Heavy hydrocarbon fate and transport in the environment

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Abstract: Heavy hydrocarbons are a heterogeneous mixture of compounds consisting mainly of alkylated cyclics, resins and asphaltenes and, depending on the source, can form a significant proportion of crude oil. Their prevalence is expected to increase in the future as heavy oil reserves are increasingly exploited for growing worldwide energy demands. Despite their growing use, heavy hydrocarbons are generally overlooked when assessing the risk of hydrocarbons to human health, ecology and water reserves. Although their human and environmental health risks are considered low, heavy hydrocarbons are known to persist in the environment. This review considers the fate, transport and toxicity of heavy hydrocarbons. It provides a description of the possible mechanisms involved in heavy hydrocarbon attenuation and offers some interpretation of data that provides insight into their persistence in the environment.

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Petroleum hydrocarbon compounds can enter groundwater owing to spills or leaks associated with exploration, production and distribution of oil and gas. Releases can also enter the subsurface as a result of natural oil and gas seeps. These releases may result in contaminated sites that pose an unacceptable risk to human health, ecology and/or water resources, and have prompted research on the environmental fate and transport and consequent risk of a range of petroleum hydrocarbons found in crude oil or refined products. These include relatively soluble and volatile compounds, such as benzene, toluene, ethyl-benzene and xylene (BTEX) and more recalcitrant compounds such as polyaromatic hydrocarbons (PAHs). An alternative approach is to assess risks for a number of defined hydrocarbon fractions (e.g. C8–C10, C10–C15 up to C44) using representative toxicity and physico-chemical parameters for each fraction (CONCAWE 1996; TPHCGW 1997; Verbruggen 2004). Whereas there is a reasonable understanding of the fate and toxicity of these selected components up to carbon length of C44, the behaviour of heavier hydrocarbons has received far less attention.

In general, heavy (i.e. high molecular weight) hydrocarbons are considered less mobile and less (eco)toxic, which implies that associated health and environmental risks are also lower compared with lighter hydrocarbons. The persistence of heavier hydrocarbons, however, is also much greater compared with lighter fractions. This raises the question of how to deal with cases of heavy hydrocarbon soil and groundwater contamination, knowing that the risks to human health, ecology and water resources are small, yet on the other hand biodegradation and natural attenuation processes are such that the contamination may persist for a significant length of time (years). This is especially relevant to spills of fresh heavy crude oils and weathered light crude oils. It is also an issue for the redevelopment of legacy brownfield sites (with ubiquitous residual heavy hydrocarbon contamination) where problem-owners and regulators are faced with decisions on how best to manage these low-toxicity, yet persistent, impacts.

To address these issues and contribute towards developing an appropriate risk management strategy, this paper presents a literature review of the fate of heavy petroleum hydrocarbons. The review describes the following: (1) heavy hydrocarbons and their occurrence in crude oil; (2) the physical and chemical properties of heavy petroleum hydrocarbons; (3) major attenuation mechanisms and reasons for persistence in the environment; (4) their fate, transport and associated risks to man and the environment.

Defining heavy hydrocarbons

Crude oil is a complex mixture of hydrocarbon- and non-hydrocarbon-containing constituents. Hydrocarbons, molecules containing only hydrogen and carbon, consist of a large array of linear, branched, cyclic and aromatic components, whereas non-hydrocarbon fractions, termed resins (carbazoles, thiophenes and oxygenated hydrocarbons) and asphaltenes, contain additional elements, such as nitrogen, sulphur and oxygen. Hydrocarbons exist at a range of molecular weights, from very light (C8, 16 g mol\(^{-1}\)) to very heavy (C4200 g mol\(^{-1}\)). Asphaltenes are generally considered to be one the largest components in crude oil with molecular weight up to 1000 g mol\(^{-1}\) (Mullens 2007, 2008).

Crude oil is refined in part by distillation to separate products by boiling point. Much of the lighter, more valuable hydrocarbon is used as a feedstock for gasoline and jet fuel, whereas the heavier boiling point hydrocarbons may be used for diesel, heavy-duty fuels and lubricating oils. For the purposes of this review heavy hydrocarbons are defined as the fraction that cannot be distilled under atmospheric and vacuum distillation (McMillen et al. 2001). This is equivalent to starting boiling temperature of c. 550°C at atmospheric pressure. Very little heavy hydrocarbon finds its way into fuel and lubricant products and most will end up as bitumen, petroleum pitch or asphalt at the end of the petroleum manufacturing and refining processes. As boiling points are dependent on molecular structure, chemical composition and molecular weight, hydrocarbons with a range of carbon numbers will constitute the starting point that defines the heavy hydrocarbon fraction. The
proportion of heavy hydrocarbon in crude oils can vary considerably. A survey of 41 crudes by McMillen et al. (2001) found that heavy hydrocarbons ranged between 0.6 and 57% and had a mean value of 23%. This broadly agrees with work by Coleman et al. (1978), who showed heavy hydrocarbon to be 0–70% in an assessment of over 800 US crudes.

Characterization of heavy hydrocarbons in environmental samples

The principal problem in characterizing hydrocarbon contamination in soils and waters is that crude oil consists of a complex mixture of components, rather than a single chemical. The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) grouped hydrocarbons, up to C₃₅, into a number of fractions based on carbon number ranges and structure (aliphatic or aromatic). This was justified by differences in solubility and other fate and transport characteristics (TPHCWG 1997). This approach, using gas chromatography with flame ionization detection (GC–FID), was extended by the American Petroleum Institute in 2001 (Douglas et al. 2001) to include hydrocarbons up to equivalent carbon (EC) number 44. No standard analytical method exists for the detection and measurement of heavy hydrocarbons beyond EC44. Douglas et al. (2001) proposed the use of vacuum distillation to quantify hydrocarbons beyond the operating limit of GC. Although this method is reliable and provides an accurate measurement of heavy hydrocarbon content, it can only be undertaken using specialist equipment. Other ways to estimate the total mass of heavy hydrocarbon concentration in environmental samples include gravimetric hydrocarbon measurement after solvent extraction (e.g. ASTM 2016a) or by simulated distillation by GC (e.g. ASTM 2016b). It should be noted that gravimetric approaches will generate a total hydrocarbon measurement, and estimation of the heavy fraction can be achieved only by determining the proportion of the lighter hydrocarbon (≤ C₄₄) fraction using GC or similar methods. Whichever approach is used, the choice of solvent for extraction of hydrocarbons from the environmental matrix requires further investigation, as they are known to affect the miscibility of asphaltenes (Miadonye & Evans 2010) and potentially have an impact on the effectiveness of the extraction step.

Although these techniques provide insight into the fraction of heavy hydrocarbons, they do not provide information on the compositional makeup of the heavy hydrocarbons. The most commonly used analytical technique to characterize complex hydrocarbon mixture analysis, combined gas chromatography–mass spectrometry (GC–MS) (Hsu & Drinkwater 2001), often lacks sufficient chromatographic resolution and mass resolving power to characterize the heavy hydrocarbon fraction. Other methods are better suited for this analysis, such as fractionation coupled with field ionization mass spectrometry (FIMS) (Boduszynski 1985; Malhotra et al. 1993), thin layer chromatography with flame ionization detection (TLC-FID) (Ugochukwu et al. 2013), or Fourier transform ion cyclotron resonance (FT-ICR) (Marshall & Rodgers 2008; Hegazi et al. 2012).

FIMS uses nominal mass resolution to its advantage by providing one mass (m/z) value for all of the isomers present for a particular compound. Analysis by this method shows heavy hydrocarbons to be a mixture of alkylated cyclic, aromatic and naphthenoaromatic hydrocarbons that have up to seven ring structures, but typically three to four (Fig. 1). They are extensively alkylated, with chain lengths of between C₁₅ and C₄₀ (Simminghe Damté et al. 1991; Lu et al. 2011), and constitute 25–40% of the heavy hydrocarbon fraction. Very high molecular weight (>500 g mol⁻¹) resins and asphaltenes will form a substantial component of this fraction. Based on studies by Tissot & Welte (1984) and Boduszynski (1985) resins and asphaltenes constitute between 40 and 80% of the heavy hydrocarbon fraction. Smaller fractions of n- and iso-alkanes will also be present (up to 5%). Carbon chain lengths can reach beyond C₅₀ but a range between C₂₀ and C₆₀ is more typical (Tissot & Welte 1984). TLC-FID is a semi-quantitative method used to determine the relative percentage distribution of the saturates, aromatics, resins and asphaltenes (SARA) fractions in oil. Although this technique does not have high reproducibility, it can be used to rapidly assess gross changes in heavy hydrocarbon composition (Ugochukwu et al. 2013). The relatively recent development of Fourier transform ion cyclotron resonance (FT-ICR) coupled with electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) mass spectrometry has further opened up the field of hydrocarbon characterization. These techniques provide the highest resolving power, mass accuracy and dynamic range amongst all types of mass spectrometers and have revolutionized our understanding of the composition and characterization of crude oils, refined petroleum products and their degradation metabolites (Marshall & Rodgers 2008; Hegazi et al. 2012; Lemkau et al. 2014). One area in which FT-ICR MS may prove to be an extremely useful technique is the analysis of hydrocarbon biodegradation intermediates. Recent work by Islam et al. (2016) applied the technique to characterize dissolved organic carbon (DOC) downgradient from a crude spill site. This work was able to clearly identify products of hydrocarbon biodegradation and differentiate them from natural (background) DOC. Others have also used FT-ICR to follow the biodegradation processes of oil released into marine environments (Chen et al. 2016) to show the identification and fate of oxygenated compounds in marine sediments.

Fate and behaviour of heavy hydrocarbons

The fate of crude oil in the environment is an important aspect of risk assessment because it determines the exposure of a human or ecological receptor to the mixture (McMillen et al. 2000). To achieve this, information on hydrocarbon behaviour and distribution, concentration and potential exposure is essential (Coulon et al. 2010). A conceptual diagram of heavy hydrocarbon fate and transport is presented in Figure 2 to highlight the major processes involved in the fate of heavy hydrocarbons when released into the environment. It is assumed that heavy hydrocarbons are present together with lighter hydrocarbon fractions that are found in most crude oils. The conceptual diagram is split into three stages that describe transport and transformation processes: (1) initial surface release of crude oil and infiltration into the unsaturated zone; (2) partitioning of a non-aqueous-phase liquid (NAPL) body near the water table; (3) attenuation of oil resulting in progressive increase in proportion of heavy hydrocarbons and mass subsequent removal of heavy hydrocarbons by biodegradation. These stages can be used to infer at what point heavy hydrocarbons impart the greatest potential exposure to human health and the environment.

Initial surface release and infiltration into the unsaturated zone

If crude oil is released in sufficient quantities, there is the potential to infiltrate into the subsurface and form an NAPL body at the water table. The rate and extent of infiltration will depend on the soil properties (porosity, pore size, moisture levels) as well as the physical properties (viscosity, density, surface tension) and the volume of the oil spilled. Generally, the greater the soil permeability and the lower the product viscosity, the greater the rate and extent of soil penetration (API 1972; Brost & DeVaul 2000; Keller & Simmons 2005). Spilled oil will penetrate the soil to a point where the NAPL head is insufficient to overcome pore entry pressures, and further migration ceases. As such, the volume of NAPL migrating decreases as immobile residual NAPL is left behind owing to retentive capillary forces in the soil column. The result is a partially
saturated mass zone in the soil that is subsequently subjected to the various attenuation and transport processes typical of hydrocarbon contaminants (McCarty & Ellis 2002; Bear & Cheng 2010). A number of studies have shown that downward migration towards the water table is not an issue when hydrocarbons are present at low concentrations in the soil. Raymond et al. (1976) assessed migration in a range of soils (silty loam, sandy loam and black clay loam) with several oils dosed at 2% (w/w). In that study 99% of the oil mixed in a range of soils (silty loam, sandy loam and black clay loam) with variances was in part attributed to differences in soil types, with much lower values observed in coarse soils.

Partitioning of NAPL

If residual soil saturation points are overcome, then NAPL will descend through the soil column until it reaches the water table. Dissolution of hydrocarbons from the NAPL into the groundwater may then generate contaminant plumes that are transported to sensitive receptors. Mass transfer of hydrocarbons from NAPL into the aqueous phase is determined by Raoult’s law. Level I fugacity models, developed by Pollard et al. (2008), illustrate the basic equilibrium partitioning behaviour in air, water, NAPL and soil systems. Calculations with heavy hydrocarbons show an extreme preference for partitioning into NAPL and soils (Table 1) compared with water and air. This analysis indicates that mass transfer of heavy hydrocarbons into groundwater will be extremely limited. Subsequent transport of dissolved hydrocarbons relative to groundwater can be estimated using retardation factors (Nham et al. 2015). Based on the physical and chemical properties proposed by McMillen et al. (2001), the estimated retardation factor for heavy hydrocarbons is very high (Table 1), suggesting that potential transport after dissolution in groundwater will be tremendously limited. As a consequence, heavy hydrocarbons are unlikely to be transported any meaningful distance via groundwater flow. Karstic geological environments may be an exception to this position, where suspended solids and/or NAPL may potentially be transported over significant distances. Although long-distance transportation is possible, recent research (Schwarz et al. 2011) suggests the likelihood of karstic transport of heavy hydrocarbons causing an unacceptable impact on groundwater is low. Based on these considerations, heavy hydrocarbons are unlikely to be of interest in hydrogeological risk assessments. Conversely, consideration of heavy hydrocarbons is substantially more important during the risk management of soils or free-floating NAPLs to control points of exposure.

Attenuation mechanisms of heavy hydrocarbons

Based on level II fugacity modelling proposed by Coulon et al. (2010), the ultimate fate of heavy hydrocarbons will be dependent on the effectiveness of biodegradation (data not shown), although other attenuation mechanisms such as photo-oxidation may contribute to mass removal mechanisms. Further details of these processes are described in the next section.

Photo-oxidation

Photo-oxidation has the potential to transform the composition of oil spills at the soil surface. The process requires oil spills to be exposed to sunlight and involves the absorption of photons by molecules within the crude oil mixture, which then initiates oxidation reactions by two main mechanisms: singlet oxygen and radial chain oxidation (Shankar et al. 2015). The result is an increase of oxygenated hydrocarbons that may be more susceptible to biodegradation (Maki et al. 2001; Lee 2003). It has been suggested that photo-oxidation could be an effective attenuation mechanism for heavy hydrocarbons. Garrett et al. (1998) proposed that photo-oxidation preferentially transformed and oxygenated high molecular weight aromatic hydrocarbons. In agreement with this, Prince et al. (2003) and co-workers used PAHs to demonstrate increasing levels of photo-oxidation with increasing aromaticity and alkylation. This pattern of photo-oxidative loss is very different than that seen during biodegradation (as described in the next section). Less in known about the photo-oxidative propensity of asphaltenes or resins, which can form a significant component of heavy hydrocarbons. Current knowledge suggests that these species are not subject to significant photo-oxidative destruction (Prince et al. 2003).

Most of the understanding relating to photo-oxidation has been generated using marine-based studies. Less is known about the significance of photo-oxidation of hydrocarbons in soils. As the process requires direct sunlight it will be effective only at the soil surface. Braddock et al. (2003) attributed poor removal rates of crude oil in soil horizons (>8 cm from the surface) to a lack of photo-oxidation caused by limited sunlight penetration over a
Processes working on fresh spill (time scale days to weeks):
- Evaporation of volatile light HCs (especially for high API crudes)
- Spreading, depending on viscosity and topographical gradient
- Infiltration, depending on viscosity and soil texture

Processes working on freshly infiltrated oil:
(time scale weeks to months):
- Infiltration and formation of NAPL layer on water table
- Sorption of oil to soil matrix
- Volatilization of light HCs from NAPL
- Dissolution of soluble HCs and formation of a dissolved phase plume
- Biodegradation of dissolved phase and vapors
- Enrichment of NAPL in heavy HCs

Processes working on heavily weathered oil:
(time scale years to decades):
- Surface oil hardens / aggregates
- Very limited volatilization
- Biodegradation induces methanogenic conditions in groundwater
- Incomplete biodegradation may result in accumulation of polar metabolites
- Further enrichment of NAPL in heavy HCs

Fig. 2. A conceptual model of heavy hydrocarbon fate and transport in the environment. Heavy hydrocarbons are typically released together with lighter hydrocarbon fractions that are found in most crude oils. This modifies the physical and chemical properties that significantly affect the transport on soils and in the subsurface. Releases of viscous refined bitumen or extremely heavy crude oils (API° < 12) are unlikely to travel any significant distance in the soil or subsurface.

25 year period at a Alaskan test site. Whether this limitation can be overcome through simple soil turning (tilling) has not yet been determined; however, the potential benefits of photo-oxidation warrant further investigation of this mechanism as a form of attenuation.

Biodegradation
Biodegradation is a major attenuation process for hydrocarbons released into the environment. The underlying mechanisms that ultimately drive the mineralization of hydrocarbons have been
The subject of numerous studies (Atlas 1981; Leahy & Colwell 1990; Cerniglia 1992; Boonchan 2001; Seo 2000; Widdel & Rabus 2001; Meslé 2002). Much of this knowledge has been established through the study of lighter hydrocarbon components, whereas knowledge of heavy hydrocarbons biodegradation is still in its infancy. This disparity is highlighted in the number of identified enzymes known to be involved in heavy hydrocarbon biodegradation. To date only one enzyme, a novel monooxygenase from Acinetobacter sp. DSM 17874 (Throne-Holst et al. 2007), has been identified in the biodegradation of hydrocarbons, which contrasts completely with lighter hydrocarbons for which multiple enzymes in multiple pathways are known. Heavy hydrocarbon biodegradation has mainly been demonstrated through laboratory-scale microcosm studies. For example, long-chain n-alkanes have been shown to completely degrade under aerobic conditions (Sakai et al. 1994; Wang et al. 2002). Similarly, asphaltene and resins are degradable to varying degrees under aerobic and anaerobic conditions (Kim et al. 2005; Strapoč et al. 2008; Uribe-Alvarez et al. 2011; Singh et al. 2012; Tahatabae et al. 2012; Furrmann et al. 2013; Meslé et al. 2013). Thus from a biochemical viewpoint, heavy hydrocarbons are expected to be susceptible to biodegradation. This is supported by Gibbs free energy calculations, which show that potential energy available through biodegradation is only marginally affected by hydrocarbon size under most redox conditions (Fig. 3).

### Observations of biodegradation in the field

Efforts to understand heavy hydrocarbon biodegradation through laboratory-based studies, performed under ideal conditions, do not accurately reflect observations and experiences in the field. Many studies have shown the rate and extent of hydrocarbon biodegradation to be limited under field conditions. Hydrocarbons present in surface soils and subject to predominantly aerobic conditions are known to degrade extensively (Kincannon 1972; Francke & Clark 1974; Raymond et al. 1976) but complete removal is often unachievable. In these circumstances removal of lighter hydrocarbons is predominant, leaving behind a residue of heavy hydrocarbons. Huesemann (1995) found that about 30% heavy saturates and at least 75% of heavy aromatics remained from a range of crude oils and petroleum products after 1 year of landfarming. In a longer study, Loehr et al. (1992) demonstrated that a recalcitrant fraction (20 – 24%) of an oily sludge remained after 2 years of land treatment. Others have shown similar trends. Salanitro et al. (1997) tested the limits and extent of hydrocarbon biodegradation soils containing crude oils with heavy, medium and light API gravity (14, 30 and 55 respectively). In agreement with other studies, a recalcitrant fraction was observed after 11 months of treatment. Heavy oil contamination, containing the greatest proportion of heavy hydrocarbons, was biodegraded the least, with only 6 – 44% removed during the experiment. The large range in removal rates was attributed to differences in non-hydrocarbon organic carbon.

### Table 1. The physical properties for heavy hydrocarbons compared with lighter saturated and aromatic hydrocarbons as described by TPHCWG (1997) and McMillen et al. (2001)*

|                        | Water solubility (mg l⁻¹) | Vapour pressure (atm) | Log Koc (cm³ g⁻¹) | H (cm³ cm⁻³) | Retardation factor, Rf | Fugacity level I partitioning (%) |
|------------------------|---------------------------|-----------------------|-------------------|--------------|------------------------|----------------------------------|
| EC > 12-16 aliphatic   | 7.6 × 10⁻⁸                | 4.8 × 10⁻⁵            | 6.7               | 520          | 1.3 × 10⁶              | 1.8 × 10⁻⁷ Air                    |
|                        |                           |                       |                   |              |                        | 1.9 × 10⁻⁵ Water                 |
|                        |                           |                       |                   |              |                        | 70.0 Soil                         |
| EC > 12-16 aromatic    | 5.8                       | 4.8 × 10⁻⁵            | 3.7               | 5.3 × 10⁻²   | 1.3 × 10³              | 4.7 × 10⁻⁴ Air                    |
|                        |                           |                       |                   |              |                        | 4.9 × 10⁻² Water                  |
|                        |                           |                       |                   |              |                        | 24.2 NAPL                       |
| EC > 16-35 aliphatic   | 2.5 × 10⁻⁶                | 9.8 × 10⁻⁷            | 8.8               | 4.9 × 10³   | 1.6 × 10¹⁰             | 5.4 × 10⁻⁴ Air                    |
|                        |                           |                       |                   |              |                        | 6.1 × 10⁻⁸ Water                  |
|                        |                           |                       |                   |              |                        | 88.0 NAPL                       |
| EC > 16-21 aromatic    | 0.65                      | 1.1 × 10⁻⁶            | 4.2               | 1.3 × 10⁻²   | 4.0 × 1⁶               | 3.4 × 10⁻⁴ Air                    |
|                        |                           |                       |                   |              |                        | 1.5 × 10⁻⁵ Water                  |
|                        |                           |                       |                   |              |                        | 28.6 Soil                         |
| EC > 21-35 aromatic    | 6.6 × 10⁻³                | 4.4 × 10⁻¹⁰           | 5.1               | 6.7 × 1⁴    | 3.2 × 1⁰⁶             | 1.9 × 10⁻⁶ Air                    |
|                        |                           |                       |                   |              |                        | 1.6 × 1⁰⁻⁵ Water                  |
|                        |                           |                       |                   |              |                        | 38.9 NAPL                       |
|                        |                           |                       |                   |              |                        | 61.1 Soil                         |
| EC > 44 heavy hydrocarbon | 1.0 × 1⁴⁻⁴             | 4.1 × 10⁻¹²           | 8.7               | 4.1 × 1⁰⁻⁸ | 1.3 × 1⁰⁻¹⁶           | 1.2 × 1⁰⁻¹⁴ Air                   |
|                        |                           |                       |                   |              |                        | 1.7 × 1⁰⁻⁷ Water                  |
|                        |                           |                       |                   |              |                        | 74.4 NAPL                       |
|                        |                           |                       |                   |              |                        | 25.6 Soil                         |
| Benzo[a]pyrene         | 3.8 × 1⁰⁻³               | 2.1 × 10⁻¹⁰           | 5.9               | 5.7 × 1⁰⁻⁴ | 2.0 × 1⁰⁻⁷            | 1.4 × 1⁰⁻⁷ Air                    |
|                        |                           |                       |                   |              |                        | 1.4 × 1⁰⁻⁴ Water                  |
|                        |                           |                       |                   |              |                        | 4.6 NAPL                         |
|                        |                           |                       |                   |              |                        | 95.4 Soil                         |

*The equivalent carbon (EC) number of a hydrocarbon is related to its boiling point (b.p.) normalized to the boiling point of an n-alkane series, or its retention time on a non-polar b.p. gas chromatographic (GC) column (TPHCWG 1997).

1Aquifer properties: effective porosity 0.25, fSOC 0.025 to 0.0025 and bulk density 2500 kg m⁻³. Rf = 1 + ((Koc × bulk density)/porosity). Koc is the soil organic carbon – water partitioning coefficient. H is Henry’s Law Constant.

2Fugacity model level I generated as described by Pollard et al. (2008) with fSOC 0.025 and air/water/NAPL/soil ratio of 0.23:0.13:0.003:0.64 based on McKone (1996). Data for benzo[a]pyrene are shown for comparison only.
content of the soils tested, with soils containing the greatest amount of organic carbon demonstrating the least amount of oil biodegradation. McMillen et al. (2001) took the correlation between crude oil API gravity and extent of biodegradation a step further. Their work demonstrated an inverse correlation between API gravity and extent of biodegradation, showing that heavy hydrocarbons are a major determinant of the final extent of oil removal from soils.

The potential for heavy hydrocarbon biodegradation in the subsurface, where anaerobic conditions are prevalent, is much more limited than in surficial soils (Grishchenkov et al. 2000). A number of well-studied sites have demonstrated limited removal of hydrocarbons many years after the original spill. A study by Reddy et al. (2002) of subsurface soils revealed very little evidence of biodegradation from a No. 2 fuel oil spilled 30 years previously in West Falmouth (MA), USA. Their work showed that much of the oil remained within the first 20 cm of the soil surface and that only partial degradation of the alkane fraction had occurred. A similar lack of biodegradation was observation by Wang et al. (1998) on a 25-year-old crude spill in Alberta, Canada. Again, oil found just beneath the soil surface, at 10–40 cm, was relatively fresh and showed little sign of biodegradation. The biodegradation of hydrocarbons in NAPL, where water, electron acceptors and nutrients are limiting, supports the idea of slow hydrocarbon removal rates in sub-optimal environments. Lundegard & Johnson (2006) found that hydrocarbons were removed at a rate of 0.1–1.0 kg m⁻² a⁻¹ at a 3000 acre oilfield site in California, USA. This is equivalent to an average zero-order attenuation rate constant of 1.5 × 10⁻³ a⁻¹ and a half-life of over 400 years. Others have shown similar findings. McCoy et al. (2015) used CO₂ traps to estimate NAPL biodegradation at a disused refinery. Based on their measurements, average rates of biodegradation were found to be 6.3 × 10⁻³ a⁻¹ and the calculated half-life was 108 years. These observations highlight the long-term persistence of oil in the subsurface. As heavy hydrocarbons are likely to be the most refractory to biodegradation, their persistence in the subsurface environment will be greater.

Factors causing heavy hydrocarbon persistence

Structure

The relative susceptibility of different classes of heavy hydrocarbon is not fully understood. Because thousands, or possibly millions, of chemical compounds constitute the compositional fraction of heavy hydrocarbons (CONCAWE 2012), the extent of biodegradation is not easily predicted and broad statements regarding biodegradation are more appropriate in describing the susceptibility of these hydrocarbons to biodegradation. Based on information from lighter fractions they are expected to degrade in the following order (Leathy & Colwell 1990): n-alkanes > (branched) iso-alkanes > naphthenic and polyaromatic hydrocarbons > heteroatom-containing species. Asphaltenes, resins and highly condensed alkylated polyaromatics (with more than three rings) are more resistant to biodegradation than other components owing to their condensed and fused aromatic ring structures.

One aspect that may influence recalcitrance is physical size. It has been proposed that heavy hydrocarbons are too large to be biodegraded by intracellular mechanisms considered typical for microorganisms (Lehmann & Kleber 2015). Overcoming this obstacle, however, may be achieved through the production of extracellular enzymes that ‘break down’ or convert large hydrocarbons into more metabolically manageable products. For example, white-rot fungi produce ligninolytic enzymes, such as peroxidases and laccases, that have activity towards hydrocarbons (Hammel 1995; Cerniglia & Sutherland 2010). Extracellular esterase and lipase are other classes of enzyme considered candidates for hydrocarbon biodegradation. Recent studies suggest that they can hydrolyse both C–C and C–O bonds at much higher levels than previously thought (Alcaide et al. 2013). Work using Phanerochaete chrysosporium by Wang et al. (2009) showed that the same extracellular oxidases responsible for PAH biodegradation were also excreted during the biodegradation of soil organic matter. This is significant because it suggests that the same enzymatic mechanism can be used to degrade heavy hydrocarbons. Further support for this mechanism can be found in studies on coal biodegradation that have shown coals such as lignite can be liquefied through the action of extracellular enzymes produced by microbes (Fakoussa & Hofrichter 1999). Fungi are generally aerobic organisms and require some oxygen to function (McGinnis & Tyeing 1996). Therefore, their contribution to overall degradation rates under strongly anaerobic conditions may be questioned. Studies have shown, however, that several species (Aspergillus sp., Trichocladium canadense and Fusarium oxysporum) are able to degrade PAHs under low-oxygen conditions (<1% O₂) (Silva et al. 2013).
et al. (2009), suggesting that fungal catalysed degradation of hydrocarbons in oxygen-poor environments may be understated. Bacteria are also sources of extracellular enzymes that may be active against heavy hydrocarbons. For example, recent work by Zeng et al. (2016) demonstrated the oxidation of PAHs by a laccase derived from Bacillus subtilis, and Shekohiyani et al. (2016) showed that Pseudomonas spp. and Bacillus spp. produced peroxidases that are active against hydrocarbons in a setup to treat waste.

**Bioavailability**

Microbial degradation of hydrocarbons requires physical contact between the microorganism and the hydrocarbon. Therefore bioavailability, or the amount of hydrocarbon that is accessible to the microorganism, is a key factor in the overall effectiveness of the biodegradation of hydrocarbons. Matrices, such as NAPL and soil organic and mineral matter, that interfere with the contact between hydrocarbon and microorganism represents a major obstacle for biodegradation (Brassington et al. 2007). Owing to their lower water solubility and vapour pressure and higher hydrophobicity, heavy hydrocarbons show a greater tendency to remain in NAPL or partition into soil compared with lighter fractions. As such, bioavailability is relatively more important as a determinant of biodegradation of heavy hydrocarbon than that of lighter fractions. Partitioning of heavy hydrocarbons between NAPL and soil is determined by the concentration of oil present, the organic carbon content of the soil and the hydrophobicity ($K_{oc}$) of the hydrocarbon, and can be estimated using level I fugacity modelling (Table 1). In most circumstances, biodegradation will occur at the interface of both NAPL and soil matrices. In cases where hydrocarbon mass is decreasing (biodegradation) or soil organic content is high, partitioning into soils becomes more predominant (supplementary material). This conceptualization is important when considering the processes that influence bioavailability and biodegradation described in the subsequent sections of this review.

Many hydrophobic soil contaminants show biphasic biodegradation behaviour, whereby, in the initial phase, the rate of removal is high and is primarily limited by microbial degradation kinetics. In the second phase, the rate of removal is low and is generally restricted by mass transfer limitations (Barnier et al. 2014). In an experiment using several PAHs in contaminated sediments, Kan et al. (1994) demonstrated extremely slow desorption of contaminants compared with the initial sorption process. In this work only 30–50% of the adsorbed pollutant could be desorbed. It is generally accepted that sequestration of hydrocarbons is caused by diffusion into the soil particles and entry into soil micro- and nanopores (Reid et al. 2000). Subsequent desorption from the soil matrix then becomes a rate-limiting step for biodegradation (Semple et al. 2003; Trinidad et al. 2005; Dungait et al. 2012). The main sorbent for hydrophobic molecules is the organic matter of soils, and this fraction is assumed to be where hydrophobic molecules become entrapped (Alexander 2000), although partitioning into the mineral soil matrix is also possible (Reid et al. 2000). The age of the contamination is also known to affect bioavailability, with sources of hydrocarbon becoming less bioavailable in soils with time (Barnier et al. 2014; Wu et al. 2014).

The interactions between bioavailability and biodegradation in oil-contaminated soils have been well studied. Efforts by Oleszczuk (2007, 2009) demonstrated that changes in soil organic matter (SOM) composition can result in significant changes in the bioavailability of adsorbed hydrocarbons. It was proposed that a weakening of the sorption between organic matter and hydrocarbon, through mineralization, results in increased bioavailability. This finding was further developed by others. Wu et al. (2013b,c) added various composts to contaminated soils to increase organic carbon matter. They found that after an initial period of high sorption to the SOM, bioavailability and biodegradation of PAHs increased significantly. These increases were partly attributed to the presence of humic acids that were probably generated during the composting process. Humic acids are considered important because they act as a carrier to provide mass transport (Wu et al. 2013b) and increase hydrocarbon bioavailability (Smith et al. 2011). Modelling using molecular dynamic (MD) simulation has contributed further to understanding. Wu et al. (2015) assessed the intricate interactions between heavy hydrocarbons and soil at the molecular scale. They demonstrated that although soil organic matter (humic acid) increased the overall hydrocarbon adsorption capacity of the soil, it also increased mobilization and bioavailability by driving oil from the NAPL and mineral soil phases. It is this mechanism, termed competitive sorption, that probably describes observations that increased organic matter enhances the biodegradation of heavy hydrocarbons in soils (Liu et al. 2017). For example, Tang et al. (2012) found that the addition of humic acid, dosed at 0.02 g kg$^{-1}$, resulted in an increase of aromatic and polar (asphaltene and resin) biodegradation after 210 days of incubation and Gao et al. (2015) demonstrated that the presence of low molecular weight organic acids increased the bioavailability of PAHs in soils. Interestingly, low molecular weight organic acids, derived from plants, are also known to increase removal of hydrocarbon in soils (Martin et al. 2014), suggesting that phytoremediation may facilitate the remediation of heavy hydrocarbons.

Several studies have shown a correlation between extent of hydrocarbon biodegradation and laboratory-based methods to measure bioavailability in soils (Rhodes et al. 2008; Dandie et al. 2010; Adetutu et al. 2013). Most make use of the cyclodextrin extraction to determine bioavailability of hydrocarbons, although other methods, involving mild organic solvents or solid-phase adsorbents such as XAD resin or Tenax are available. Further work with high molecular weight PAHs has suggested a direct correlation between the rapidly desorbing fractions and the extent to which removal by biodegradation or chemical treatment is feasible (Richardson & Aitken 2011; Lemaire et al. 2013; Barnier et al. 2014). This correlation, however, remains to be validated, as do other forms of the technique, for heavy hydrocarbons. For example, Dandie et al. (2010) showed that a number of bioavailability techniques overestimated the biodegradative propensity of a C$_{17–40}$ hydrocarbon fraction by up to a factor of three, and Wu et al. (2013b) highlighted the potential inefficiencies of cyclodextrin as a method for predicting the bioavailability of PAHs with a high molecular size or polar substituents. Although this predictive tool shows promising signs, more research is required to validate its use for heavy hydrocarbons under a range of conditions. Indeed, Umeh et al. (2017) suggested that the most appropriate bioavailability approach is still to be determined. One possible explanation for these observations can be found in work by Huesemann et al. (2004), who demonstrated that in some cases hydrocarbons that were bioavailable in soils did not undergo complete biodegradation. It was suggested that this phenomenon was due to microbial factors such as lack of cometabolic substrates or insufficient numbers of hydrocarbon-degrading populations.

**Nutrients and water availability**

Availability of inorganic nutrients, particularly nitrogen and phosphorus, is often an important control on hydrocarbon degradation in soils and in the subsurface. These nutrients are generally needed to support microbial biomass production that occurs concurrently with the biodegradation of hydrocarbons. The requirement for nutrients has been shown in both surface soils and the subsurface. Coulon et al. (2012) and Brown et al. (2017) both demonstrated that the addition of inorganic nutrients stimulated biodegradation rates of hydrocarbons in aerobic landfarmed soils.
Similarly, Essaid et al. (2011) identified nutrient limitation to be one of the main factors controlling biodegradation in subsurface contamination at Bemidji, USA, and Leevis et al. (2013) showed a similar impact in the colder climate of Alaska, USA. Many hydrocarbon-contaminated soils become hydrophobic, which reduces water retention in soils (Adams et al. 2008). As water is necessary for microbial activity, a lack of it will have a negative impact on the biodegradation of hydrocarbons. The higher propensity of heavy hydrocarbons to bind to soils suggests that they are major determinants of the process that drives soils to become more hydrophobic.

**Toxicological impact of heavy hydrocarbons**

Humans can be exposed to hydrocarbons by inhalation, by oral uptake and via dermal contact. From a mobility perspective, heavy hydrocarbon will not move significantly from the area of release via groundwater. In addition, these materials are not volatile so exposure by inhalation would not be expected. Therefore, exposure to heavy hydrocarbons would be limited to direct contact by oral or dermal routes. Basic physical and chemical properties suggest that heavy hydrocarbons are not bioavailable and therefore are unlikely to exert toxic effects. As a consequence, there is a lack of toxicological studies with heavy hydrocarbons. It is generally accepted that hydrocarbons with carbon numbers ≥C35 are not bioavailable because they cannot be absorbed via biological membranes (CONCAWE 1993; EFSA Panel on Contaminants in the Food Chain (CONTAM) 2012). As such, both oral and dermal exposure is not likely to be an issue with heavy hydrocarbons. A survey of dermal uptake coefficients for petroleum hydrocarbons was performed recently to assess the toxicity of petroleum hydrocarbons (Jakasa et al. 2015). This work demonstrated that models used to predict uptake of hydrocarbons tended to over-predict uptake of smaller molecules but were good at predicting the penetration of heavier products. When these models were applied to heavy hydrocarbons, they predicted no dermal penetration whatsoever. This suggests that acute or chronic toxicity of heavy hydrocarbons constitutes (C15–50) (API 2009). These observations are consistent with modelled toxicity predictions for heavy hydrocarbons using the PETROTOX Target Lipid Model (Redman et al. 2012), which shows that hydrocarbon constituents with octanol–water partition coefficient (Kow) values of >6.0 are predicted to be non-toxic to aquatic organisms. Recent work extending the PETROTOX to soil and sediment organisms using equilibrium partitioning (EqP) theory also demonstrated that for hydrocarbons with log Kow values >6.0 an increasing incidence of no observed toxicity consistent with the dataset for aquatic organisms was observed (Redman et al. 2014).

Recently, there has been interest in metabolic intermediate products of hydrocarbon biodegradation (Bekins et al. 2016). These components, typically more polar and soluble than their parent hydrocarbon, are likely to have higher mobility in soil and groundwater (Boll et al. 2015). The human and ecological risk of these metabolic intermediates is unclear at this point. Bekins et al. (2016) suggested that metabolites in groundwater can pose a risk to aquatic and mammalian species, whereas others such as Zemo et al. (2016) indicated they had low toxicity to humans and were not expected to pose significant risk to human health. Studies in groundwater lag behind the work in marine environments, which have been stimulated by the Deepwater Horizon oil spill in 2010. Reddy et al. (2012) was the first to show that polar compounds accounted for a significant fraction of the oil released into the Gulf of Mexico. These compounds, generated through biodegradation and photo-oxidation, have been suggested to be more persistent and toxic than their parent compound (Aeppli et al. 2012; Chen et al. 2016).

Naphthenic acids, have been identified as one potential source of these metabolites with several studies indicating that di, tri and tetra-cyclics become increasingly predominant during biodegradation (Angolini et al. 2015; Kim et al. 2005). Whether the biodegradation of heavy hydrocarbons in terrestrial environments would yield more or less toxic compounds is not known, but would depend on their resulting structure and properties that govern hydrophobicity (i.e. log Kow). Heavy hydrocarbons contain numerous compound classes with a wide range of carbon number distributions. Therefore, addition of oxygen during biodegradation alters each compound’s hydrophobicity and toxicity in a potentially different way. The vast majority of heavy hydrocarbon constituents have log Kow values considerably greater than 6.0, which is the approximate cut-off for toxicity of hydrocarbons to aquatic, sediment and terrestrial dwelling organisms (Redman et al. 2012, 2014) Thus, significant changes in overall polarity, through increased heteroatom (N, S, O) content or a reduction in molecular mass, are necessary before heavy hydrocarbon metabolic intermediates can be expected to influence toxicity.

**Ecotoxicological impact of heavy hydrocarbons**

The ecotoxicity of petroleum hydrocarbons in soil has been studied using a range of species, including bacteria, earthworms and plants (Table 2). Factors that are known to have an impact on toxicity effects include the type and quantity of oil, the length of weathering (extent of biodegradation) of the oil and the type of soil (Chaineau et al. 1997, 2003; Dorn et al. 1998). Most studies have been undertaken using whole product mixtures or crude oils in which the proportion of heavy hydrocarbon varies. These studies have shown that products containing higher amounts of heavy hydrocarbon are much less toxic than those containing lighter fractions (Table 2). For example, Dorn et al. (1998) demonstrated that the no observed effect concentration (NOEC) in seed germination tests was up to 19.5% (195 000 mg kg⁻¹) for heavy crude oil (API 17). This contrasted significantly with light crude oil (API 55), which showed an NOEC of 2.4% in the same test. Chaineau et al. (1997) compared LD₅₀ (median lethal dose) values for light and heavy fuel oil fractions using Zea mays germination tests. The work clearly showed the heavy fuel product to be less toxic than the corresponding light fraction. Direct toxicity of hydrocarbons to organisms is strongly dependent on bioavailability (Peterson 1994). It is manifested in the organism once a critical body burden is attained, thus the organism–water partitioning (with octanol–water partitioning used as a surrogate) of the constituents is an important aspect of the process (van Wezel et al. 1995). Single hydrocarbons have different organism–water partition coefficient values that vary with molecular weight, class and molecular structure. Previous work has suggested that the bioavailability and toxicity of compounds such as heavy hydrocarbons that have extremely high log Kow values are limited (Verbruggen 2004; Redman et al. 2012). Understanding of hydrocarbon ecotoxicity has been developed mainly through studies on aquatic systems. For example, aromatic extracts of vacuum distillates, predominantly composed of alkylnated polyaromatic hydrocarbons (C₉₀–₅₀) show no acute or chronic toxicity in tests on aquatic organisms (API 2009). Similar observations were reported for lubricating oil base stocks, which are predominantly composed of saturated aliphatic hydrocarbon constituents (C₁₅–₅₀) (API 2009). These observations are consistent with modelled toxicity predictions for heavy hydrocarbons using the PETROTOX Target Lipid Model (Redman et al. 2012), which shows that hydrocarbon constituents with octanol–water partition coefficient (Kow) values of >6.0 are predicted to be non-toxic to aquatic organisms. Recent work extending the PETROTOX to soil and sediment organisms using equilibrium partitioning (EqP) theory also demonstrated that for hydrocarbons with log Kow values >6.0 an increasing incidence of no observed toxicity consistent with the dataset for aquatic organisms was observed (Redman et al. 2014).

**Issues related to heavy hydrocarbon contamination**

Surface releases of crude oil can negatively affect local flora and fauna and cause severe loss of vegetation of the area affected by the spill. The natural rehabilitation of contaminated soils may take time to accomplish and it may take months or years for plant growth to
Table 2. Selected ecotoxicity characteristics of hydrocarbons in soils

| Product                        | Composition                  | End-point                  | Comment                     | Reference |
|-------------------------------|------------------------------|----------------------------|-----------------------------|-----------|
| Crude oil, Villeperdue         | Fresh oil: 48% saturates; 26% aromatics; 26% resins and asphaltenes | Inhibition of seed germination | Oil dosed to 1.5% (w/w) in soil; 5 plant species tested | (Chaîneau et al. 2003) |
|                              | Remediated oil (480 days): 6% saturates; 15% aromatics; 79% resins and asphaltenes | Seed germination LC50 | >10% (w/w) oil in soil; 5 plant species tested | (Chaîneau et al. 1998) |
| Fuel oil, light fraction       | Unknown (fresh)              | Seed germination LC50 | 0.73% (w/w) oil in soil; 5 plant species tested | (Adams et al. 2016) |
| Light crude oil                | Fresh oil API 55: 87% saturates; 6% aromatics; 1% resins and asphaltenes | Seed germination NOEC | <2.4% (w/w) oil in soil; 5 plant species tested | (Adams et al. 2016) |

Management of sites contaminated by heavy hydrocarbons

Risk assessment is an established requirement for effective management of contaminated land, and is now a widely used support tool for environmental management decisions. Heavy hydrocarbons are unlikely to be major risk drivers during contaminated land management but need to be considered because they will generally be a component of the larger mixture of hydrocarbons. Fugacity modelling (Pollard et al. 2008; Coulon et al. 2010) demonstrates that there are limited exposure pathways with heavy hydrocarbons (Table 1). Based on these assumptions the most relevant exposure scenario is via contact with hydrocarbon-affected soils. Remedial actions for soil clean-up may be triggered by soil hydrocarbon concentrations greater than calculated or arbitrary screening values or through non-risk-based measures such as stakeholder concerns over soil aesthetics or impacts to soil texture.

A shift to sustainable remediation practices recently (Bardos et al. 2011) has pushed soil treatment options towards active biological treatments such as landfarming or biopiling. These approaches use return. The process can be further delayed by the residual, non-toxic effects of oil that remains in the soil. For example, water repellency reduces the rate of wetting and retention of water in soils which in turn will create a less than ideal environment plant growth (Roy et al. 2003). Water repellency reduces the rate of wetting and retention of water in soils, which in turn will create a less than ideal environment for plant growth (Roy et al. 2003). This process has been observed in soils of all textures as well as organic-rich soils, but there seems to be a greater probability of it developing in sandy soils (Doert et al. 2000). Oil contamination is one of many ways in which soil can become hydrophobic and repel water. Water repellency may also develop after episodes of fire, through the breakdown of plant matter or the action of microbes (Doert et al. 2000). Its prevalence in agricultural soils has prompted the development of strategies to overcome this phenomenon using wetting agents (Hallett 2008). Despite success in agriculture, this approach is not likely to be useful for oil-contaminated soils, where the risk of remobilizing subsurface oil would be a source of concern.

Alternative approaches to treat water repellency in hydrocarbon-contaminated soils have been explored with some success recently. Adams et al. (2016) found that washing with alkali (0.1M NaOH) significantly reduced water repellency in soils. In other work, Cann (2000) showed that addition of clay had a similar impact in reducing water repellency. Because of the simplicity of these methods they lend themselves to implementation under field conditions and it is worth monitoring their progress in the future.

The formation of ‘tar crusts’ on the surface of soils is another physical impact that can hinder the rehabilitation of an area (Fig. 4). These crusts are formed by either extensive weathering (Volk 1980) or burning of oil through artisanal refining. In some cases, tar crusts can exist for decades (UNEP 2011). They form a physical barrier that can smother the soil, reduce the ingress of oxygen and limit the initial rooting of plants (Coulon et al. 2012), thus making re-vegetation very difficult. For example, Murygina et al. (2016) described the occurrence of a large asphalt crust in Siberia, Russia. It could withstand a weight up to 60 kg without being destroyed and had zero plant growth 20 years after the spill. There are other similar examples across most oil-producing regions in the world. Eliminating the physical barrier caused by these crusts, by homogenization or removal, is likely to be the simplest means of stimulating natural rehabilitation of the affected area. It should be noted, however, that these crusts are usually associated with lighter hydrocarbons, which have a different risk profile and may require additional consideration during treatment.
biodegradation as the principal form of contaminant destruction and thus require conditions that are favourable to microbial growth. One major limitation of this remediation option is that it is less effective with soils containing high levels of contamination (>50 000 mg hydrocarbon kg\(^{-1}\) soil) (Kuppusamy et al. 2017). In these circumstances innovative alternatives have been proposed. For example, Wu et al. (2013a) carried out a laboratory trial of a combined solvent extraction and bioremediation process to reduce oil contamination in soil from Shengli Oilfield, China. They found that this process reduced contamination from 140 000 to <4000 mg kg\(^{-1}\) but required the use of bioaugmentation (Bacillus subtilis F006) and biosurfactant (rhamnolipid) for full effectiveness. Whether this process competes on a cost-effective basis at larger scale remains to be seen, but it does highlight efforts to develop strategies to tackle highly contaminated soils. For in-situ treatment of heavy hydrocarbons, smouldering technologies, such as Self-sustaining Treatment for Active Remediation (STAR), have proven successful recently and have effectively treated subsurface heavy coal tar and crude oil contamination (Pironi et al. 2011; Scholes et al. 2015).

A number of tools are now available to assist with determining risk-based remediation end-points and timeframes. Level II fugacity modelling has been used successfully to predict the removal of hydrocarbons from constructed biopiles (Coulon et al. 2010). In this work partitioning propensity and fate of hydrocarbon fractions were modelled to produce time explicit data that adequately predicted hydrocarbon fate during the remediation. There is growing awareness that determination of remediation end-points should account for the bioavailability of hydrocarbons in soils (Harmsen & Naidu 2013; Kördel et al. 2013; Umeh et al. 2017). From a risk assessment and bioremediation perspective it is the bioavailable hydrocarbon fraction that is important rather than total concentration.

Fig. 4. Tar crusts formed after extensive weathering of crude oil (a–c) or the undistillable waste products after artisanal refinement (d). Scale bar = 0.1m.
(Guo et al. 2016). Wu et al. (2013c) demonstrated the applicability of various machine learning models to predict changes in PAH bioavailability, based on soil physicochemical properties, during composting of contaminated soils (Wu et al. 2013c). These models were found to be useful for determining remediation end-points based on bioavailability and could be applied to other remedial situations with relative ease. In similar work Harmsen & Naidu (2013) used Tenax extraction to predict PAH biodegradation based on various levels of bioavailability. Further developments in modelling are considering the interactions between factors that influence remediation and their relative contribution to predicting remediation success (Wu et al. 2014). The bioavailability of hydrocarbons has substantial ramifications for the remediation of contaminated soils. If it can be demonstrated that greater levels of contamination can be left in soil without additional risk, lower costs and smaller remediation volumes could be achieved (Wu et al. 2013b). There is evidence, however, that bioavailability is not fixed in time. Changes in environmental conditions can affect the bioavailability of hydrocarbons, as demonstrated in work by Wu et al. (2013). This indicates that a better understanding of the impacts of bioavailability of hydrocarbons is required to fully comprehend the risks associated with residual contamination. Most of the current tools used for assessing risk posed by hydrocarbons that determine the end-point of remedial activities are based on total extractable concentrations and do not account for bioavailability. Clearly framework guidance documents to support wide regulatory adoption of the bioavailability concept have recently been published (reviewed by Umeh et al. 2017). There has been some limited recognition by European-based environmental regulators (in Germany, the Netherlands and the UK) that bioavailability can be an aspect of contaminated land risk management, but generally regulatory and public acceptance is still limited (Harmsen & Naidu 2013).

Conclusions and future perspectives

In most circumstances, the unintentional release of heavy hydrocarbons will result in soil contamination and, depending on the volume released, the formation of free phase NAPL. Given the low volatility and solubility, the only attenuation mechanism of biodegradation, which, from thermodynamic considerations, can be expected to occur under different redox conditions. Field evidence shows that biodegradation is dependent on the prevailing environmental conditions and that heavy hydrocarbon contamination can persist over long time periods in the subsurface (years to decades). Recent developments in modelling have demonstrated that humic acids can influence the partitioning of heavy hydrocarbons in NAPL and soil. Experimental observations support this and have demonstrated that humic acids and soil organic matter can improve the bioavailability and biodegradation of heavy hydrocarbons. Although the low bioavailability of heavy hydrocarbons limits their toxicity, sites contaminated with heavy hydrocarbons may still require action to overcome the physical effects they may have on soils, including increased hydrophobicity, negatively affected soil texture, or the formation of oil crusts limiting oxygen diffusion into the soil. Overall, it is concluded that further research is needed to understand the fate and transport of heavy hydrocarbons. This includes developing a better understanding of heavy hydrocarbon biodegradation, which is required to determine their ultimate fate and risks. This will assist with the development of more effective remediation strategies, provide a scientific basis for establishing remediation end-points and help shed light on whether heavy hydrocarbons are a significant source of metabolic intermediates that change the risk profile of contaminated soils or become mobile in groundwater. Recent analytical and modelling techniques can contribute to this goal. Improved analytical capabilities will contribute to characterizing the composition of heavy hydrocarbon fractions and degradation intermediates. More detailed understanding of heavy hydrocarbon composition is needed to develop more realistic physical and chemical properties for this highly heterogeneous fraction. These data can be used to develop modelling methods that encompass the overall biodegradation route to establish science-based remediation end-points including bioavailability for heavy hydrocarbons. The combination of higher resolution analytical data with process-based models can also help to identify bottlenecks in biodegradation and potentially open up new sustainable remediation options for soils that contain a high proportion of heavy hydrocarbon. This includes understanding and developing strategies to overcome some of the gross contamination issues discussed in this review (soil hydrophobicity, oil crusts, soil texture) that may affect the rehabilitation of the contaminated soil.

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