

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.

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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 10s 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 pH is mildly to moderately acidic ($pH \sim 4.5$ – 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 CaCl₂ (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 (³H₂O, 116 ± 2 pCi/mL) as a non-reactive tracer of water movement. A pulse of 1.4 PV (~23 days) of ³H₂O-electrolyte was injected, followed by another 4.8 PV of ³H-free electrolyte solution. A second 1.3 PV pulse of ³H₂O-electrolyte solution was then introduced to the monolith followed again by ³H-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 ³H₂O 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 Na₂SO₄, 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 ³H tracer.

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

2900TR, PerkinElmer, Boston, MA) – 2 mL of effluent sample was mixed with 10 mL of scintillation cocktail (Packard Ultima Gold, Boston, MA) and counted for 20 min.

2.4. Contaminant distribution in the monolith

At the end of the 377-day experiment, the electrolyte solution in the monolith was allowed to drain under gravity and the crude coal tar source was removed. Six mini-core samples from one half of the monolith, ranging in depths of 13–22 cm, were extracted using a 2.2 cm ID stainless steel soil probe (AMS, American Falls, ID). The cores were split into 3.5–5 cm long sub-sections for extraction of coal tar compounds using an accelerated solvent extractor (ASE 300, Dionex, Sunnyvale, CA). The extraction protocols and quality control procedures were according to US EPA Method 3545A [12]. All matrix samples were spiked with bromonaphthalene to measure extraction efficiency. The final extracts were concentrated to 2.0 mL and stored at -20°C pending GC/MS analyses.

2.5. Measurement of coal tar compounds with GC/MS

All extracts from water and soil samples were analyzed using GC/MS (Agilent 6890/5973N, Santa Clara, CA) according to US EPA Method 8270D (method to analyze semivolatile organic compounds by GC/MS) [12].

2.6. Preparation of thin-sections

The saprolite monolith was cut in half along the center of the monolith and one half was air-dried in a fume hood for approximately 30 days and then impregnated with polyester boat resin, and sliced into smaller sections. The trimmed samples were cut into smaller segments, coated with Hillquist[®] 7A and B formula thin-section epoxy resin, polished, and slices were cut off from the soil billets using a low-speed microtome equipped with a diamond saw blade. These slices were then mounted on a microscope slide and polished to optical thickness of about $30\ \mu\text{m}$, using methods described previously [7]. The thin sections were examined with polarized-light microscopes equipped with epi-fluorescence (UV) attachments, to determine pore structure and the extent of migration of immiscible tar into the fractures and macropores.

2.7. Moment analyses

Moment analysis was applied to the breakthrough curves for estimating the mass and mean travel time (\bar{t}) of the center of mass of each compound recovered in the effluent as

$$\text{mass} = \sum_{i=1}^n C_i$$

$$\bar{t} = \frac{\sum_{i=1}^n C_i t_i}{\sum_{i=1}^n C_i} - \bar{t}_0 \quad (1)$$

where C_i is the concentration, t_i is sampling time and \bar{t}_0 is the mean travel time of the corresponding step input [13–15]. As a first approximation, the coal tar source in the monolith was considered to be an infinite source for all coal tar chemicals and hence a step input. These calculations were performed only on data from the initial 233-day period (i.e., $\bar{t}_0 = 233/2 = 116.5$ days). Retardation factors (R) were also calculated by normalizing mean travel time of each compound with that of $^3\text{H}_2\text{O}$ tracer.

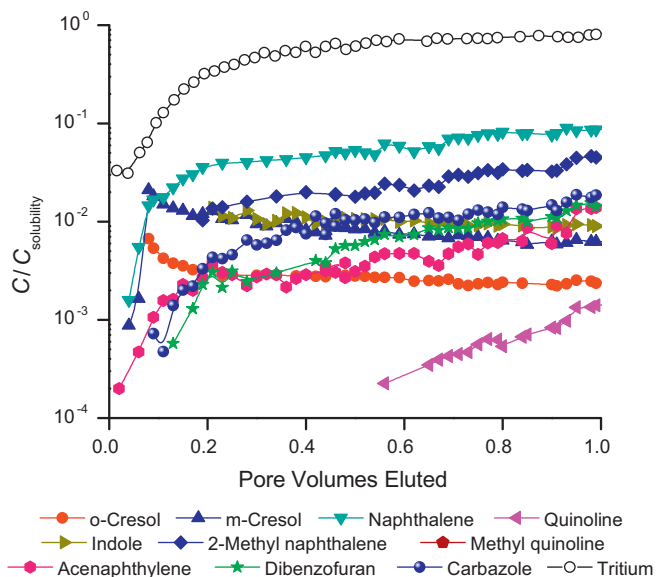


Fig. 1. First pore volume of elution curves of 10 coal tar compounds. Tritium tracer breakthrough curve is also shown. Note the tritium concentration is expressed as ratio of initial tritium concentration and coal tar concentrations are expressed as ratios of aqueous solubilities estimated using Raoult's Law.

3. Results

3.1. Tritium transport in residuum monolith

Tritiated water arrived in the effluent within the first 0.1 PV following both tracer pulse injections (Figs. 1 and 2). Breakthrough curves for both $^3\text{H}_2\text{O}$ pulses were nearly identical indicating that water flow did not change significantly within the monolith over the course of the experiment (Fig. 2). Nearly 80% of the injected tracer was recovered in the effluent for both pulses, with the remainder presumably diffused in the residuum matrix. The asymmetrical shape of the breakthrough curves (Fig. 2) was also nearly identical for both pulses. Electrolyte injection through the monolith was interrupted for 32 days after 233 days. When flow was resumed (Fig. 2), $^3\text{H}_2\text{O}$ concentrations in the effluent were approximately twice that observed immediately before the flow interruption and then quickly declined to pre-interruption levels, which demonstrates that matrix diffusion plays an important role in solute transport in this material.

3.2. Dissolution and transport of coal tar compounds in residuum monolith

The 10 target compounds made up approximately 14% by mass of the crude coal tar (Table 1). Naphthalene was the most dominant compound (8.6% by mass), followed by acenaphthalene (1.67%), dibenzofuran (0.97%), and 2-methyl naphthalene (0.91%). Since aqueous solubilities are only available for pure organic compounds, Raoult's Law was used to estimate the effective aqueous solubility of these compounds in complex mixtures by multiplying the mole fractions with corresponding aqueous solubility of the pure liquid organic compound [e.g., 16, 17]. Of the monitored compounds, cresols were the most soluble and dibenzofuran was the least soluble (Table 1). Nine of the 10 coal tar compounds monitored appeared in the effluent within the first PV of the injection (Fig. 2). Concentrations of most compounds in the effluent initially rose sharply followed by a slower increase for 233 days (14.4 PV, Fig. 2). The main exceptions were cresols and indole, for which concentrations rose sharply to their highest levels within the first 0.2 PV and then progressively decreased over time. During the initial

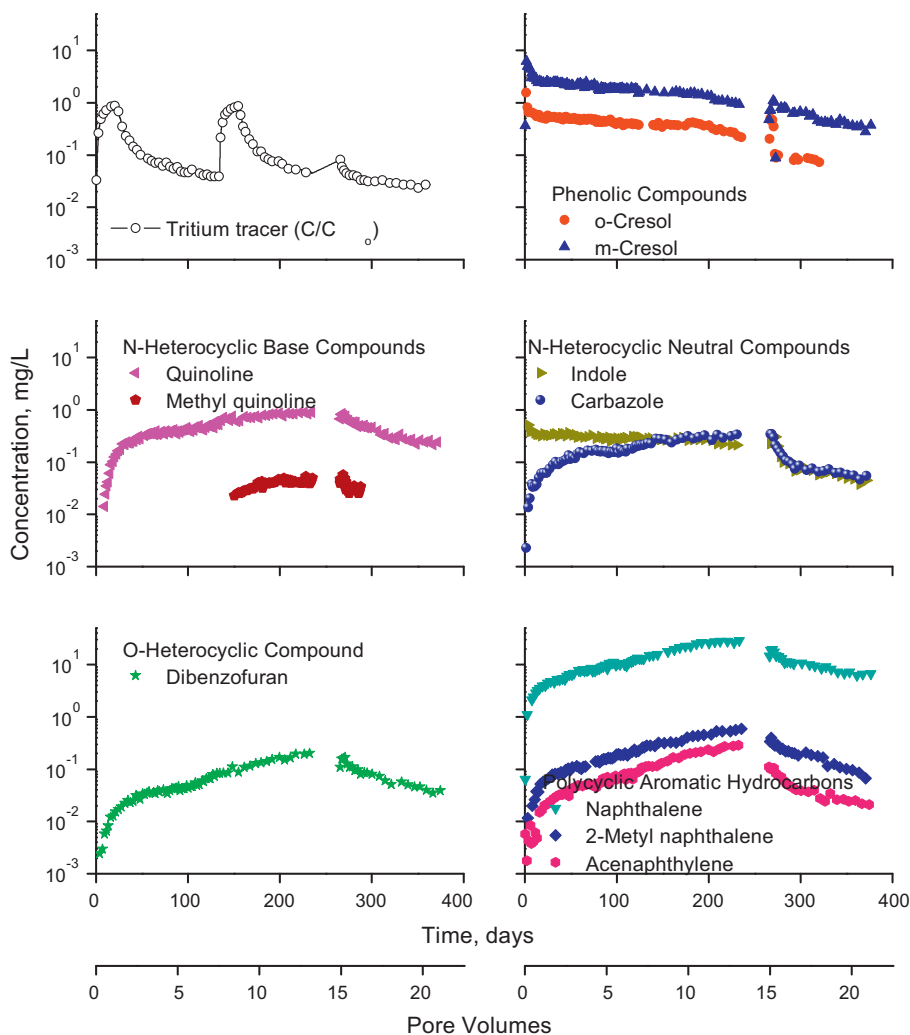


Fig. 2. Breakthrough of 10 coal tar compounds from the residuum monolith. Tritium breakthrough curve is also plotted in the first panel. The compounds appear in separate panels classified according to their structure. Notes: Flow through the monolith was interrupted for approximately 32 days after the monolith was flushed for 233 days. Tritium tracer is expressed as normalized concentration (C/C_0). The symbols indicate specific coal tar compounds and follow the same color and symbol scheme as shown in Fig. 1.

233 days, the maximum effluent concentration for most coal tar compounds was significantly lower than the corresponding effective solubility. Only naphthalene (107%) and 2-methyl naphthalene (155%) effluent concentrations exceeded corresponding effective solubilities. Maximum effluent concentrations for cresols, indole, quinoline, and methyl quinoline were $2.5 \pm 1.4\%$ (\pm SD) of their effective solubilities while those of carbazole, acenaphthylene, and dibenzofuran were 27–58% of corresponding values.

Due to nonideal behavior during transport, moment analysis was applied to estimate the mass, mean travel time (\bar{t}), and retardation factor (R) of each compound recovered in the effluent (Table 1). The R values for all compounds were >1 – for cresols and indole, R was between 2.5 and 8.5, and was >20 for the remaining compounds (Table 1).

The estimated mass recoveries for the 10 coal tar compounds at the end of 377 days were compared with the mass of coal tar emplaced in the monolith. A significant mass of the emplaced coal tar compounds were retained in the monolith, as indicated by the relatively low recovery of those compounds in the effluent. Recovery of *o*-cresol and *m*-cresol were estimated to be 27% and 56%, respectively, while naphthalene, quinoline, and indole were estimated to be between 23 and 33%. Of the remaining compounds, $<5\%$ of their initial mass eluted from the monolith (Table 1).

After the electrolyte injection into the monolith was resumed following a 32-day interruption, the concentrations of some coal tar compounds in the effluent briefly increased compared to concentrations measured just prior to flow interruption (Fig. 2). However, the concentrations of all compounds declined soon thereafter. This decline was gradual in most cases, but the rate was faster in case of indole and carbazole. Methyl quinoline was not detected in the effluent approximately 20 days (0.9 PV) after the electrolyte injection was resumed. In addition, *o*-cresol was also not detected in the effluent 65 days (4.0 PV) following resumption. The calculated masses from the post-interruption elution were insignificant compared to that eluted prior to the interruption.

3.3. Distribution of coal tar in the monolith

The 10 coal tar compounds were detected in all soil cores (Fig. 3), even though the cores were extracted at different depths and distances from the immiscible coal tar source. The highest concentrations in the fine-grained matrix were located at different regions of the monolith for different compounds – naphthalene and quinoline hotspots appeared close to edge of monolith while *m*-cresol, dibenzofuran, and carbazole hotspots appeared closest to the source. The concentrations were usually higher in the upper

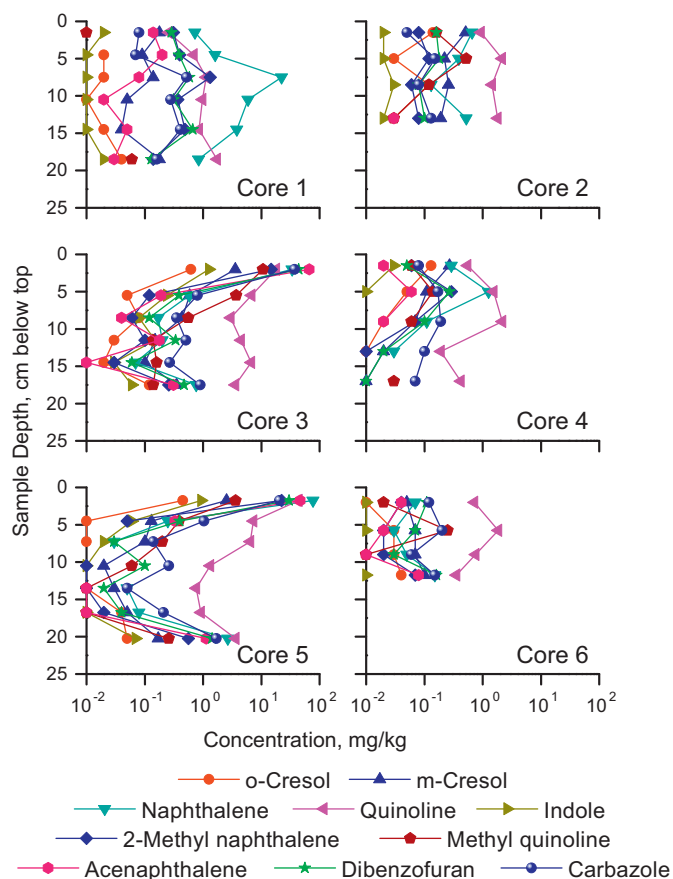


Fig. 3. Vertical distribution of the coal tar compounds measured in subsamples from the six cores. The symbols indicate specific coal tar compounds and follow the same color and symbol scheme as shown in Fig. 1.

5–10 cm and decreased with depth (the source was placed to a depth of 6.7 cm below top of the monolith). Petrographic analysis of thin-sections prepared from the undisturbed portion of the monolith indicated transport of tar (1–2 mm) into the adjacent fine-grained matrix (Fig. 4), while tar entered up to 1 cm into macropores and fractures adjacent to the source. This confirms that the immiscible tar source was nearly immobile during the elution experiment. Bright regions of fluorescence were observed in all thin-sections when exposed to UV light indicating presence of aromatic hydrocarbons. The matrix adjacent to some macropores also shows strong indication that coal tar compounds had diffused into the matrix while transport of dissolved compounds occurred within the macropores. The residuum matrix is inherently low in natural organic matter and hence, the fluorescence is attributed to the presence of coal tar derived-aromatic hydrocarbons as was confirmed from the chemical analysis of core samples. Similar fluorescence was observed from thin-sections prepared from fine-grained material at a coal tar contaminated site [18].

4. Discussion

Eight out of ten compounds did not reach Raoult's Law estimated solubility limits in effluent concentrations (Fig. 2) due to a combination of factors such as dilution, dissolution, and sorption. In general, concentrations of neutral compounds were closer to the estimated solubility limits compared to concentrations of ionic compounds. Measured values of aqueous solubilities tend to be lower than those estimated using Raoult's Law [e.g., 19, 20].

Most of the emplaced source was still present in all injection holes (based on volume estimates) at the end of the experiment,

even though the chemical composition had changed due to dissolution of higher solubility coal tar compounds. Thin section photomicrographs of the source area indicated that coal tar did not migrate far (<1–2 mm) from the source, confirming that transport of immiscible coal tar was negligible and that the primary mode of transport was dissolution followed by advective transport through the fractures and macropores, as well as through diffusion into the fine-grained matrix. The fast initial solute breakthrough patterns (<0.2 PV for 7 of 10 compounds, Fig. 1) indicated that dissolution occurred rapidly at the source. The subsequent more gradual increase in concentration (Fig. 2) is attributed to two factors: (i) diffusion of coal tar compounds from inside the emplaced source to tar–water interface is kinetically driven and hence affects dissolution and subsequent transport and (ii) slower advective and diffusive transport that occurs primarily in the fine pores of the matrix, where the potential for retardation by sorption is also greater.

Solute retardation, measured by comparing mean arrival time of solutes with that of the $^3\text{H}_2\text{O}$ tracer, was used as an indicator of sorption (Table 1). With the exception of cresols and indole, all compounds were significantly retarded ($R > 10$) during transport. Cresols, which are weak acids, and indole are present in neutral form at experimental conditions (pH 4–5), and were relatively less retarded due to their higher solubility and lower sorption affinity. Quinoline and methyl quinoline are organic cations at pH 4–5 and were significantly retarded, potentially due to sorption to negatively charged clay-rich residuum matrix (Table 1). The residuum matrix is moderately acidic with pH between 4.5 and 6, increasing the potential for sorption of cations. In addition, sorption seemed to increase for N-heterocyclic compounds that have methyl group attached to the parent compound (methyl quinoline vs. quinoline). Broholm et al. [23] reported that several heterocyclic bases were strongly sorbed in natural clayey tills by multilayer sorption or condensation. Neutral compounds (PAHs, carbazole, and dibenzofuran) can sorb either to organic coatings on minerals [24], or to the mineral surfaces themselves in the case of geologic materials with very low organic content [e.g., 11, 25]. However, it is expected that the low solubility of these compounds decreased the solute mass available for sorption and hence apparently high retardation. Quantitative prediction of R values using independent sorption and diffusion transport experiments has previously been shown to be difficult [21,23]. The contributions of diffusion and sorption are usually inseparable and strongly influence retardation of organic compounds. Diffusion and sorption coefficients were not independently measured for the compounds in this study and hence it was not possible to quantitatively predict R values. The potential for sorption increases due to exposure of solutes to a greater volume of porous media during diffusion [19,20].

Concentrations of almost all of the coal tar compounds decreased significantly the following 32 days of flow interruption (Fig. 2) and the decline continued for the rest of the experiment. A temporary decline in the concentration was expected, due to diffusion from the fast flow pathways into the matrix, but surprisingly the decline persisted. One possibility is that a “skin” may have developed on the tar source during the period of quiescence that impeded further dissolution. This has been observed in complex NAPL mixtures (coal tar, petroleum, etc.) where interfacial films (skin) on the surface of immiscible phase NAPLs that have been in contact with water when aged for few days in quiescent conditions [26,27]. Alternately, the decline in concentrations could occur due to enhanced microbial mediated degradation of coal tar compounds [e.g., 28, 29]. Sodium azide was added to the influent water is a microbial inhibitor, but it is possible that the flow interruption in some way allowed the microbial communities to recover and begin degrading the coal tar compounds.

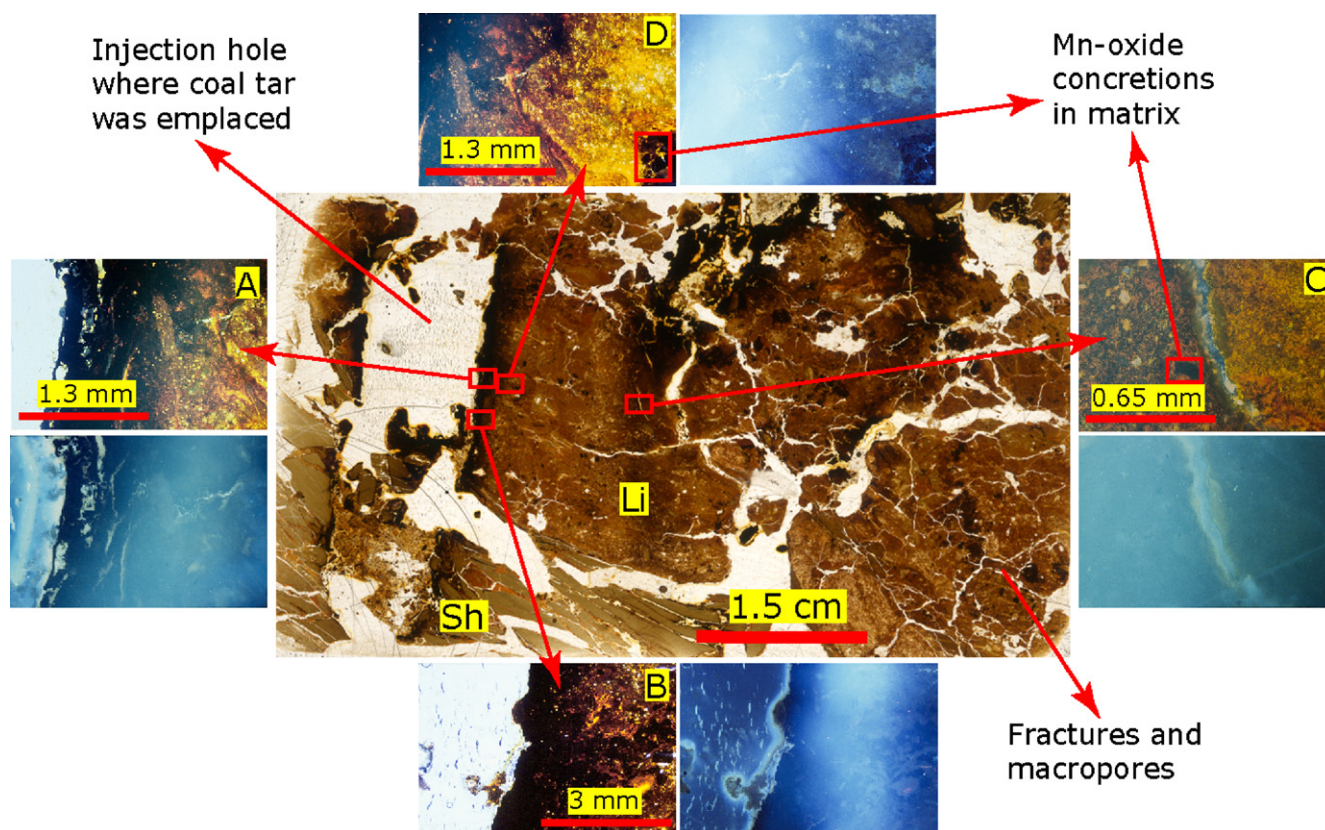


Fig. 4. A thin-section prepared for a section of column along the holes drilled for coal tar emplacement (center image). Smaller images are photomicrographs of different areas within the thin section along injection hole (A and B), a macropore (C) and limestone matrix (D). Discrete and interbedded limestone (Li) and shale (Sh) lithological sub-units are identified. The photomicrographs were taken under plane-polarized light (PPL) and under wideband ultraviolet (WUV) light. Clear areas in PPL photomicrographs are pores filled with epoxy; some pores are natural whereas others were enhanced by desiccation-induced shrinkage during thin-section preparation. The small areas on the thin-section (A–D) as seen under WUV light fluoresce brightly (blue images) indicating the presence of organic compounds within the matrix or macropores. Note that the black Mn-oxide concretions in the matrix and some fractions of coal tar do not fluoresce under WUV light. Abundant fractures and macropores are also visible throughout the thin sections. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

5. Conclusions

The emplaced immiscible coal tar was not mobile in the highly fractured clay-rich residuum, with only a few large fractures showing signs of penetration by immiscible coal tar. However, coal tar compounds from the emplaced source quickly dissolved and were transported throughout the residuum even though only a small portion of the surface area of the emplaced source (1–3%) was exposed to the fast-flow pathways along the fractures and macropores. This suggests that diffusion into the fine-grained matrix and slow advection in fine pores plays a significant role in dissolution and transport of compounds from DNAPL sources in this kind of material. The study clearly showed that a wide variety of dissolved PAH compounds, including those with relatively low solubility, can experience substantial transport in groundwater in fractured clay-rich materials. Coal tar can act as a persistent source of PAH contamination in groundwater as evidenced by the large percentage of many PAHs remaining in the residuum monolith after 377 days of flushing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.12.023.

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