demonstrate that degradation of petroleum hydrocarbons occurs under most subsurface conditions at a rate that means that dissolved phase plumes reach a steady-state (i.e. the plume stops expanding) within a relatively short distance from the source. This is typically found to be within about 100 m for a release of a few thousand litres (or less) from a retail petrol filling station. However, the rate of degradation depends on a number of factors such as electron acceptor (respiratory substrate) supply, temperature, redox potential, groundwater flow velocity, and contaminant concentration. Assumptions regarding degradation should therefore be supported by site-specific evidence.

Some substances that can be associated with petroleum hydrocarbon plumes (notably MTBE and ethyl tert-butyl ether (ETBE)) frequently do not degrade as rapidly as the crude oil-derived compounds (for example, BTEX) and the risks from such compounds require separate assessment.

Approaches that support the development of evidence that degradation occurs include:

- **Examining lines-of-evidence** as described in the Environment Agency's guidance on monitored natural attenuation (MNA) (Environment Agency, 2000). The lines of evidence are:
  - **Primary:** documented loss of contaminant mass or decrease in concentration in the field;
  - **Secondary:** geochemical and biochemical indicators which demonstrate the natural attenuation process that results in the reduction in contaminant concentration;
  - **Tertiary:** microbiological data to support the occurrence of biodegradation. This is rarely needed given that hydrocarbon biodegradation is well understood and widely accepted.
- **Evaluating the geochemical environment.** The rate of degradation will depend on the geochemical environment. In general, petroleum hydrocarbons degrade more rapidly in aerobic rather than anaerobic environments. An assessment of the redox state of the groundwater environment should therefore be undertaken. Dissolved oxygen concentrations of <1 mg/l are indicative of anaerobic conditions.
- **Undertaking an electron balance** to demonstrate whether there are sufficient oxidants (oxygen, nitrate, sulphate, iron and manganese) to degrade the mass of hydrocarbon in the aquifer. This should be used as guidance only as methanogenic conditions, brought about by a lack of other oxidants, will also stimulate biodegradation.
- **Using appropriate analytical or numerical models** to represent degradation and to calculate the extent of the plume.

It is not necessary to undertake all these to provide sufficient evidence that biodegradation is occurring. A combination of the evidence appropriate to the site setting, complexity and level of risk will suffice.

Published degradation rates (or half-lives) for carbon band ranges are not widely available. One approach is therefore to use conservative degradation rates for indicator substances within a carbon band range (Section 7.3). For example, for the aromatic carbon band range >EC10-EC12, naphthalene (EC 11.7) may be an appropriate indicator compound; the half-life of naphthalene quoted in the literature ranges from 100 to 1,000 days (Environment Agency, 2002). Where literature values are used, it is essential that:

- The degradation rate chosen for the substance is appropriate for the environmental conditions found for the site of interest; and
- There is supporting evidence that degradation occurs at the site.

The remedial targets worksheet options that allow the user to select (Environment Agency, 2006<sup>d</sup>):

- “*Apply degradation rates to dissolved substances only*”. This is applicable where degradation rate is obtained from laboratory studies of the substance in the water; and
- “*Apply degradation rates to substances in all phases*”. This is applicable where the degradation rate is observed from field observations, e.g. long-term groundwater monitoring or laboratory experiments have been undertaken using groundwater and the aquifer matrix. With regard to petroleum hydrocarbons, there are large studies published that collate field biodegradation rates and present statistical summaries of field data. For example, Suarez and Rifai (1999).

Monitoring data should also be examined to determine whether hydrocarbons migrate from the source and if plumes are continuing to expand. Software such as GWSDAT ([www.claire.co.uk/gwsdat](http://www.claire.co.uk/gwsdat)) may be useful in visualising plume stability and attenuation.

If plumes are stable (that is they are not expanding) or shrinking, then management of the plume by monitored natural attenuation is likely to be appropriate (Environment Agency, 2000) provided receptors are not currently impacted.

# 7. Concluding remarks

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This section summarises the advice on assessing the risks to groundwater and groundwater-dependent receptors from petroleum hydrocarbons contained in this guidance and gives suggestions on how to put the guidance into practice.

Where hydrocarbons are present in soil or groundwater beneath a site, a risk assessment will be required to determine whether the hydrocarbons pose an unacceptable risk to controlled waters. The risk assessment should be undertaken in accordance with the Remedial Targets Methodology (Environment Agency, 2006<sup>a</sup>) and take into account the guidance set out in this document. The understanding of the site should be set out in a CSM that identifies the type of hydrocarbon(s) present based on a review of site history, current use and site investigation results. The CSM should also describe the forms of hydrocarbon present, i.e. whether it is present as NAPL, contaminated soil or dissolved in groundwater and the condition of the hydrocarbon source (degree of weathering). In addition, it should describe the location of the source spatially and vertically, the source dimensions and the expected pathways operating. As with any risk assessment, the areas of uncertainty should be documented together with the potential implications of the uncertainty.

Undertaking a risk assessment for hydrocarbons poses particular challenges that may require specific detailed consideration, including:

- They are complex mixtures defined by the analytical methods employed and where component interactions can affect transport and attenuation;
- They are present in different phases, including NAPL;
- Source terms will change with time;
- The selection of CoPC for the assessment of hydrocarbon mixtures; and
- The importance of establishing those site factors that are important in determining the level of risk posed (e.g. biodegradation, groundwater flow velocity, etc).

## 7.1 Analytical requirements

Site-specific data must include detailed analysis of hydrocarbons in soils and groundwater. The detailed analysis, which must be tailored to the hydrocarbon mixture present at the site and level of risk posed by its components, should include one or more of TPHCWG, VOC, SVOC, PAH and 'individual' CoPC analyses.

## 7.2 Presence of NAPL

Where NAPL is present, it represents a source of contamination and will require consideration in the risk assessment. The concentration in soil, perched water or groundwater at the source in contact with the NAPL, which determines the risk, can be derived by direct analysis of hydrocarbon concentration in groundwater, soil or perched water adjacent to the source; or by theoretical calculation of the NAPL-water equilibrium concentration using Raoult's Law or fugacity methods.

NAPL may also present a direct risk by migration. Although the assessment of mobility risks from NAPL is beyond the scope of this guidance, it is covered in other guidance (Environment Agency, 2003<sup>a</sup>; CL:AIRE, 2014) and should be included within the risk assessment where necessary.

### 7.3 Selection of CoPC

The risk assessment should evaluate risks for CoPC present at the site. Hydrocarbon mixtures generally comprise a large range of individual compounds and it is impossible to quantify all compounds through analysis and to undertake risk assessment for each. Rather, the assessment should focus on those individual compounds, or groups of compounds, that pose the greatest risk to controlled waters; these are the CoPC. In general, the CoPC are those compounds that are relatively mobile and have a water quality assessment criterion (a drinking water or environmental quality standard); examples include benzene and naphthalene. However, individual compounds will not always be present at concentrations that distinguish them as risk drivers, the original source of hydrocarbons may be unknown and/or several sources may be present. Where this is the case, the approach advocated here is to identify the hydrocarbons in specific carbon band ranges as the risk drivers. Table 7.1 summarises the approach to deriving remedial target concentrations in a range of situations.

**Table 7.1. Summary of criteria for selection of the approach to hydrogeological risk assessment for hydrocarbons**

Phase/matrix	Hydrocarbon characterisation/condition	Approach to deriving remedial target concentrations
NAPL / Soil / Groundwater	High proportion of individual compounds identified by detailed analysis (BTEX, naphthalene and other PAHs) for which there are water quality assessment targets (WQTs)	Assess risks for <b>individual compounds</b> only.
	Low proportion of individual compounds for which there are WQTs.	Assess risks for <b>indicator compounds</b> for the carbon band ranges that present the highest risk (based on a ranking of their risk and on their relative abundance).
	No / very low proportion of individual compounds	Assess risk for <b>carbon band ranges</b> that present the highest risk (from ranking of their risk and on their relative abundance).

### 7.4 Biodegradation

The risk assessment must consider the evidence for biodegradation. Biodegradation is an important process that can act to reduce concentrations and associated risk. Ignoring biodegradation will result in a conservative assessment that may overstate risk. However, biodegradation should only be incorporated where there is reasonable evidence that it is occurring. It is important that evidence for biodegradation, using a lines-of-evidence approach (Environment Agency, 2000) is collected during site investigation.

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# Glossary

Term	Definition
Aliphatic hydrocarbons	Straight and branched chain hydrocarbons, including alkanes and alkenes
API	American Petroleum Institute
Aqueous solubility	The amount of material that will dissolve in water at standard temperature and pressure
Aromatic hydrocarbons	Hydrocarbons containing one or more benzene rings, including BTEX and PAHs
BSI	British Standards Institute
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
Carbon number	Number of carbon atoms in a hydrocarbon molecule
Carbon bands	A range of carbon numbers used to group organic compounds within hydrocarbon mixtures
CoPC	Constituents of Potential Concern
ConSim	A risk assessment programme for assessing risks to groundwater developed for the Environment Agency by Golder Associates
Controlled waters	Waters defined in Section 104 of the Water Resources Act 1991
DIPE	Di-isopropyl ether – an additive to some unleaded petrol (very rarely present in the UK market)
DNAPL	Dense Non-Aqueous Phase Liquid – denser than water
DOC	Dissolved Organic Carbon
DQRA	Detailed Quantitative Risk Assessment
DRO	Diesel Range Organics
EC number	The equivalent carbon (EC) number concept allows compounds with similar boiling points to be grouped into specific carbon bands. For <i>n</i> -alkanes, the carbon number and the EC number are the same. Benzene has an EC number of about 6.5.
ETBE	Ethyl-Tert-Butyl-Ether – an additive to unleaded petrol to improve exhaust emissions quality
EQS	Environmental Quality Standard
FAME	Fatty Acid Methyl Ester – a biofuel component used in biodiesel
$f_{oc}$	Fraction organic carbon
GC-FID	Gas chromatography–flame ionisation detector
GC-MS	Gas chromatography–mass spectrometry
GRO	Gasoline Range Organics (sometimes referred to as PRO or Petrol Range Organics)
$K_d$	Soil/water partition coefficient
$K_{oc}$	Organic carbon-to-water partition coefficient
LNAPL	Light Non-Aqueous Phase Liquid – less dense than water
MCERTS	Monitoring certification scheme for the chemical testing of soils
Mineral oil	Aliphatic hydrocarbons in the range C <sub>15</sub> to C <sub>50</sub>
MNA	Monitored Natural Attenuation
Mole fraction	The number of molecules of a substance compared to the total number of molecules in the system

<b>Term</b>	<b>Definition</b>
MTBE	Methyl-Tert-Butyl-Ether – an additive used in some unleaded petrol
NAPL	Non-Aqueous Phase Liquid
PAHs	Polycyclic Aromatic Hydrocarbons – hydrocarbons containing more than one benzene ring
PID	Photo ionisation Detector
PRO	Petrol Range Organics (equivalent to gasoline range organics, GRO)
QA	Quality Assurance
QC	Quality Control
QRA	Quantitative risk assessment
Speciate/speciated	In the context of petroleum hydrocarbons, a species is a compound or group of compounds (e.g. within a carbon band) that have similar properties. Speciation is analysis to determine the concentration of that species.
SGV	Soil Guideline Value
SuRF-UK	Sustainable Remediation Forum UK
SVOC	Semi-Volatile Organic Compound
TAME	Tertiary-Amyl Methyl Ether – oxygenate used in some unleaded petrol
TIC	Tentatively Identified Compounds
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
UKAS	United Kingdom Accreditation Service
USEPA	United States Environmental Protection Agency
16 USEPA	A set of 16 PAHs (also referred to as 16-PAH) identified by the USEPA as priority pollutants. They are: <ul style="list-style-type: none"> <li>• acenaphthene</li> <li>• acenaphthylene</li> <li>• anthracene</li> <li>• benz[<i>a</i>]anthracene*</li> <li>• benzo[<i>a</i>]pyrene*</li> <li>• benzo[<i>b</i>]fluoranthene*</li> <li>• benzo[<i>g,h,i</i>]perylene</li> <li>• benzo[<i>k</i>]fluoranthene*</li> <li>• chrysene*</li> <li>• dibenz[<i>a,h</i>]anthracene*</li> <li>• fluoranthene</li> <li>• fluorene</li> <li>• indeno[1,2,3-<i>cd</i>]pyrene*</li> <li>• naphthalene</li> <li>• phenanthrene</li> <li>• pyrene</li> </ul> Those marked with an asterisk are probable human carcinogens and make up a sub-set known as 7-PAH.
VOC	Volatile Organic Compound