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Desorption of polycyclic aromatic hydrocarbons from field-contaminated soil to a two-dimensional hydrophobic surface before and after bioremediation

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HIGHLIGHTS

- We evaluated PAH desorption from field-contaminated soil to a hydrophobic surface.
- PAHs desorbed at soil loadings in excess of monolayer coverage.
- Transport of PAHs through the vapor phase is an important mechanism.
- Bioremediation eliminates PAHs capable of desorbing to the hydrophobic surface.

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ABSTRACT

Dermal exposure can represent a significant health risk in settings involving potential contact with soil contaminated with polycyclic aromatic hydrocarbons (PAHs). However, there is limited work on the ability of PAHs in contaminated soil to reach the skin surface via desorption from the soil. We evaluated PAH desorption from a field-contaminated soil to a two-dimensional hydrophobic surface (C18 extraction disk) as a measure of potential dermal exposure as a function of soil loading (5–100 mg dry soil cm^{-2}), temperature (20–40 °C), and soil moisture content (2–40%) over periods up to 16 d. The efficacy of bioremediation in removing the most readily desorbable PAH fractions was also evaluated. Desorption kinetics were described well by an empirical two-compartment kinetic model. PAH mass desorbed to the C18 disk kept increasing at soil loadings well above the estimated monolayer coverage, suggesting mechanisms for PAH transport to the surface other than by direct contact. Such mechanisms were reinforced by observations that desorption occurred even with dry or moist glass microfiber filters placed between the C18 disk and the soil. Desorption of all PAHs was substantially reduced at a soil moisture content corresponding to field capacity, suggesting that transport through pore air contributed to PAH transport to the C18 disk. The lower molecular weight PAHs had greater potential to desorb from soil than higher molecular weight PAHs. Biological treatment of the soil in a slurry-phase bioreactor completely eliminated PAH desorption to the C18 disks.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of great concern because of their known or suspected genotoxicity, mutagenicity and carcinogenicity (Santodonato, 1997; Bostrom et al., 2002). Dermal exposure can represent a significant health risk in settings involving potential contact with complex materials containing PAHs, including PAH-contaminated soil or sediment (Boffetta et al., 1997; Sobus et al., 2009). Most previous work has been concerned with integrated uptake of chemicals through the skin and not with how a contaminant reaches the skin surface in the first place. However, only a contaminant that reaches the skin surface is available for dermal absorption (Roy et al., 1998; Shatkin et al., 2002). Desorption properties, such as dynamic conditions by which soil contacts the skin, interactions of the soil with the skin surface and chemical interaction with the soil, have been identified to influence dermal uptake of chemicals (McKone and Howd, 1992; Spalt et al., 2009). Therefore, it is important to understand desorption of PAHs from contaminated soil or sediment to the skin surface.

To account for the association of hydrophobic contaminants such as PAHs with compartments of varying sorptive strength in soil (Alexander, 1995; Xing and Pignatello, 1997; Cornelissen et al., 2005), a so-called two-compartment desorption model assumes a simplified situation in which a fraction of the contaminant is released relatively rapidly and the remainder is released

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relatively slowly (Cornelissen et al., 1998; Hawthorne et al., 2001; Zhu et al., 2008). By incorporating two-compartment desorption kinetics into a fugacity model, Shatkin et al. (2002) illustrated that a greater rapid-desorbing fraction of a chemical would result in greater dermal uptake. In most previous experimental work on dermal uptake of contaminants from soil, an individual contaminant was introduced into the soil through a solvent that subsequently evaporated (Spalt et al., 2009). However, exposure to a spiked chemical does not account for the effect of contaminant aging that would have occurred in field-contaminated soil (Roy et al., 1998; Stroo et al., 2000; Spalt et al., 2009), which is well known to decrease its bioavailability (Alexander, 2000).

The objective of this study was to evaluate desorption of PAHs from field-contaminated soil from a former MGP site to a two-dimensional hydrophobic surface (Empore™ C18 extraction disk) as a measure of potential dermal exposure. Various factors affecting desorption were investigated, including soil loading, temperature, soil moisture content (SMC), and exposure time. We also compared desorption to the C18 disk to a conventional method of evaluating potential contaminant bioavailability in soil, desorption to Tenax® beads in a well-mixed aqueous slurry (Loehr et al., 2003). The efficacy of bioremediation (in a slurry-phase bioreactor) in removing the most readily desorbable PAH fractions was evaluated with both methods.

2. Materials and methods

2.1. Materials

Source soil used in this study was collected from a former MGP site in Salisbury, North Carolina, USA. Samples were air-dried, sieved (250 μm mesh) and maintained at 4 °C prior to use. The total organic matter fraction (f_{oc}) was 0.16 (dry mass basis, wt/wt), SMC was 2.0% (wt/wt), field capacity was 40% (wt/wt), and soil particle density was 2.57 g cm^{-3} (methods are identified in Table S1, Supplementary Material). The total concentration of 14 target PAHs (the 16 priority PAHs, excluding acenaphthylene and indeno[*1,2,3-cd*]pyrene) was 780 ± 10 mg kg^{-1} (dry mass basis, wt/wt; individual PAH concentrations are shown in Table S2); the most abundant PAHs were phenanthrene (PHE, 322 ± 5.1 mg kg^{-1}) and pyrene (PYR, 121 ± 0.05 mg kg^{-1}). Soil samples were mixed with de-ionized water to reach desired SMC levels prior to desorption experiments. Treated soil was the slurry from a continuously stirred, semi-continuous (draw and fill), laboratory-scale aerobic bioreactor (Zhu et al., 2008) treating the source soil. The treated soil had a total PAH concentration of 121 ± 8 mg kg^{-1} (individual PAH concentrations are shown in Table S2).

Empore™ C18 extraction disks (25 mm diameter, 0.5 mm thickness) were obtained from 3 M (St. Paul, MN, USA) and cleaned by acetone extraction overnight and air-dried before use. Tenax® TA beads (60/80 mesh) were purchased from Alltech (Deerfield, IL, USA) and cleaned by Soxhlet extraction in acetone: hexane (50:50, v/v) mixture overnight and air-dried before use. PAH standards (EPA 610 PAHs Mixture) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Anthracene-D10 was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Solvents were high-pressure liquid chromatography (HPLC) grade and were obtained from Fisher Scientific (Pittsburgh, PA, USA).

The C18 extraction disks were used to evaluate variables that might influence the transfer of PAHs from soil to a static hydrophobic interface. This method is analogous to the Tenax beads method for evaluating PAH desorption kinetics in slurry systems (Loehr et al., 2003), in that both C18 extraction disks and Tenax beads serve as an infinite sink; however, we believe that the C18 disk is more relevant to the application of soil to skin in a dermal exposure scenario.

2.2. Desorption experiments

Desorption of PAHs from soil samples to C18 disks was determined at three different temperatures (20 °C, 30 °C and 40 °C), four SMC levels (2%, 8%, 20% and 40%) and seven soil loadings (5–100 mg dry soil cm^{-2}) over periods of 6 d, when total PAHs desorbed from soil to a C18 disk reached an apparent equilibrium (Fig. S1). Kinetics for desorption of PAHs from soil to C18 disks were investigated over periods of 16 d. The sorption capacity of C18 disks was evaluated by repeated soil loading of the same disk; results indicated that the sorption capacity greatly exceeded the amount of PAHs desorbed in any given experiment (Table S3). Soil with a specified SMC level was spread as evenly as possible (under microscopic observation) onto the C18 disk, which was then transferred with an aluminum spatula onto an aluminum weighing dish. Soil weight was determined by weight difference of the C18 disk before and after soil loading. The aluminum weighing dish was then transferred into a sealed container and kept in the dark in a constant-temperature room set to the desired temperature. After each desired time interval, disks were removed and rinsed with de-ionized water three times for subsequent PAH extraction. To investigate possible mechanisms of PAH transport from soil to the hydrophobic surface, dry or moist Whatman glass microfiber filters (pore size 0.7 μm, pre-baked at 400 °C for 4 h) (Fisher Scientific, Pittsburgh, PA, USA) were placed between the C18 disk and the soil. Triplicates of procedure blanks (no soil) were included. Total PAH recovery over all experiments was 94 ± 6% (individual PAH recoveries are shown in Table S4), calculated by comparing the initial PAH mass in the soil with the PAH mass desorbed to the C18 disk and the PAH mass remaining in the soil after desorption.

Desorption of PAHs from soil to Tenax beads was carried out at 20 °C. Approximately 3 g of soil (dry wt.) and 0.2 g Tenax beads were suspended in 20 mL phosphate buffer (pH 7.5) amended with 4.15 g L^{-1} NaN_3 in a 30-mL glass serum vial with a PTFE-lined septum and screw cap. The vials were placed on a wrist-action shaker at 240 rpm in the dark. After 1, 2, 4, 8 and 16 d, the vials were centrifuged at 3500 rpm for 15 min, Tenax beads were removed from the vials for subsequent extraction as described by Zhu et al. (2008), and the supernatant was discarded. For all but the 16-d time point, 20 mL fresh medium was added along with 0.2 g fresh Tenax beads into the vials. The mass recovery of Tenax beads over all time points was 97 ± 2%. Total PAH recovery was 92 ± 10% for combined experiments with source soil and treated soil (individual PAH recoveries are in Table S4).

2.3. PAH extraction and analysis

C18 disks and Tenax beads were extracted with 10 mL acetone and 10 mL methanol, respectively, in a 20-mL test tube with a PTFE-lined septum and screw cap; each tube was amended with 20 μL anthracene-D10 (100 μg L^{-1}) as recovery surrogate. The tubes were placed on a wrist-action shaker at 240 rpm in the dark for 24 h. A 1-mL aliquot of extract from the C18 disk was then removed for HPLC analysis. The extract from Tenax beads was filtered through a Millipore (Billerica, MA, USA) nylon membrane (pore size 0.20 μm) to remove the beads and subsequently analyzed by HPLC. Soil samples were extracted overnight twice each with a mixture of 10 mL acetone and 10 mL dichloromethane as described elsewhere (Zhu et al., 2008). All extracts were analyzed by HPLC (Zhu et al., 2008).

2.4. Data analysis

SPSS® (v16.0, SPSS Inc.) was applied for data analysis. One-way ANOVA followed by Tukey's test was employed to test for differences among multiple groups. The maximum soil loading required