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Dissolution and transport of coal tar compounds in fractured clay-rich residuum

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ABSTRACT

We investigated the dissolution and transport of organic contaminants from a crude coal tar mixture in a monolith of fractured clay-rich residuum. An electrolyte solution was eluted through the residuum monolith containing a small emplaced source of coal tar under biologically inhibited and mildly acidic conditions. Concentrations of 10 coal tar compounds, representing mono-, poly-, and heterocyclic aromatic hydrocarbons that constitute crude coal tar were monitored in the effluent over a period of 377 days. Most compounds appeared in the effluent within the first 0.1 pore volume eluted indicating the importance of rapid dissolution and transport through the fracture networks. The concentrations continued to rise but did not reach the corresponding effective solubility limit in most cases. Compounds that were less soluble and those that were more susceptible to sorption or matrix diffusion eluted at a much slower rate. Analysis of contaminant concentrations in microcore residuum samples indicated that all 10 compounds had spread throughout the entire monolith and had diffused into the fine-grained matrix between fractures. These data suggest that the predominantly fine pore structure did not appear to inhibit coal tar dissolution and subsequent transport, even though only a small portion of tar was in direct contact with fractures and macropores that control most flow.

1. Introduction

Coal tar compounds were commonly disposed of in the environment as byproducts of the coal gas manufacturing industry in the US and Western Europe [1]. This resulted in extensive contamination of surface water, soil, and groundwater by coal tar components such as polycyclic and heterocyclic aromatic hydrocarbons [2,3]. Coal tar is a complex mixture of monocyclic, polycyclic, and heterocyclic aromatic hydrocarbons exhibiting a wide range of chemical and physical properties [2]. It is generally assumed to be relatively immobile in fine-grained subsurface porous media because of its high viscosity and interfacial surface tension, combined with the low permeability and small average pore size of the fine-grained materials. However, field and laboratory investigations in a variety of clay-rich materials, including glacial tills [4], lacustrine deposits [5,6] and residuum derived from sedimentary rock [7] show that these fine-grained materials often contain fractures, rootholes and other macropores, which can act as conduits for flow and transport of dissolved contaminants. Only a few experimental studies address transport of immiscible phase contaminants such as TCE [8] and creosote [9] in these materials. They show that (i) immiscible contaminants can, in some cases, enter fractures or macropores at relatively low capillary pressures (few 10 s of cm of head) and (ii) relatively high solubility contaminants, such as TCE, can rapidly dissolve in fractures because of the high surface area/volume ratio of the fracture and because of diffusion of the dissolved TCE into the fine-grained matrix. However, it is not clear whether dissolution rates will be environmentally significant for complex mixtures of low solubility compounds, such as coal tar, particularly in cases where the tar source is concentrated in a small area and is mainly in contact with the low permeability clay matrix, rather than being distributed along the fast flow pathways in the fractures and macropores.

The goal of this research is to determine the influence of fractures and clay-rich matrix on dissolution and transport of moderate to low solubility organic compounds from an immiscible coal tar source in fractured clay-rich residuum typical of East Tennessee. These materials are highly fractured (spacing of <2 cm), but the

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fracture or macropore porosity (1–3%) constitutes a small portion of total porosity (40–50%) [10]. Our main hypothesis is that diffusion through the fine-grained matrix adjacent to immiscible coal tar sources is sufficiently rapid such that the low hydraulic conductivity of the matrix will not act as a major impediment to dissolution and transport of coal tar compounds. To investigate this process, we emplaced a source of crude coal tar in an undisturbed monolith of fractured limestone-shale residuum and monitored the elution of a suite of 10 organic compounds that represent the major chemical classes present in typical crude coal tar mixtures – phenolic and polycyclic/heterocyclic aromatic hydrocarbons.

2. Materials and methods

2.1. Coal tar composition

“Fresh” crude coal tar with a specific gravity of 1.1 g/mL at 20 °C, a boiling point of 150 °C, and a vapor pressure of <5 mm Hg at 20 °C was used in the experiment (data provided by manufacturer). Mass fractions of 10 coal tar compounds (Table 1) were measured by dissolving approximately 2.6 g of crude coal tar in 41 mL of methylene chloride (MeCl) at 22 °C. Following a 24-h equilibration period, coal tar compounds (Table 1) were analyzed using gas chromatograph/mass spectrometer (GC/MS) as described in Section 2.5. The mass fraction (g/g) and mole fraction (mol/mol) of each compound in the crude coal tar was calculated from the concentration of specific compound in the MeCl extract (g/mL) and the molecular mass of the crude coal tar sample. The average molecular mass for the crude coal tar was determined, using vapor pressure osmometry (Galbraith Laboratories, Knoxville, TN), to be approximately 272 g/mol.

2.2. Residuum monolith description

An undisturbed residuum monolith was obtained from an extensively characterized research site in the Solid Waste Storage Area #7 (SWSA7) at the U.S. Department of Energy’s Oak Ridge Reservation, Oak Ridge, Tennessee, USA [e.g., 10, 11]. The residuum is derived from in situ weathering of the underlying sedimentary bedrock, which is composed of interbedded shale, siltstone, and limestone [7]. The carbonates have been leached leaving a highly porous, fine-grained, detrital matrix that retains much of the structure of the parent bedrock. Hydraulic conductivity values for monoliths previously collected at SWSA7 ranged from 2.7×10^{-4} to 4.5×10^{-9} m/s [10]. Residuum-derived soil is typically clay-rich (illite, vermiculite, and kaolinite) and fracture surfaces present in the matrix are often coated with Fe- and Mn-oxides. The soil *p*H is mildly to moderately acidic (*p*H ~ 4.5–6), with CEC values ranging between 7 and 16 cmol_c/kg, and fractional organic carbon content (f_{OC}) of 0.05% [11].

The monolith (23 cm diameter and 25 cm tall) was collected at ~2 m below ground surface and ~1 m above the residuum-bedrock contact and was prepared for flow-through experiments as previously described [10]. Based on a matrix porosity of 45% [10,30], the pore volume (PV) was estimated to be 4.7 L.

2.3. Flow-through monolith experiment

The monolith was saturated with an electrolyte solution containing 0.5 mM of $CaCl_2$ (representative of the ionic strength of groundwater in the area) and 1 g/L sodium azide to inhibit microbial activity. After saturation, seven holes of ~1.27 cm inner diameter (ID) were drilled into the top of the residuum monolith to a depth of 6.7 ± 0.6 cm and 63.8 g of coal tar was poured into the holes until they were nearly filled. The monolith was capped and downward flow (0.2 mL/min) was established using the electrolyte solution spiked with tritiated water (^3H_2O, 116 ± 2 piCi/mL) as a non-reactive tracer of water movement. A pulse of 1.4 PV (~23 days) of ^3H_2O-electrolyte was injected, followed by another 4.8 PV of ^{3}H-free electrolyte solution. A second 1.3 PV pulse of ^3H_2O-electrolyte solution was then introduced to the monolith followed again by ^3H_2O-free electrolyte solution until the end of the experiment. The flow of solution through the monolith was temporarily stopped between 233 and 265 days to investigate the effects of matrix diffusion. The injection was stopped after 377 days.

Effluent from the monolith was collected at a rate of 1–4 samples/day and was sub-sampled for ^3H_2O and coal tar compounds. Dissolved coal tar compounds were extracted by equilibrating 5.0 mL of each water sample with 2.0 mL of diethyl ether spiked with bromo naphthalene for 1 h. Following equilibration, 1 mL of diethyl ether was sampled, dried using anhydrous Na_2SO_4, and stored in GC vials at −20 °C pending GC/MS analysis. Tritium was analyzed using a liquid scintillation counter (Packard Tri-Carb

Table 1
List of coal tar compounds monitored in this study, their mass balance, and retardation estimates.

Chemical	Aqueous solubility[a] (mg/L)	Mass in coal tar[b] (mg)	Mole fraction[c]	Calculated solubility[d] (mg/L)	Total mass flushed[e] (mg)	Mean time of arrival[f] (days)	Retardation factor[g]	Fraction of total eluted[h] (%)
o-Cresol	28,700	101	0.004	114	27.3	15	6	27%
m-Cresol	22,000	235	0.009	204	132	6.1	2.5	56%
Naphthalene	111	5460	0.18	20.2	1250	59	24	23%
Quinoline	6710	139	0.005	30.8	46.3	53	22	33%
Indole	6740	74.6	0.003	18.3	21.7	21	8.5	29%
2-Methyl naphthalene	31.6	581	0.017	0.552	22	61	25	4%
Methyl quinoline	6720	34.5	0.001	6.91	0.86	86	35	2%
Acenaphthalene	18.3	1060	0.03	0.546	9.06	63	26	1%
Dibenzofuran	24.2	621	0.016	0.382	7.53	64	26	1%
Carbazole	168	365	0.009	1.57	16.8	51	21	5%
Tritium, pulse 1						2.4	1	79.90%
Tritium, pulse 2						2.5	1	77.50%

[a] Pure compound solubility data from Mackay et al. [31]. For organic compounds that are solids at 25 °C, subcooled liquid solubilities were estimated as outlined in Schwarzenbach et al. [32].

[b] Measured in this study.

[c] Estimated from mass fractions and molecular weight of crude coal tar (measured in this study).

[d] Estimated from mole fractions and aqueous solubilities using Raoult’s Law.

[e] Calculated zeroth moment of the breakthrough curves.

[f] See Eq. (1) for estimation.

[g] Calculated as ratio of mean travel times of the coal tar compound and ^{3}H tracer.

[h] Ratio (as %) of mass of compound eluted at end of experiment versus mass emplaced in monolith.