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Fugacity modelling to predict the distribution of organic contaminants in the soil:oil matrix of constructed biopiles

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Abstract

Level I and II fugacity approaches were used to model the environmental distribution of benzene, anthracene, phenanthrene, 1-methylphenanthrene and benzo[*a*]pyrene in a four phase biopile system, accounting for air, water, mineral soil and non-aqueous phase liquid (oil) phase. The non-aqueous phase liquid (NAPL) and soil phases were the dominant partition media for the contaminants in each biopile and the contaminants differed markedly in their individual fugacities. Comparison of three soils with different percentage of organic carbon (% org C) showed that the % org C influenced contaminant partitioning behaviour. While benzene showed an aqueous concentration worthy of note for leachate control during biopiling, other organic chemicals showed that insignificant amount of chemicals leached into the water, greatly reducing the potential extent of groundwater contamination. Level II fugacity model showed that degradation was the dominant removal process except for benzene. In all three biopile systems, the rate of degradation of benzo(a)pyrene was low, requiring more than 12 years for soil concentrations from a spill of about 25 kg (100 mol) to be reduced to a concentration of 0.001 μg g^{-1}. The removal time of 1-methylphenanthrene and either anthracene or phenanthrene was about 1 and 3 years, respectively. In contrast, benzene showed the highest degradation rate and was removed after 136 days in all biopile systems. Overall, this study confirms the association of risk critical contaminants with the residual saturation in treated soils and reinforces the importance of accounting for the partitioning behaviour of both NAPL and soil phases during the risk assessment of oil-contaminated sites.

Keywords: Biopiling; Bioremediation; Fugacity; Modelling; Organic contaminants; Oil

1. Introduction

Constructed biopile technology (Battelle Environmental restoration department, 1996) is one means of reducing risks to human health and environment from soils contaminated with hydrocarbons. Risk reduction is heavily dependent on the physicochemical behaviour of risk critical compounds in the oil–soil matrix, and on their bioaccessibility and bioavailability to microorganisms (Doick et al., 2005; Allan et al., 2006). We have long been concerned with the environmental fate, partitioning and toxicity of risk critical compounds within hydrocarbon-contaminated soils (Pollard et al., 1992, 1999; Zemanek et al., 1997a,b; Whittaker et al., 1999; Pollard et al., 2004; Brassington et al., 2007). In these soils, an oil–soil matrix is universally present as the principal source of the organic contaminants that

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drive risk assessments (e.g. benzene, benzo(a)pyrene) and remedial actions at these sites.

However, within exposure assessment models for hydrocarbon-contaminated sites, the partitioning of risk critical compounds to their host matrix, the oil (Boyd and Sun, 1990; USEPA, 1991; Walter et al., 2000; Heyes et al., 2002) is rarely represented. As an oil matrix weathers, it develops into a more condensed, asphaltenic structure (Westlake et al., 1974) representing, in principle, an even stronger partition medium for contaminants in weathered hydrocarbon matrices and their post-treatment residues. Further, the oil becomes physically entrained within the soil matrix over time and hydrophobic contaminants are increasingly sequestered through partitioning into soil organic matter and/or diffusion into nanopores (Huesemann et al., 2005). As a result, contaminant molecules are released very slowly into the aqueous phase of the oil–soil matrix (Pignatello and Xing, 1996; Hatzinger and Alexander, 1997; Huesemann, 1997; Alexander, 2000). The rate of contaminant biotransformation in aged soils is thus limited by the rate of release from the matrix (Huesemann et al., 2003, 2004).

The application of fugacity modelling to the challenges of solid wastes is increasing. Previous applications include its use for directing site remediation decisions (Pollard et al., 1993; She et al., 1995), for quantifying vapour emissions from contaminated sites (Mills et al., 2004), and to predict the fate of organic compounds at landfill sites (Kjeldsen and Christensen, 2001; Shafi et al., 2006). However, there have only been limited attempts to include the source term (e.g. oil) for organic waste matrices (Nieman, 2003). Here, we investigate the capacity of oily waste source terms to act as a sink for priority contaminants within the oil–soil matrix of a biopile during bioremediation. Our research is part of an ongoing investigation by a research consortium (PROMISE) to place biopiling within a risk management framework and improve end-user confidence in this technology. Level I and II fugacity models were developed that included four phases within the soil matrix, namely: air, water, mineral soil and non-aqueous phase liquid (NAPL) to represent the source term. The model was parameterised using physical and chemical characteristics of three soils collected from sites historically contaminated with oily wastes. Our interest is in (i) to what extent this conceptualisation of partitioning in a biopile allows us to optimise treatment and (ii) what implications emerge from the modeled concentrations of key contaminants in individual media (air, water, soil) for the environmental regulation of biopiling, including the derivation of practical remedial targets for residual hydrocarbons.

2. Materials and methods

2.1. Soil characterisation

Archived soils (A, B and C; Table 1) were obtained from three sites in the UK, historically contaminated with petroleum hydrocarbons. Soil A was from a site that had undergone biopiling until the total petroleum hydrocarbon (TPH) load was reduced to the satisfaction of the regulatory authorities. Soils B and C were sampled from unremediated sites that had a long history of contamination with heavy petroleum.

Samples were prepared and characterised using standard procedures (Allan, 1989). Extractions for nitrate and ammonium analysis were performed using 4.0 ± 0.5 g (dry weight) soil and 40 ml of 1 M KCl. These were shaken on an end-over-end shaker for 30 min. Phosphate extractions were performed with 0.5 ± 0.1 g (dry weight) soil with 40 ml 2.5% v:v acetic acid using an end-over-end shaker for 2 h. Extracts were filtered through Whatman 44 paper prior to analysis on a flow injection analyzer (FIAstar). Carbon dioxide production, as a surrogate for respiration, was measured by weighing 1 ± 0.5 g (dry weight) soil into 11 ml vacuettes. Sealed vacuettes were incubated for 24 h at 15 °C and the headspace analysed for carbon dioxide using a gas chromatograph (Chrompack 9001) equipped with a methanizer and a flame ionisation detector (FID). An aliquot of between 50 and 100 µl was taken using a 250 µl gastight glass Hamilton syringe, and immediately injected onto an 80/100 mesh Poropak Q column (2 m × 1/8″ OD × 2 mm). The carrier gas was nitrogen at a flow of 20 ml min^{-1}. Temperatures of oven, injector and detector were 250 °C, 100 °C and 350 °C, respectively. A standard curve was prepared using certified gas mixtures (Linde Gases, Aberdeen). Three replicate blank vials were incubated and analysed with the samples to account for background carbon dioxide levels (Paton et al., 2006).

Microbial numbers for heterotrophic microorganisms and hydrocarbon degraders were estimated using the "most probable number" (MPN) method (Kirk et al., 2005). Soil (0.5 ± 0.2 g; dry weight) was extracted with 0.1% w:v sodium pyrophosphate in Ringer's solution using an end-over-end shaker for 2 h. Extracts (20 µl) were added to three different 96-well microtiter plates containing 180 µl media amended with 0.25 g l^{-1} INT (*p*-iodonitrotetrazolium violet) solution. The media were tryptic soya broth (TSA) for heterotrophs and Bushnell-Haas amended with 2 µl filter-sterilised diesel per well for hydrocarbon degraders or unamended for the control. The plates were incubated for two and four weeks at 25 °C for heterotrophic and hydrocarbon-degrading microorganisms, respectively.

Soil pH was measured using deionised water and a solution of 0.01 M $CaCl_2$. The measurement was performed by weighing 4 g (wet weight) into 50 ml centrifuge tubes and adding 20 ml solution. Tubes were shaken using an end-over-end shaker for 30 min and left to settle for at least 30 min. The pH was recorded when there was no change in the pH value in the second decimal point after 10 s (see Fig. 1).

2.2. Hydrocarbon extractions

Prior to extraction, samples (10 g) of each soil were blended with 10 g Na_2SO_4 to obtain a free flowing mixture.

Table 1
Soil characteristics and volumetric composition of the three biopiles

Soil and volumetric characteristics	Soil A		Soil B		Soil C	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Bulk density, kg l^{-1}	0.973	–	0.823	–	0.576	–
Moisture content, %	15	0.79	21	0.77	34	1.56
Moisture content, % at WHC*	38	3	44	1	46	1
pH in water	6.8	0.4	7.5	0.1	6.8	0.2
pH in 0.01 M $CaCl_2$	6.5	0.0	6.6	0.0	6.1	0.1
LOI**%	12	1	15	7	26	3
Org. C, %	7	0	9	4	15	1
C (TPH)NAPL, %	2.27	–	3.15	–	1.97	–
Org C soil, %	4.73	–	5.85	–	13.03	–
Dissolved org. C, μg g^{-1}	65	18	120	47	88	26
Dissolved total C, μg g^{-1}	143	11	221	92	152	27
% C	9	1	8	1	18	3
% N	5	1	2	1	1	0
Heterotrophic MPN per g in TSA	8.44×10^2	2.98×10^2	6.05×10^5	1.56×10^5	7.02×10^4	2.08×10^4
Degrading MPN per g in BH with 0.1% diesel	1.50×10^5	7.44×10^3	1.13×10^5	1.32×10^4	5.81×10^5	1.17×10^5
TPH, mg kg^{-1}	22700	–	31500	–	19700	–
Total biopile volume, m^3	625	–	625	–	625	–
Air volume, m^3	310	–	337	–	399	–
%	49.6	–	54.0	–	63.9	–
Water volume, m^3	91.1	–	108	–	122	–
%	14.6	–	17.3	–	19.6	–
Soil volume, m^3	209	–	162	–	96.1	–
%	33.5	–	26.0	–	15.4	–
NAPL volume, m^3	14.4	–	16.8	–	7.49	–
%	2.30	–	2.70	–	1.20	–

* Water holding capacity.
** Loss on ignition.

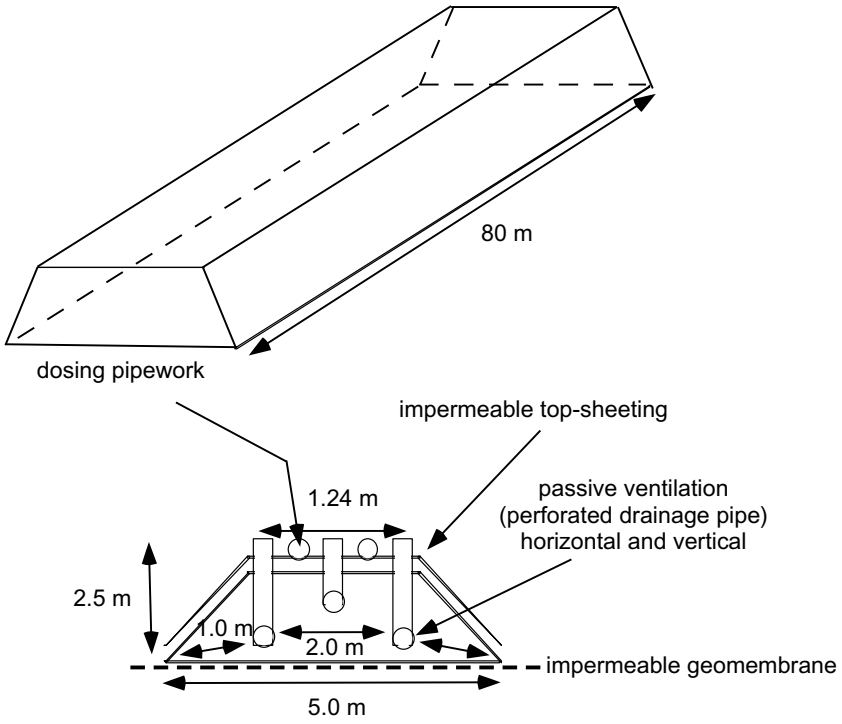

Fig. 1. Schematic and cross-section of the biopile 'evaluative environment'. The final biopile construction has a volume of 624 m^3 and weighs *ca.* 7.5×10^5 kg.

A layer of Na_2SO_4 (5 g) was placed in a series of Soxhlet thimbles followed by the soil samples. To each thimble, 1 ml of 50 mg l^{-1} *o*-terphenyl in methanol was added as a surrogate standard. Further blank (Na_2SO_4), blank spike (Na_2SO_4 with 1 ml of a 10 000 mg l^{-1} diesel/mineral oil in pesticide grade methanol solution) and reference (air-dried and ground soil reference material) samples were prepared. All glass thimbles were placed into soxhlet extractors and connected to 500 ml round bottom flasks containing 200 ml dichloromethane/acetone (90:10) solution. Samples were refluxed at 30 °C for 6–8 h and extracted samples concentrated down to 1 ml by Kurderna–Danish, using a 3-ball macro synder column. Concentrations of total petroleum hydrocarbon (TPH) were determined using GC–FID on a Perkin Elmer elite 5-MS capillary column (30 m × 0.25 mm × 0.25 μm) with helium carrier gas at a flow rate of 1 ml min^{-1}. The initial oven temperature of 40 °C was raised to 300 °C at a gradient of 4.4 °C min^{-1}. The soils characterisation is presented in Table 1.

2.3. Fugacity model development

Soil characteristics (Table 1) were used to parameterise Level I and II fugacity models representative of a 'typical' constructed biopile. Initially, a Level I fugacity model (Level 1 Fugacity calculator version 1.2; Nieman, 2003) was used to examine the general partitioning behaviour and preferential partitioning in a constructed biopile environment. An evaluative environment was constructed using a typical biopile design (Battelle Environmental restoration department, 1996). It was assumed that the soil matrix consisted of four compartments: air ('A', pore space), water ('W', soil pore water), non-aqueous phase liquid ('NAPL') and mineral soil ('S') (Fig. 2). The total mass of contaminant in the system (T, mol) is described by

$$T = V_A C_A + V_W C_W + V_{NAPL} C_{NAPL} + V_S C_S \quad (1)$$

where T is the total mass of contaminant in the system, V represents the volume of each compartment (m^3), and C represents the concentration of the contaminant in each compartment (mol m^{-3}).

To estimate the fluxes between the compartments (depicted as connecting lines in Fig. 2), the relationships between C_A, C_W, C_{NAPL} and C_S were estimated by deriving partition coefficients (Eq. (2)). The partition coefficients can be used to characterise the distribution of the contaminant within the system (Eq. (3))

$$\left(\frac{C_{NAPL}}{C_W}\right) = K_{NAPLW} \quad (2)$$

$$T = V_A\{K_{AW} C_W\} + V_W\{K_{WNAPL} C_{NAPL}, K_{WA} C_A\} + V_{NAPL}\{K_{NAPLS} C_S, K_{NAPLW} C_W\} + V_S\{K_{SNAPL} C_{NAPL}\} \quad (3)$$

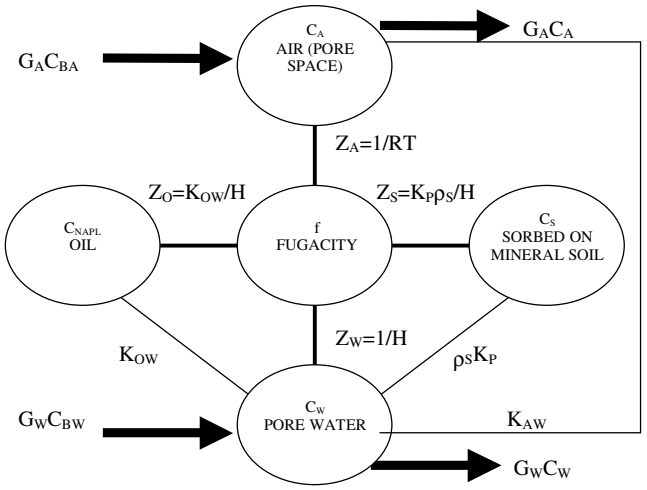

Fig. 2. Schematic of the fugacity model developed for each soil including definition of fugacity capacities used for each compartment. Z is the proportionality constant (mol m^{-3} Pa); H is the Henry's Law constant (Pa m^3 mol^{-1}); R is the gas constant = (8.314 m^3 Pa K^{-1} mol^{-1}); Temperature (K); K_S represents a partition coefficient (l kg^{-1}). ρ_S is the soil bulk density (kg l^{-1}). The inflow and outflow of air and water through the biopile system, and the losses of contaminants, are represented by the bold arrows.

where V represents the volume of each compartment in Fig. 2 (m^3), and C represents the concentration of the contaminant in each compartment (mol m^{-3}).

Under the fugacity approach, the concentration term, C, is replaced with the fugacity term Zf. This employs the relationship between concentration, C, and fugacity, f, which may be defined as the proportionality constant, Z (Eq. (4)) (MacKay, 2001). Definitions of the fugacity capacities Z_A, Z_W, Z_O and Z_S used in the Level I model are indicated in Fig. 2

$$C = Zf \quad (4)$$

To parameterise Eq. (1), the volumetric composition of each biopile was derived using a mass fraction based on the bulk density of each soil (Table 1), and a biopile volume of 625 m^3 (Battelle Environmental restoration department, 1996). The concentration of NAPL was assumed to be equal to the measured concentration of TPH (Table 1). The volumetric composition of the three biopiles is reported in Table 1. The volume of water, NAPL and mineral soil were calculated using literature-derived densities: water 1000 kg m^{-3}; NAPL was assumed to have an average bulk density of 970 kg m^{-3} (Woolgar, 1997); mineral soil was assumed to have a particle density of 2400 kg m^{-3} (Rowell, 1997). The volume of air was calculated as the total volume minus the sum of the other three volumes. A hundred moles of five priority compounds (Table 2) were introduced into the models and the partitioning of these compounds within the three soil matrices estimated.

The Level II fugacity model accounted for advection processes and degrading reactions in the form of residence times and half lives. The calculations assumed steady-state conditions – *i.e.* the amount entering the system was mass

Table 2
Input parameters

Chemical	Benzene	Benzo[*a*]pyrene	Anthracene	Phenanthrene	1-Methylphenanthrene
Molecular weight, g mol^{-1}	7.81×10^{1}	2.52×10^{2}	1.78×10^{2}	1.78×10^{2}	1.92×10^{2}
Water solubility, mg l^{-1}	1.78×10^{3}	3.80×10^{-3}	4.50×10^{-2}	1.1×10^{0}	2.69×10^{-1}
Vapor pressure, mmHg	7.60×10^{1}	5.49×10^{-9}	1.08×10^{-5}	2.01×10^{-4}	7.27×10^{-5}
Henry's Law constant, atm m^3 mol^{-1}	5.43×10^{-3}	1.80×10^{-5}	3.38×10^{-5}	3.98×10^{-5}	4.27×10^{-1}
Log K_{ow}	2.13×10^{0}	6.06×10^{0}	4.45×10^{0}	4.46×10^{0}	5.14×10^{0}
Log K_{oc}	1.81×10^{0}	6.74×10^{0}	4.10×10^{0}	4.10×10^{0}	4.17×10^{0}
$\tau_{1/2}$ Air	1.70×10^{1}	1.70×10^{2}	5.50×10^{1}	5.50×10^{1}	1.70×10^{1}
$\tau_{1/2}$ Water	1.70×10^{2}	1.70×10^{3}	5.50×10^{2}	5.50×10^{2}	1.70×10^{2}
$\tau_{1/2}$ Soil	5.50×10^{2}	1.70×10^{4}	5.50×10^{3}	5.50×10^{3}	1.70×10^{3}
$\tau_{1/2}$ NAPL	1.70×10^{3}	5.50×10^{4}	1.70×10^{4}	1.70×10^{4}	5.50×10^{3}

balanced by the amount leaving the system. If a chemical is introduced at a rate of E mol h^{-1}, then the rate of removal must also be E mol h^{-1}. If the amount in the system is M mol, then on an average the amount of time, τ, each molecule spends in the steady-state system is (Eq. (5))

$$\tau = M/E; \quad M = \tau E \tag{5}$$

There are two primary mechanisms by which a chemical may be removed from a biopile system: advection and reaction. Since a steady-state applies, we assume that inflow and outflow are equal and that a mass-balance applies. If G is the advecting medium (m^3 h^{-1}) and C is the concentration of the contaminant in G (mol m^{-3}), then the rate of advection, N, is GC (mol h^{-1}). The total influx of the chemical is at a rate $G_A C_{BA}$ in air, $G_W C_{BW}$ in water, $G_{NAPL} C_{BNAPL}$ in NAPL, and $G_S C_{BS}$ in mineral soil. Therefore, the total influx I is (Eq. (6))

$$I = E + G_A C_{BA} + G_W C_{BW} + G_{NAPL} C_{BNAPL} + G_S C_{BS} \tag{6}$$

If we assume a constant fugacity, f, to apply within the biopile system and to the out-flowing media (air and water), then we can write (Eqs. (7) and (8))

$$\begin{aligned} I &= (G_A Z_A f + G_W Z_W f) + (V_A Z_A k_A f + V_W Z_W k_W f \\ &\quad + V_{NAPL} Z_{NAPL} k_{NAPL} f + V_S Z_S k_S f) \\ &= f \Sigma D_{Ai} + f \Sigma D_{Ri} \end{aligned} \tag{7}$$

$$F = \frac{I}{\Sigma (D_{Ai} + D_{Ri})} = \frac{I}{\Sigma D_T} \tag{8}$$

3. Results and discussion

The fugacity of a chemical in a multiphase system is analogous to the partial pressure of an ideal gas and related to concentration through the fugacity capacity (Mackay, 2001). For the three soils as an entire environmental compartment, there were no significant differences ($P > 0.05$) between the estimated Level I fugacities (f) for the five priority contaminants, though the contaminants differed markedly in their fugacities (Table 4).

Here, we are principally interested in the relative phase partitioning of these contaminants (Table 3) and, from the Level II calculations, their time dependent behaviour (Fig. 3 and Table 4) within modeled biopiles. The results for phenanthrene are not presented because its Level II model output was not significantly different to anthracene.

NAPL and soil are the dominant partition media for these contaminants in each biopile systems (Table 3). The partition behaviour of the compounds is mainly influenced by their water solubility and the percentage of organic carbon in soil. In comparison to NAPL and soil phase concentrations, the water and air phase concentrations are very small except for benzene (Table 3). Benzene expresses an aqueous concentration worthy of note for leachate control during biopiling; the air phase concentrations appear insignificant in relation to NAPL and soil phase concentrations. The model provides some comfort, but odour events at biopiling facilities are sufficiently common to warrant further examination of air phase fluxes of risk critical contaminants.

Interestingly, benzene and anthracene in soil C shows a greater propensity to transfer to the soil compartment, than in soils A and B. This appears to be due to the higher percentage of organic carbon in soil C compared to the other soils (Table 3). In addition, benzo(a)pyrene being the least soluble organic compound used in these models shows a systematic preference for the soil compartment in all biopile systems. Thus, recognition of both NAPL and soil compartments, as partition media are important for risk analysts, regulators and remediation engineers. The overriding dominance of the NAPL phase for hydrophobic contaminants is theoretically established but rarely incorporated, in practice, into the exposure assessment tools used to derive soil screening levels and guideline values. This is an oversight that is likely to have a marked influence on soil assessment criteria at hydrocarbon-contaminated sites. Its significance comes into play when one considers the residual risk posed by post-treatment residues. For biopiling, there is a long-standing debate regarding the nature and extent of the hazard posed by post-treatment residues left *in situ* following treatment. For example, Zemanek et al. (1997a) showed that between 71 and 96% w:w of PAH in weathered diesel-contaminated loams were partitioned to residual oil (at 2–6% w:w of the total soil composition) in petroleum and weathered creosote-contaminated soils, with 84% w:w of benzo(a)pyrene partitioned to the residual oil phase. Woolgar and Jones

Table 3
Partitioning behaviour of the five organic compounds within the air, water, soil and NAPL phases of the three biopiles

Organic compound	Phase	Soil A		Soil B		Soil C	
		Moles	%	Moles	%	Moles	%
Benzene	Air	1.93×10^{0}	1.9	1.94×10^{0}	1.9	2.85×10^{0}	2.8
	Water	2.51×10^{0}	2.5	2.76×10^{0}	2.8	3.85×10^{0}	3.9
	Soil	4.22×10^{1}	42.2	3.75×10^{1}	37.5	6.13×10^{1}	61.3
	NAPL	5.33×10^{1}	53.3	5.78×10^{1}	57.8	3.19×10^{1}	31.9
Anthracene	Air	6.19×10^{-5}	0.0	6.23×10^{-5}	0	9.51×10^{-5}	0.0
	Water	1.30×10^{-2}	0.0	1.42×10^{-2}	0	2.07×10^{-2}	0.0
	Soil	4.25×10^{1}	42.5	3.77×10^{1}	37.7	6.42×10^{1}	64.2
	NAPL	5.75×10^{1}	57.5	6.23×10^{1}	62.3	3.58×10^{1}	35.8
Methyl-phenanthrene	Air	2.35×10^{-1}	0.2	2.25×10^{-1}	0.2	4.77×10^{-1}	0.5
	Water	3.90×10^{-3}	0.0	4.06×10^{-3}	0.0	8.21×10^{-3}	0.0
	Soil	1.50×10^{1}	15.0	1.26×10^{1}	12.6	2.99×10^{1}	29.9
	NAPL	8.74×10^{1}	84.7	8.71×10^{1}	87.1	6.96×10^{1}	69.6
Benzo(a)pyrene	Air	1.58×10^{-7}	0.0	1.75×10^{-7}	0.0	1.72×10^{-7}	0.0
	Water	6.20×10^{-5}	0.0	7.49×10^{-5}	0.0	7.02×10^{-5}	0.0
	Soil	8.88×10^{1}	88.8	8.66×10^{1}	86.6	9.51×10^{1}	95.1
	NAPL	1.12×10^{1}	11.2	1.34×10^{1}	13.4	4.95×10^{0}	4.9

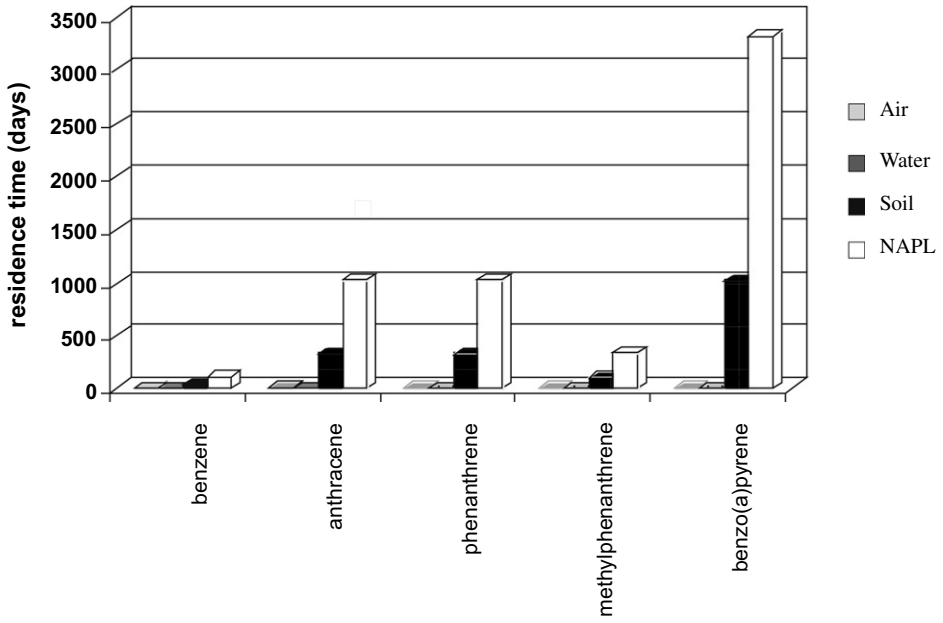

Fig. 3. Representative partitioning and degradation behaviour of the five model compounds within the soil:oil biopile matrix A.

(1999) estimated oil–water partition coefficients (termed log K_{mw}) for a series of polynuclear aromatic hydrocarbons ranging between 4.5 and 6.5 (log) dependent on the nature of the source term. Under these conditions, highly partitioned constituents are likely to be biologically inaccessible to microbial communities and resistant to biotransformation. Further, their inaccessibility may also, but not necessarily, restrict the dose available to receptors. The corollary of this debate also has implications. Attempts by remediation technologists to improve the bioavailability of these components to microorganisms through, for example, the use of biosurfactants may also result in increased human and environmental exposure. Notwithstanding the demonstration of the importance of the oil source term in this study, the behaviours modeled in Table 3 represent only a partial picture. The changes in structural composition of oil as it is biotransformed (Westlake et al., 1974; Whittaker et al., 1999) and its depletion with time mean that hydrophobic and recalcitrant contaminants become both concentrated and more tightly bound within the oil matrix as biopiling progresses. To date, the modelling above does not account for these secondary effects, but would need to if we were to present a truly representative account of partitioning behaviour in the NAPL phase over time.

In practice, biopiling timeframes are typically of the order of 3–6 months (~90–180 days). The discussion that follows

Table 4
Environmental losses including advection and degradation processes for the five model compounds in each biopile systems

		Fugacity (f) Pa	Total reaction rate ($\sum D_R f$), mol h^{-1}	Total advection rate ($\sum D_A f$), mol h^{-1}	Overall residence time (days)
Biopile soil A	Benzene	1.52×10^{1}	1.64×10^{-1}	4.66×10^{-1}	136
	Anthracene	4.87×10^{-4}	7.72×10^{-3}	2.37×10^{-3}	1335
	1 Methyl-phenanthrene	1.85×10^{0}	2.64×10^{-2}	1.47×10^{-3}	434
	Benzo(a)pyrene	1.24×10^{-6}	3.76×10^{-3}	1.14×10^{-5}	4434
Biopile soil B	Benzene	1.40×10^{1}	1.61×10^{-1}	4.32×10^{-1}	136
	Anthracene	4.51×10^{-4}	7.31×10^{-3}	2.20×10^{-3}	1355
	1 Methyl-phenanthrene	1.63×10^{0}	2.53×10^{-2}	1.29×10^{-3}	435
	Benzo(a)pyrene	1.26×10^{-6}	3.70×10^{-3}	1.16×10^{-5}	4334
Biopile soil C	Benzene	1.74×10^{1}	2.22×10^{-1}	5.35×10^{-1}	137
	Anthracene	5.81×10^{-4}	9.57×10^{-3}	2.83×10^{-3}	1356
	1 Methyl-phenanthrene	2.91×10^{0}	4.05×10^{-2}	2.32×10^{-3}	434
	Benzo(a)pyrene	1.05×10^{-6}	3.94×10^{-3}	9.61×10^{-6}	4335

with respect to the depletion times of risk critical compounds needs to be viewed in light of these practical realities. For all three soils, the majority of modeled benzene (100 mol) remained present in the NAPL compartment until 102 days when benzene was no longer present in all three biopiles (132 days; Table 4). Benzo(a)pyrene is fully eliminated from the three biopile systems after 4334 days (12 years). As shown in Fig. 3, benzo(a)pyrene remains at least 9 years in NAPL phase and ~3 years in soil phase. Elimination of anthracene and 1-methylphenanthrene from the soil phase is observed after 23 and 8 months, respectively. In contrast, anthracene and 1-methylphenanthrene remain 2.8 years and 27 months, respectively in NAPL phases (Fig. 3).

This discussion is somewhat artificial when one considers the authentic conditions under which biopiling is used. In practice, we expect the persistence (if not concentration) of these compounds in oily post-treatment residues, albeit with a restricted bioavailability. This paradox between mass and availability has proved to be a rich territory for discussion between the oil and manufactured gas plant industries and environmental regulators. In the United States, a substantive research effort has focused on integrating hydrocarbon fate and transport, petroleum microbiology and environmental diagnostics to inform regulatory processes for site management under the Superfund Program. ThermoRetec (2000), reporting for the petroleum environmental research forum (PERF), provide an authoritative account of the central importance of partitioning within soil-bound hydrocarbons in developing environmentally acceptable endpoints (remedial objectives). Drawing on a detailed understanding of NAPL and residual oil fate and behaviour, this work is now influencing the development of more realistic and defensible remediation criteria for petroleum hydrocarbon in soils for human health, groundwater and ecological receptors, and a reappraisal of the level of residual petroleum hydrocarbons that can be left at remediated sites without posing an unacceptable risk. In England and Wales, the Environment Agency (2003) have also recognised the importance of an authentic representation of partitioning in their consultation, and subsequent framework, (Environment Agency, 2005) on evaluating the human health risks from petroleum hydrocarbons in soils. We will be exploring these influences and attempting to validate the modeled behaviours described here with data from microcosms and pilot biopile trials. Ultimately, we are interested in providing a more sound evidence base for the derivation of realistic soil assessment criteria and directing remedial efforts towards risk critical compounds, exposures and environmental media.

4. Conclusions

We have demonstrated the propensity for risk critical compounds in hydrocarbon-contaminated soils to be preferentially partitioned to the NAPL and soil phases and modeled their behaviour using typical biopile design parameters. Small differences in the partitioning behaviours of the compounds studied between individual soils were dwarfed by the relative partitioning observed between the air, water, NAPL and soil phases in the evaluative environments. Modeled depletion times for individual contaminants in the context of authentic biopiling are immaterial and thus research efforts should be focused on the likely exposures of humans and other receptors to residual saturation at hydrocarbon-contaminated sites. Further, the results indicate the need for modifications to the exposure assessment models used to generate soil screening guidelines or guideline values, so to better represent contaminant fate in the multimedia systems.

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