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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 $\mu g\ g^{-1}$. 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 ($2\ \text{m} \times 1/8''\ \text{OD} \times 2$ mm). The carrier gas was nitrogen at a flow of $20\ \text{ml min}^{-1}$. 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 $0.25\ \text{g l}^{-1}$ 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.