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Enhanced Concentrations of PAHs in Groundwater at a Coal Tar Site

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Concentrations of polycyclic aromatic hydrocarbons (PAHs) in groundwater at a coal tar site were elevated by factors ranging from 3 (pyrene) to 50 (indeno[1,2,3-*cd*]-pyrene) over purely dissolved concentrations. Air−groundwater surface tension measurements (70.6 ± 3 dyn/cm) were not sufficiently different from air−pure water measures (72.2 ± 0.1 dyn/cm) to ascribe the observed enrichments to either cosolvents or surfactants in the groundwater. Excess pyrene was associated with colloids that passed an ultrafilter at ambient pH but became ultrafilterable when the groundwater pH was lowered to 1. This suggested pyrene association with humic acids. Given the decrease in groundwater total organic carbon (TOC) of 4 mg_C/L upon acidification and ultrafiltration, a partition coefficient of 10^5 L/kg_C was estimated for this pyrene association. Use of the results for pyrene and scaling for the differences in PAH hydrophobicities enabled good predictions of the observed enrichments of less water-soluble PAHs in the groundwater. This is strong field evidence indicating colloid-facilitated transport of HOCs in groundwater. Assuming that humic-bound PAHs were as mobile as the dissolved PAHs, the fluxes of individual PAHs (e.g., benzo[*a*]pyrene) from the tar source were as much as 20 times greater than estimates based solely on tar−water partitioning predictions.

Introduction

The total masses of hydrophobic organic compounds (HOCs) that are mobile in groundwater may include both dissolved and colloid-associated species. Dissolved forms may include HOC molecules solvated by water or mixtures of water and nonaqueous solvents. Colloid-associated species include HOC molecules carried in water-borne media such as macromolecular humic substances, biogenic exudates, micelles, microorganisms, and nanometer-to-micrometer-sized suspended mixed-phase solids (e.g., organic-coated kaolinite.) To the extent that various species are important relative to the fully water-solvated species, “facilitated” subsurface HOC transport may occur. As a result, sensitive receptors, such as groundwater wells and surface water bodies, may receive HOCs sooner, and the HOC fluxes may be greater than would be expected in the absence of such “facilitating” species. Indeed, efforts to cleanup subsurface sites using surfactant-generated micelles are cases of promoting facilitated transport.

In order for facilitated transport *by colloids* to be important: (i) colloids must be present, suspended in the groundwater; (ii) HOCs must associate with these colloids sufficiently to enhance the mobile load; and (iii) the colloids must be substantially transportable through the subsurface (*1*). Evidence for each of the three conditions has been found at various field sites and in focused laboratory studies. Laboratory studies have shown that various colloidal materials may increase the total aqueous concentrations of HOCs. These include humic substances (*2*−*4*), organic matter-coated mineral particles (*5*), anthropogenic surfactants/micelles (*6*, *7*), microorganisms (e.g., bacteria; *8*), and microbial exudates (*9*, *10*). Enhanced mobilization of HOCs in the presence of these agents has been demonstrated through the use of miscible displacement experiments with laboratory soil columns (*4*, *6*, *8*, *10*, *11*). [Note that the mass fraction of mobile HOC that is colloid associated is a function of both the HOC colloid−water partition coefficient and the abundance of colloids (*12*).]

Several field studies also suggest the potential facilitated transport of HOCs in contaminated aquifers. Polycyclic aromatic hydrocarbon (PAH) concentrations in groundwater from a coal tar site were greater than levels estimated from the tar composition using Raoult’s law (*13*). In this case, it was suggested that colloids were present in the groundwater; however, the colloid phase was not isolated or characterized. Colloids, capable of binding HOCs, have been verified in groundwater from a crude oil site (*14*) and a sewage plume (*15*) by spiking hydrophobic compounds into groundwater samples. However, no evidence was obtained for “enhanced” HOC groundwater concentrations or fluxes at these sites. Colloid-associated PAHs were quantified in size-separated samples from two creosote-contaminated sites (*16*). In this case, it was suggested that the hydrophobic compounds were associated with clays and quartz- and iron-containing colloids. Colloid-associated polychlorinated biphenyls (PCBs) and PAHs have also been quantified in size-separated samples from a landfill leachate plume (*17*). In that instance, most of the contaminant mass was associated with particles greater in size than 1 μm. Consequently, it seems unlikely that these particles were substantially mobile under the ambient groundwater gradient at this site. Thus, while other studies of varied sites have shown some evidence for enhanced HOC transport due to colloids, no field observations have shown conclusive evidence by simultaneously demonstrating enhanced in situ mobile HOC concentrations and the presence of substantially mobile colloidal species, which may facilitate HOC tranport.

The purpose of this study was to assess whether colloid-associated species contributed significantly to the mobile PAH load in groundwater at a coal tar site. Aqueous PAH concentrations were evaluated using both calculations based on the site’s tar composition and tar−water equilibrations in the laboratory. These dissolved concentrations were then compared with total PAH levels in groundwater samples carefully collected by prolonged slow pumping at the site. Fractionated extractions of groundwater were used to determine in situ colloid-associated PAHs after further prolonged settling (5 months) and again after precipitating humic acids using acidification and ultrafiltration. Colloid−water partition coefficients were quantified using these fractionated extractions and by fluorescence quenching in the raw groundwater. The results were used to estimate the effect of colloid-facilitated transport on PAH fluxes away from the coal tar source.

Methods

Chemicals. Solvents used for extraction of groundwater and dissolution of compounds were methanol, methylene chlo-

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ride, and hexane (OmniSolve, EM Science). Internal standards of deuterated phenanthrene, *p*-terphenyl, and *m*-terphenyl were obtained from Ultra Scientific (North Kingstown, RI). External PAH standards were obtained as EPA 525 Mix A (Supelco, Bellefonte, PA). Pyrene was obtained from Aldrich (Milwaukee, WI). Other compounds included sodium sulfate (Fisher Scientific, Fairlawn, NJ), silica gel (100−200 mesh, EM Science), potassium hydrogen phthalate (Sigma, St. Louis, MO), hydrochloric acid (Fisher), and phosphoric acid (Mallinckrodt, Paris, KY). Purified water (18 MΩ·cm) was from an Aries purification system (Vaponics, Rockland, MA).

Sample Collection. The groundwater samples were collected from a shallow, water-bearing unit composed of anthropogenic fill materials at a mid-Atlantic coal tar site. As is typical of such sites (*18*), the tarry deposits occur in land adjacent to a surface water body. Seven stainless steel multi-level wells with 0.6-m-long stainless steel screens (0.05-cm slots) were installed in December 1994 using hollow-stem auger drilling with no drilling fluids. Groundwater samples were collected during five field campaigns between December 1995 and September 1996. Slow pumping techniques, with continuous monitoring of sample turbidities, were employed to minimize entrainment of immobile particles in groundwater samples (*13*). Packers were used to isolate the 60-cm screens from the overlying standing water. The pump flow rate (25−35 mL/min) was set so that the well screen withdrawal velocity did not exceed the local groundwater velocity. After prolonged purging, 2-L samples were collected in amber bottles for total (dissolved + colloid-associated) PAH analysis. Groundwater was also collected in all-glass biological oxidation demand (BOD) bottles for organic carbon analysis. Groundwater (0.5−2 mL, followed by 10 mL of purified water rinse) was also filtered through 30-nm poresize Nuclepore (Pleasanton, CA) filters for microscopic analysis of groundwater particles. Well W40M consistently showed the greatest PAH concentration enhancements. Therefore, replicate samples were collected from this well in September 1996 in foil-wrapped BOD bottles for fluorescence quenching studies and fractionation efforts aimed at elucidating the in situ pyrene speciation. These duplicate samples were stored undisturbed (i.e., allowing particle settling) at 4 °C for 5 months before use.

Ancillary Data. Groundwater turbidity, conductivity, pH, and E_H were measured in the field. Conductivity (HI8333, Hanna Instruments), pH (Orion), and redox potential (platinum electrode, Orion) were monitored continuously during pumping. Turbidity was measured periodically by redirecting the pumped flow through another flow-through cell and a calibrated turbidimeter (DRT-15CE, HF Scientific, Inc.) Dissolved oxygen and sulfide were measured periodically using colorimetric assays (Chemettes, Chemetrics, Calverton, VA).

Levels of inorganic ions in the groundwater were determined by ion chromatography (Dionex Ion Chromatograph 16.) A 1-mL sample was transferred to the AS4A-SC column (Dionex) and eluted with 3 mM sodium bicarbonate/2.4 mM sodium carbonate buffer flowing at a rate of 2 mL/min. Ions were quantified using response factors determined with external standards. Metal concentrations were determined by graphite furnace atomic absorption spectrometry using a Perkin-Elmer 4100ZL instrument. Standards were made up in Q-water (Millipore, Bedford, MA). Alkalinity titrations were performed by Gran titration with 20 mM HCl and an Orion pH electrode/meter.

PAH Analyses. Groundwater PAH concentrations were quantified by liquid−liquid extraction and gas chromatographic separation. Immediately after sample collection, an internal recovery standard of deuterated phenanthrene in methanol was added to each sample. Methylene chloride (100 mL) was then added to the bottles to begin the extraction process and to preserve the samples during transportation. At the laboratory, a second recovery standard of *p*-terphenyl in methanol was added without disturbing the methylene chloride layer. A total of three methylene chloride extractions (100 mL each) were made, combined, and dried with anhydrous sodium sulfate. The extract was reduced to a small volume in a Kuderna−Danish concentrator and then transferred into hexane for further concentration to 1 mL under a stream of nitrogen. A PAH fraction was isolated by silica gel chromatography [2 g of fully activated SiO_2, eluted with 24 mL of hexane, 5 mL of 8:1 hexane:methylene chloride, and finally 15 mL of 3.4:1 hexane:methylene chloride (*19*)]. The PAHs were quantified by capillary gas chromatography using a flame ionization detector (FID) (Carlo Erba, HRGC, on-column injection, 30 m DB5-MS column, 0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA). An injection standard of *m*-terphenyl was added just prior to analysis to quantify the final volume of the extract. The temperature program began at 70 °C with a ramp of 12 °C/min to 120 °C, followed by a ramp of 3 °C/min to 175 °C, a ramp of 8 °C/min to 300 °C, and a final hold time of 5 min at 300 °C. Compounds were quantified by using response factors from contemporaneous injections of known external PAH standards. Phenanthrene and anthracene concentrations were corrected with deuterated phenanthrene recoveries, and all other PAHs were corrected for recovery with *p*-terphenyl, a hydrophobic internal standard ($\log K_{ow} = 6.03$; *20*) that could be detected by FID.

Tar−Water Equilibrations and Tar Analysis. A sample of free-flowing tar was pumped from W40M in April 1996. PAH concentrations in this tar were quantified by gas chromatography, as described above (start temperature 35 °C), after diluting an aliquot of tar into methylene chloride. This tar sample was assumed representative of all the wells sampled, as the greatest distance between any well and W40M was only 18 m. This was ultimately borne out as PAH concentrations in other tar samples obtained 1 (A. A. MacKay, unpublished results) and 30 m (*21*) from W40M differed by less than 10% from levels found in the W40M tar.

Tar (3 mL) was also mixed with 2 L of purified water containing sodium chloride (1 g/L) to match the site groundwater conductivity and mercuric chloride (1 mg/L) to inhibit compound biodegradation. The two phases were mixed with a stir bar for 2 days, and the dispersed tar droplets were allowed to settle for 2 months before sampling. The aqueous phase was carefully siphoned into a separatory funnel using aluminum tubing, primed with purified water. This sample was spiked with deuterated phenanthrene and *p*-terphenyl and extracted as outlined above.

Fractionated Extractions of Groundwater. Pyrene was quantified in a series of fractions of the W40M groundwater. First, solids were allowed to settle from solution over a 5-month standing period. (Assuming Stokes settling and a particle density of 1.05 g/cm^3, all particles greater than 1.2 μm in diameter would have settled in this time.) Next, the supernatant was gently siphoned from the BOD bottle, leaving a small, undisturbed volume of water containing the settled solids. (The siphon tube was a piece of aluminum tubing primed with purified water, introducing less than 8 mL to the 270 mL transferred volume.) The small volume of water remaining in the original sample bottle was spiked with an internal standard of *p*-terphenyl and extracted in the bottle with methylene chloride. This extract was denoted the “settled solids + walls” fraction and contained pyrene associated with settled solids and any pyrene species that may have adhered to the glass walls, including tar-associated pyrene.

The siphoned supernatant contained the dissolved species plus any pyrene associated with stable colloids. This fraction (initially at pH 5.6) was acidified to pH 1 with hydrochloric acid. The sample was allowed to stand for 3 days while acid-

TABLE 1. Physical and Chemical Groundwater Parameters from Several Wells at a Coal Tar Site in September 1996[a]

	well id						
parameter	W20M	W20S	W40M	W40S	W100D	W100M	W100S
pH	5.4	5.5	5.6	5.4	5.3	5.5	5.6
turbidity (NTU)	1.4	2.3	0.5	1.6	7.2	7.8	4.3
conductivity (mS)	1.95	1.37	1.76	1.32	1.50	2.23	2.44
redox potential (mV, H° scale)	−51	−82	−31	−110	−16	29	−76
dissolved oxygen (μM)	<1	<0.3	<0.3	6	<6	5	<0.5
alkalinity (meq/L)	27.2	15.7	19.2	14.6	15.4	18.6	15.1
nonpurgeable organic carbon (mg/L)	45	34	34	28	33	33	40
$S^{2-}{}_{total}$ (μM)	<80	1600	<80	1600	<80	<80	800
$SO_4{}^{2-}$ (μM)	2000	300	<1	1400	na	20	1400
Al_{total} (μM)	30	20	4	7	17	31	80
$Al_{dissolved}$ (μM)	1	1.4	2	1	9	2	10
Fe_{total} (μM)	13	37	40	5	100	370	83
$Fe_{dissolved}$ (μM)	3	70	3	3	12	4	7
Si_{total} (μM)	na	na	1500	na	na	na	1600
$Si_{dissolved}$ (μM)	na	na	1000	na	na	na	1300

[a] na indicates samples that were not analyzed.

precipitated material settled out. The siphoning procedure was then repeated. The remaining volume was spiked, extracted, and referred to as the "pH 1 precipitate" fraction. The second siphoned supernatant contained dissolved pyrene and any colloids not precipitated under acidic conditions. This volume of water was also spiked with *p*-terphenyl and extracted with methylene chloride. This fraction was called the "pH 1 dissolved" fraction. The methylene chloride extracts were transferred to hexane and analyzed by capillary gas chromatography, as described above.

Fluorescence Quenching. Fluorescence quenching (*15*, *22*) measurements were made with water samples siphoned from the collection vessels to include only the colloids stable over a 5-month period. Fluorescence of an added pyrene probe was measured with a Perkin-Elmer LS50B luminescence spectrometer. The excitation wavelength was 334 nm (slit width 4 nm), and the emission wavelength was 373 nm (slit width 4 nm). The absorbances at these two wavelengths were measured on a Beckman DU 640 spectrophotometer to correct for the inner filter effect (*22*). The linearity of a Stern−Volmer plot was verified by a dilution series (minimizing coagulation artifacts that might have occurred with a colloid concentration approach). Subsequently, single-point measurements were made at only one quencher concentration. Background fluorescence readings of a 3-mL water sample were taken before pyrene addition. Four 50-μL aliquots of a pyrene in methanol stock solution were sequentially added to the cuvette. The cuvette was allowed to stand for 10 min after each addition before fluorescence measurements were made. In all cases, fluorescence response was linear, suggesting that the relatively high carrier solvent concentration did not change the probe partition coefficient. Thus, the maximum error that would result from this approach was estimated from the 1.6% methanol in water solution (i.e., 50 μL of stock aliquot) and found to underestimate the colloid−water partition coefficient by 20% (*12*). Fluorescence response was quantified as the slope of a plot of background-subtracted fluorescence versus added-pyrene concentration. A duplicate sample with 3 mL of oxygen-free (<0.3 μM, Chemettes, Chemetrics, Calverton, VA) purified water was treated identically to quantify pyrene fluorescence in the absence of O_2 quenching. All sample manipulations were made in an argon or nitrogen atmosphere.

Organic Carbon Measurements. Total organic carbon (TOC) in water samples was determined with a high-temperature Shimadzu TOC-5000 organic carbon analyzer. Samples were acidified to pH 3 with phosphoric acid and bubbled with nitrogen or argon for 10 min to remove inorganic carbon. Triplicate TOC measurements were made, and the high temperature oxidation system was externally calibrated with potassium hydrogen phthalate standards.

For the W40M groundwater with pH 1, acid-precipitated material was separated from acid-stable organic carbon by centrifuge ultrafiltration. Centricon 3 (Amicon, Beverley, MA) filter cartridges were used to separate organic carbon with a nominal cutoff of 3000 Da (*23*). Before use, the filters were washed with methanol, followed by repeated washes with purified water until the TOC of the filtrate was indistinguishable from purified water. Acidified samples were ultrafiltered by centrifuging for 2 h at 800*g*. Subsequent TOC measures of the filtrate were made as described above.

Surface Tension. Groundwater surface tension measurements were made by the falling drop method (*24*). Measurements of purified water surface tension were made to verify this method. A value of 72.2 ± 0.1 dyn/cm ($n = 5$) was calculated for purified water and compares reasonably with the reported value of 71.97 dyn/cm at 25 °C (*25*).

Calculation of Partition Coefficients. Partition coefficients of colloidal materials were calculated from enhancement factors:

$$E = \frac{C_T}{C_w} = 1 + \sum [\text{colloid}] K_{\text{colloid}} \tag{1}$$

where E is the enhancement factor, C_T (mg/L) is the total compound concentration in a bulk (dissolved + colloid-associated) water sample, C_w (mg/L) is the dissolved concentration as measured by tar−water equilibration, [colloid] (kg/L) is the colloid concentration, and $K_{colloid}$ (L/kg) is the colloid−water partition coefficient. In the case of fluorescence quenching, the total compound concentration was assumed proportional to the background-subtracted fluorescence of a supernatant after the colloid phase had been removed (F_0). The dissolved concentration was assumed proportional to the background-subtracted fluorescence in the colloid-containing sample (F_1) and assuming the colloid-associated probe is fully quenched.

Results and Discussion

Groundwater Characteristics. Groundwater, pumped slowly on five dates from seven wells at the site, exhibited a range of properties (Table 1). Some parameters were fairly invariant between wells; for example, pH values only ranged from 5.3 to 5.6, electric conductivities only varied from 1.32 to 2.44 mS, alkalinities were between 15 and 27 mM, and non-

TABLE 2. Aqueous and Tar Concentrations of Polycyclic Aromatic Hydrocarbons[a]

		equilibrium aq concn (mg/L)		Apr. 10, 1996, groundwater concn (mg/L)	
compd and abbrev	tar concn (mg/L)	calcd	measd	W40S	W40M
phenanthrene, PH	19 700	0.11	0.073	0.063 ± 0.0007	0.12
anthracene, AN	5 000	0.027	0.012	0.011 ± 0.001	0.02
fluoranthene, FL	6 500	8.7×10^{-3}	3.3×10^{-3}	$3.8 \times 10^{-3} \pm 5 \times 10^{-4}$	0.015
pyrene, PY	9 300	6.4×10^{-4}	1.4×10^{-3}	$2.5 \times 10^{-3} \pm 5 \times 10^{-4}$	0.011
benz[*a*]anthracene, BA	3 900	6.9×10^{-4}	7.7×10^{-4}	$3.8 \times 10^{-4} \pm 5 \times 10^{-5}$	7.9×10^{-3}
chrysene, CH	3 600	9.6×10^{-4}	6.8×10^{-4}	$4.2 \times 10^{-4} \pm 3 \times 10^{-5}$	6.3×10^{-3}
benzo[*b*&k]fluoranthene	4 300	*b*	2.4×10^{-4}	$1.8 \times 10^{-4} \pm 5 \times 10^{-5}$	3.4×10^{-3}
benzo[*e*]pyrene	3 700	*b*	1.9×10^{-4}	$1.4 \times 10^{-3} \pm 1.4 \times 10^{-3}$	3.4×10^{-3}
benzo[*a*]pyrene, BaP	3 600	1.1×10^{-4}	3.5×10^{-4}	$1.7 \times 10^{-4} \pm 9 \times 10^{-4}$	5.8×10^{-3}
indeno[123-*cd*]pyrene, IP	1 200	*b*	6.2×10^{-5}	$7 \times 10^{-5} \pm 4 \times 10^{-5}$	2×10^{-3}
benzo[*ghi*]perylene, BP	1 200	6×10^{-5}	1.6×10^{-4}	$6 \times 10^{-5} \pm 3 \times 10^{-5}$	2×10^{-3}

[a] W40S groundwater concentrations are the average and standard deviation of 3 samples obtained over a 36-h period. [b] Experimental solubility not available.

purgeable organic carbon varied between 28 and 45 mg_C/L. [Note that while these organic carbon concentrations appear large in comparison to pristine aquifers (*26*), 8−11 mg/L reflect dissolved coal tar components, primarily naphthalenes.] Generally, the groundwater was reducing (+29 down to −110 mV), and oxygen was very low or absent ($\leq 6\ \mu$M). Sulfide was present ($>800\ \mu$M) in the three wells screened nearest the water table, but this reduced sulfur species was not detected in the corresponding deeper groundwater ($<80\ \mu$M). Sulfate was found in the water at every well except W40M.

Some parameters suggested the presence of colloidal phases suspended in these water samples (Table 1). Although the groundwater samples were always "clear" to the naked eye after many hours of slow pumping, light scattering above instrument background (ca. 0.1 NTU) was always seen. This scattering was as low as 0.5 NTU in well W40M and as high as 7−8 NTU in wells W100D and W100M. Well-to-well variations in turbidity or total scattered light likely resulted from differences in the composition of colloidal materials at the different wells. For example, filterable iron was 2−10 times higher in wells W100D and W100M than in well W40M (Table 1). Scanning electron microscopy observations of particles collected on Nuclepore filters revealed colloids with mean diameters (number average) between 300 and 700 nm and a range of diameters from about 100 to 4000 nm. Filterable aluminum, iron, and silicon (total minus dissolved concentrations, Table 2) ranged from a few micromolar to 70 μM_{Al}, 370 μM_{Fe}, and 500 μM_{Si}, respectively. These observations indicate that inorganic colloidal phases were present, suspended in these groundwaters, at levels between 1 and 40 mg/L.

Enhanced Groundwater Concentrations. Residual tar was observed to be distributed throughout the subsurface solids recovered during well installation (*19*). Thus, we expected groundwater concentrations of dissolved PAHs in this area to exhibit equilibrium with nonaqueous phase liquid tar. Equilibrium aqueous PAH concentrations can be estimated theoretically, via application of Raoult's law with knowledge of the tar composition. One may also evaluate these aqueous concentrations empirically by experimental equilibration of the site's tar with water. Expected equilibrium dissolved PAH concentrations were determined using both of these approaches. First, using results of our measurements of the tar composition, we calculated dissolved concentrations of PAHs in water at equilibrium, assuming a sufficiently large tar-to-water ratio that tar concentrations were not depleted by PAH partitioning into the water. This calculation required knowledge of compound subcooled liquid solubilities (*27*), the tar "molecular" weight (160 g/mol; *21*), and the compound activity coefficient in tar (1; *19*, *28*, *29*). Although each of the compounds we examined occur in the tar at concentrations greater than 1000 mg/L tar, their hydrophobicities result in an expected range of groundwater concentrations from about 10^{-1} down to less than 10^{-4} mg/L water (Table 2).

We also made experimental determinations of water concentrations in equilibrium with tar using incubations in the laboratory. In general, the values calculated from tar compositions were the same as the measured ones within a factor of 3 (measured/calculated = 1.4 ± 1.0, $n = 8$ compounds). Since the measured values do not require any assumptions about PAH compatibilities with the tar mixture or mean tar molecular weight, in subsequent discussion we will assume that *the measured concentrations reflect the dissolved species in equilibrium with the site's tar*.

To ascertain whether the site's groundwater concentrations only reflected the presence of the dissolved-in-water PAH species, we compared measured tar−water equilibrium values with levels we measured in slow-pumped samples from the site (Figure 1). In many wells (e.g., W20M, W40S, W100D, W100M), concentrations of PAHs observed in slow-pumped groundwater from this coal tar site appeared to reflect equilibrium dissolution from the coal tar. However, some monitoring wells had groundwater concentrations of PAHs distinctly in excess of tar−water equilibrium values. For 7 of 25 well/date sample combinations, at least 50% of the PAH compounds monitored exhibited groundwater concentrations more than 3 times greater than measured by tar−water equilibration. Benzo[*a*]pyrene concentrations were observed up to 16 times higher than tar−water equilibrium, and indeno[1,2,3-*cd*]pyrene concentrations were up to 50 times higher. Well W40M always showed such PAH enrichments (Figure 2). Notably, in all of those cases, the ratio of observed-to-equilibrium concentrations increased with increasing compound hydrophobicity. This trend suggested the presence of dissolved or suspended materials in some of the groundwater at this site, which enabled the concentrations of PAHs in the water to exceed levels reflecting only dissolved-in-water species in equilibrium with coal tar.

For several reasons, we believe that this enhanced load of groundwater PAHs was truly mobile and not an artifact of our sampling procedure. First, in all cases the turbidity levels had reached asymptotic values (<1.5 NTU), as determined by long-term (5−9 days) slow pumping. Also, only particles less than 4 μm in diameter were obtained on filters. Finally, no correlation was seen between the occurrence of enhanced PAH concentrations and observations of tar in monitoring wells (only 10−100 μg of tar entrained in a 1-L groundwater sample would be needed to explain our observed PAH concentrations) (*19*). Convinced that our observations did not result from sampling artifacts, we

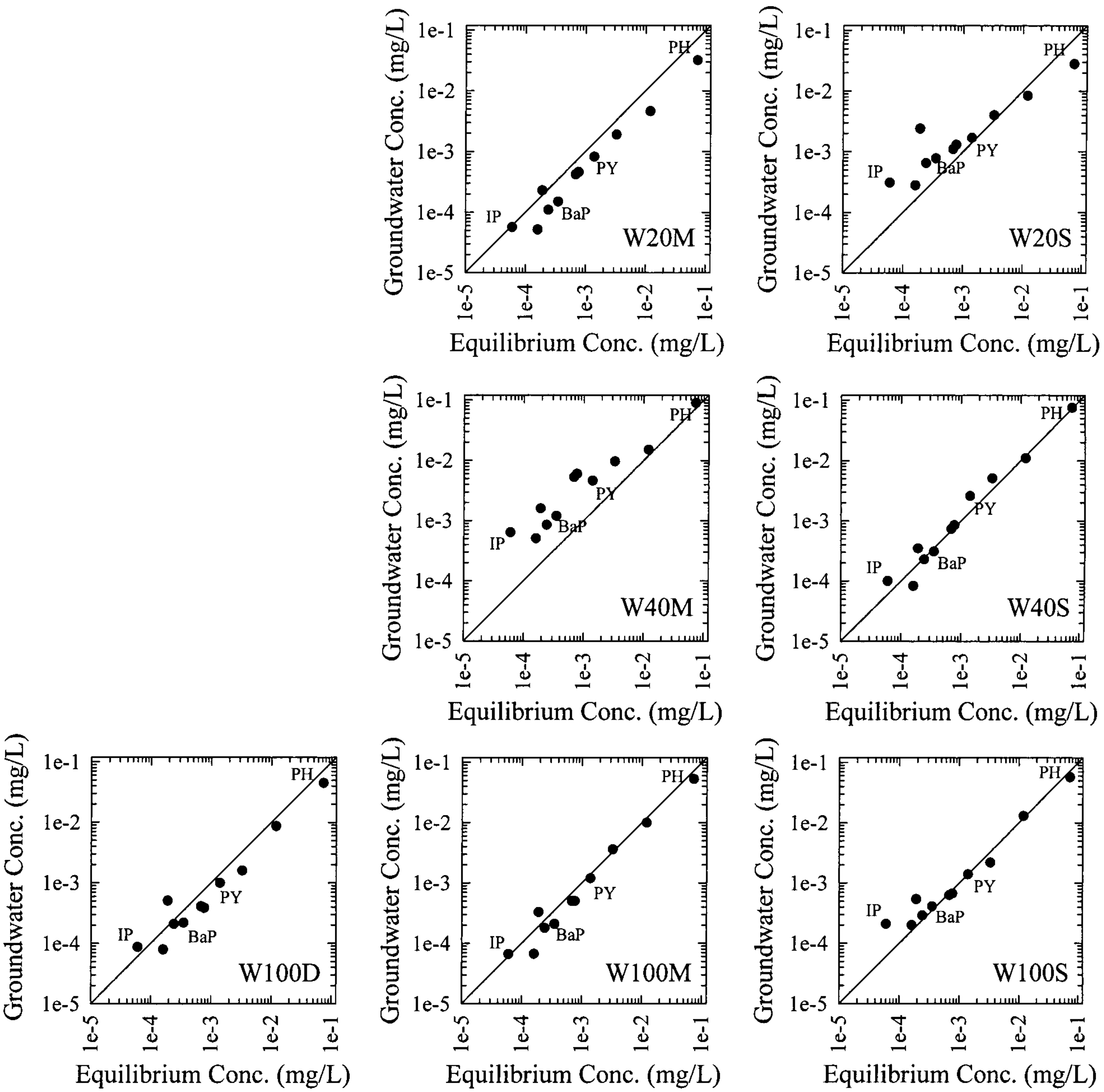

FIGURE 1. Comparison of observed groundwater PAH concentrations to measured aqueous tar–water equilibrium concentrations. Slow-pumped groundwater samples were collected from all wells in September 1996. Compound abbreviations are given in Table 2.

investigated possible mechanism(s) for enhanced solubilization of hydrophobic PAHs using samples from well W40M.

Cosolvents and Surfactants. Cosolvents or surfactants in the groundwater could enhance PAH solubilities over the measured tar–water equilibrium values (*6, 7, 30*). If such materials were present at concentrations sufficient to have a detectable concentration-enhancing effect, we would expect to observe lower groundwater–air surface tensions. We measured the surface tension of the groundwater samples from W40M to be 70.6 ± 3 dyn/cm ($n = 5$). Within the measurement variability, this value did not differ from the surface tension measured for purified water. Water that has been equilibrated with tar has a surface tension that is not significantly different from purified water (*31*), indicating that tar constituents do not lower aqueous surface tension values. The much greater variability observed for the groundwater samples than the purified water may suggest the presence of surface active species in the groundwater pumped from this well. Indeed humic substances present at 5–10 mg/L, as were observed in this groundwater (see Colloidal Materials discussion below), may lower surface tensions by 1 dyn/cm (*32, 33*).

The magnitude of this surface tension effect on the solubility of benzo[*a*]pyrene was estimated with (*12*)

$$\log \frac{C_{\mathrm{mix}}^{\mathrm{sat}}}{C_{\mathrm{w}}^{\mathrm{sat}}} = \frac{N(\sigma_{\mathrm{air:H_2O}} - \sigma_{\mathrm{air:gw}})(\mathrm{HSA})}{2.303\,RT} \qquad (2)$$

where C_{mix} and C_{w} (mg/L) are the aqueous concentrations in the presence and the absence, respectively, of any surface active agent; N is Avogadro's number; $(\sigma_{\mathrm{air:H_2O}} - \sigma_{\mathrm{air:gw}})$ (dyn/cm) is the difference in surface tensions between the two water samples; R (erg mol^{-1} K^{-1}) is the gas constant; T (K) is the temperature; and HSA (cm^2) is the molecule hydrophobic surface area, here approximated as 250 A^2 (*12*).

A decrease of 1.4 dyn/cm in surface tension from that in pure water would enable a benzo[*a*]pyrene concentration increase of a factor of about 3 in the groundwater relative to pure water. The observed BaP enhancement factor at W40M

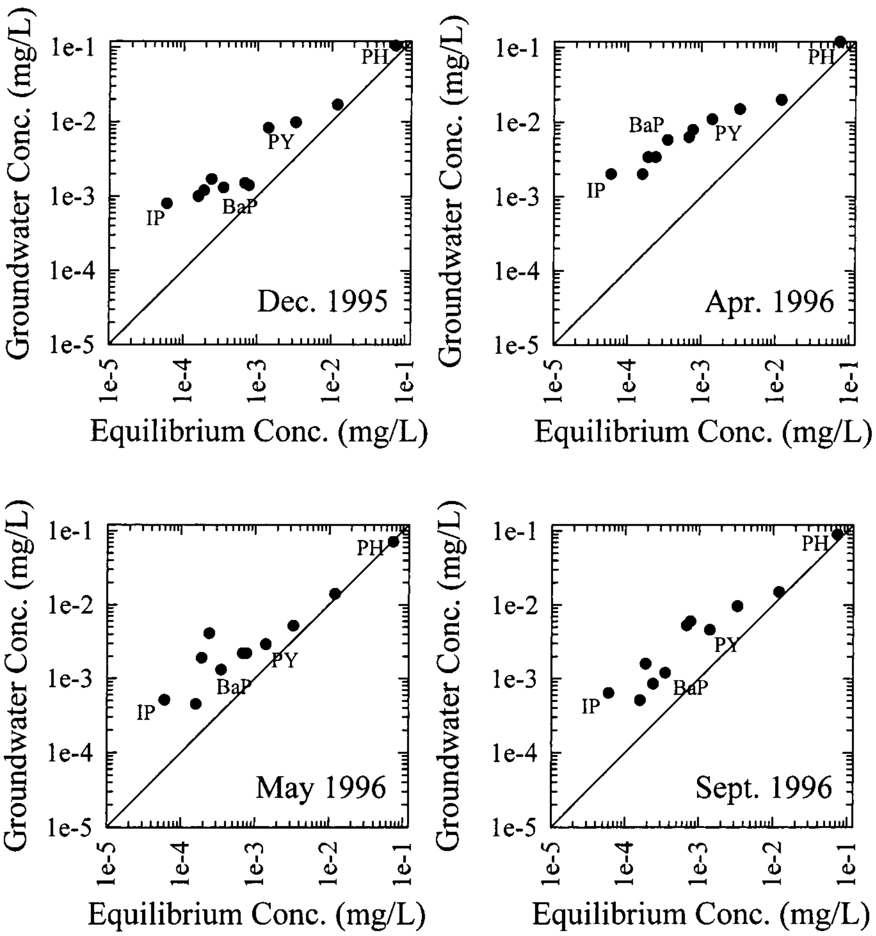

FIGURE 2. Comparison of observed groundwater PAH concentrations to measured aqueous tar–water equilibrium concentrations from well W40M.

TABLE 3. Distribution of Pyrene in Fractionated W40M Groundwater

fraction	pyrene concn (mg/L)	vol of extract (L)	mass of pyrene (μg)	fraction of total pyrene after correction for carryovers (%)
settled solids + walls	0.044	0.010	0.44	36
pH 1 precipitate	0.0071	0.039	0.28	28
pH 1 dissolved	0.0013	0.230	0.3	36
bulk groundwater	0.0036	0.279	1.02	100

[a] Bulk groundwater values are the sum total from each of the separated fractions.

was 14 in September 1996 when the surface tension was measured. A polar, methanol-like cosolvent would need to be present at gram per liter quantities to explain this enhancement (*12, 31*); however, only 34 mg/L of organic carbon was measured in the groundwater. On a carbon-basis, synthetic surfactants and biosurfactants can elevate compound solubilities at milligrams per liter concentrations but not without dramatic decreases in surface tension (*9*). Thus, surface active species did not appear to be important contributors to the enhancement of groundwater PAH concentrations at this site.

Colloidal Materials—In Situ Pyrene Distribution. Pyrene concentrations were elevated above dissolved concentrations in both the settled solids + walls and the pH 1 precipitate fractions of W40M groundwater (Table 3). The masses in each fraction were summed to give the pyrene concentration that would have been obtained by an extraction of the bulk water sample. This concentration (0.0036 ± 0.001 mg/L) was consistent with the concentration of pyrene (0.0046 ± 0.0013 mg/L) determined in 2 L of fresh W40M groundwater, indicating no compound degradation over the 5-month storage period. While the separation of the colloid fractions in W40M groundwater was likely not perfect because gravitational settling and siphoning were used for separation, the pyrene concentration (0.0013 mg/L) in the final pH 1 dissolved fraction was in agreement with the dissolved concentration in equilibrium with coal tar (0.0014 mg/L). Concentration agreement between the pH 1 dissolved fraction and the expected equilibrium with tar indicated that fulvic acids, organic materials that would remain suspended even at pH 1, were not important colloidal phases for pyrene sorption in this groundwater. Thus, all colloid-associated pyrene appears to have been removed by the settling and pH 1 precipitation steps.

The relative importance of settled solids-plus-tar and acid-precipitated organic matter on the enhancement of groundwater pyrene concentrations was calculated. In order not to suspend settled particles between successive siphon steps, a measurable volume of water was left behind at each stage. Thus, dissolved and stable organic colloid-associated pyrene was also extracted with the settled solids and walls; likewise, dissolved pyrene was in the pH 1 precipitate. The portion of the pyrene mass (reported in Table 3) for the settled solids-and-walls that originated from the inclusion of dissolved and organic colloid-associated pyrene in this volume was calculated to be 15%. In the case of the pH 1 precipitate, 18% of the pyrene mass extracted was actually dissolved and not colloid-associated. With these corrections, about 40% of the pyrene in the original water sample was associated with the

TABLE 4. Pyrene Fluorescence in W40M Groundwater after Various Treatments to Remove Organic Colloids

sample	fluorescence response (intensity units/unit of pyrene added)	TOC (mg_C/L)
purified water	3.1 ± 0.1, 3.2 ± 0.1	1.9 ± 0.4
unaltered W40M groundwater	2.2 ± 0.1	19 ± 1.5
ultrafiltered W40M groundwater	2.4 ± 0.1	17 ± 0.02
pH 1 W40M groundwater	not measured	20 ± 0.9
ultrafiltered pH 1 W40M groundwater	3.4 ± 0.2	13 ± 0.4

bottle walls or settled solids, about 30% of the pyrene was associated with colloids that were stable over 5 months, and the remaining mass was dissolved-in-water pyrene.

Colloidal Materials—Fluorescence Quenching. The presence of stable colloids in W40M groundwater was supported by observations of fluorescence quenching of pyrene added to groundwater samples. Increases in fluorescence due to pyrene additions to W40M groundwater were clearly less than corresponding responses from pyrene amendments of purified water (Table 4), indicating the presence of a quenching colloid phase in the groundwater. Ultrafiltration (3000 D) did not remove substantial amounts of the quenching phase: the pyrene fluorescence was slightly greater than in the unaltered groundwater, but the fluorescence did not approach that of pyrene in purified water. Thus, the quencher was able to pass through a nominal 3000 D filter. However, when the groundwater sample was acidified to pH 1 and then ultrafiltered, the fluorescence with pyrene additions did approach the levels of fluorescence in colloid-free water. The organic carbon concentration also decreased to 13 mg_C/L (Table 4). Acidification of the water sample would cause humic acids to precipitate and be more efficiently removed from solution by ultrafiltration. Thus, the fluorescent probe measurements also indicate that pyrene concentrations in the excess of tar—water equilibrium concentrations result from the association of pyrene with stable colloids which can be acid-precipitated.

Changes in the groundwater absorbance at 280 nm with sample manipulation also support the hypothesized presence of humic acid-like colloids. The absorbance at 280 nm decreased from 0.73 for ultrafiltered groundwater to 0.50 for pH 1 ultrafiltered groundwater. Water that was equilibrated with tar in the laboratory incubation had an absorbance of 0.45 (280 nm), and thus the groundwater absorbance after acidification and ultrafiltration likely resulted from dissolved aromatic hydrocarbons. The molar absorptivity of the 4 mg_C/L organic carbon removed by acidification was calculated to be 690 $M_C^{-1}\ cm^{-1}$. This molar absorptivity is of the same magnitude as reported for humic materials (*34*, *35*) and is much less than the molar absorptivity of polycyclic aromatic hydrocarbons (cf., benz[*a*]anthracene absorptivity of $10^4\ M_C^{-1}\ cm^{-1}$; *12*). Thus, the change in absorbance upon acidification and ultrafiltration is consistent with colloids of a humic nature rather than a tar nature.

Coupled with the results indicating pyrene in excess of tar-equilibrated concentrations occurred in situ, this is strong field evidence for association of hydrophobic organic compounds with small (< nominal 3000 Da) organic colloids in groundwater. Previous laboratory studies have demonstrated that humic substances isolated from soil (*36*) and aquatic systems (*2, 37—39*) can enhance the solubility of added HOCs. In our study, colloid-associated PAH concentrations were measured directly by increased groundwater concentrations above tar—water solubility and in extracts of separated colloid fractions. Previous fractionated extractions of contaminated groundwater have not identified humic materials as important facilitating phases (*16, 17*). HOC association with organic groundwater colloids has been inferred in other contaminant plumes through the addition of hydrophobic probes (*14, 15*). Our probe additions were consistent with in situ pyrene distributions that showed organic colloids to be important facilitating phases under certain conditions at this coal tar site.

An organic colloid—water partition coefficient for pyrene was estimated from the fluorescence quenching results. Using eq 1 and values of F_0 and F_1 taken from the ultrafiltered pH 1 groundwater and the unaltered, ultrafiltered groundwater, respectively, an enhancement factor of 1.4 ± 0.1 was calculated. The decrease in TOC concentration of 4 mg_C/L between the ultrafiltered groundwater and the pH 1 ultrafiltered groundwater (Table 1) was assumed to indicate the concentration of sorbent colloids. With this colloid concentration and an enhancement factor of 1.4, a colloid—water partition coefficient of $10^5\ mL/g_C$ was calculated for pyrene using eq 1. The magnitude of this partition coefficient is greater than observed for pyrene association with aquatic humic substances ($10^{4.3}$—$10^{4.5}$; *40*) but is of a comparable magnitude to pyrene partitioning to soil humic substances ($10^{4.9}$—$10^{5.5}$; *22, 41*). The source of colloidal organic matter at this site is unknown; however, degradation of many organic materials in the fill solids, including wood, tar, and natural organic matter (*19*), could contribute to the high dissolved organic carbon concentrations observed in the groundwater.

Predicted PAH Concentration Enhancements. Pyrene partitioning was used to calculate the expected concentration enhancements of other PAHs above tar—water equilibrium in the W40M groundwater. Compound concentrations in the bulk groundwater will be increased by PAH association with stable humic acid-like organic colloids and the material that was operationally labeled settled solids + walls in our fractionated extractions. The overall enhancement factor for a given compound in groundwater can be estimated using

$$E = \frac{C_T}{C_w} = 1 + \left[\begin{matrix}\text{organic}\\ \text{colloids}\end{matrix}\right] K_{\text{colloid}} + \left[\begin{matrix}\text{settled}\\ \text{solids}\end{matrix}\right] K_{\text{solids}} + [\text{tar}]K_{\text{tar}} \quad (3)$$

where [*i*] (kg/L) is the concentration of the colloidal phase as indicated and K_i values (L/kg) are the corresponding colloid—water partition coefficients. A tar—water partitioning term has been included in eq 3 because some of the pyrene lost to walls in the fractionation steps may have been associated with tarry colloids that have a different colloid—water partition coefficient than the settled solids. Since we found that the fractionated in situ pyrene mass distribution indicated that the settled solids-plus-walls terms are about the same magnitude as the organic colloid term (Table 3), we modified eq 3 to be

$$E^{\text{PY}} = \frac{C_T}{C_w} \approx 1 + 2\left[\begin{matrix}\text{organic}\\ \text{colloids}\end{matrix}\right] K_{\text{colloid}} \quad (4)$$

K_{colloid} values for other PAHs were estimated from the pyrene K_{colloid} value, assuming that they scaled according to the compounds relative octanol—water partition coefficients (i.e., $K_{\text{colloid}}^{\text{PAH}}/K_{\text{colloid}}^{\text{PY}} = K_{\text{ow}}^{\text{PAH}}/K_{\text{ow}}^{\text{PY}}$) (Table 5). An organic colloid concentration of 4 mg_C/L was used in the calculations. The calculated solubility enhancements (eq 4) matched closely the observed enhancements calculated by the ratio of PAH concentrations in bulk groundwater extractions to tar—water equilibrium concentrations (Table 5). As expected, less water-soluble PAHs were more susceptible to colloid enhancement. With the concentrations of colloidal materials observed, the mass of pyrene that can be transported in the groundwater

TABLE 5. Expected PAH Solubility Enhancement Factors

compd	log K_{ow}[a]	log $K_{colloid}$	calcd E	obsd E[b]
phenanthrene	4.57	4.39	1.2	1.2 ± 0.5
fluoranthene	5.22	5.04	1.9	2.4 ± 0.9
pyrene	5.18	5	1.8	2.9 ± 1.1
benz[*a*]anthracene	5.91	5.73	5.3	3.7 ± 1.4
chrysene	5.79	5.61	4.2	3.6 ± 1.4
benzo[*a*]pyrene	5.98	5.8	6	7.2 ± 2.8

[a] Ref *27*. [b] Calculated from $E = C_{groundwater}/C_w$, where $C_{groundwater}$ is the concentration in a 2-L sample collected at the same time as the fractionated samples, and C_w is the concentration from the laboratory tar−water equilibration.

is increased by a factor of 2−3 over the dissolved hydrated mass; however, over 80% of the mass of benzo[*a*]pyrene, a more hydrophobic PAH, is associated with colloidal materials, increasing the mobile benzo[*a*]pyrene mass by a factor of 6−7 times.

Environmental Significance. The results of this research may be coupled with colloid generation and transport models to predict the enhanced flux of PAHs away from the coal tar source. The low groundwater turbidities and small colloid particle sizes suggest that the PAHs observed in the bulk groundwater were mobile, at least in the vicinity of our sampling wells; however, we have no data characterizing the colloid attachment and detachment rates for the subsurface solids and colloids at this site from which to develop a colloid transport model. As an upper, conservative (i.e., fastest transport) bound, a retardation factor (R) in the presence of colloids was estimated assuming (i) linear equilibrium partitioning of the colloids to the solid phase; (ii) linear equilibrium partitioning of the PAHs between colloid and solid phases; and (iii) a constant colloid concentration (*42*):

$$R = 1 + \frac{r_{sw}K_d}{1 + \sum[\text{colloid}]K_{\text{colloid}}} \qquad (5)$$

where r_{sw} (kg/L) is the solid-to-water ratio and K_d (L/kg) is the solid−water partition coefficient. This model is applicable to organic matter colloids, which have a lesser tendency to partition to the immobile solid phase than do PAHs (*4*). For PAHs, the product of the solid-to-water ratio and the partition coefficient is generally much greater than 1, so the retardation factor for these compounds in colloid-containing groundwater is reduced by a factor of $1 + \Sigma[\text{colloid}]K_{\text{colloid}}$ ($= E$), relative to a system with no colloids. We observed enhancement factors for benzo[*a*]pyrene between 4 and 16 at this coal tar site. Thus, the retardation factor for benzo[*a*]pyrene would be reduced by a factor of 4−16, relative to predictions assuming no colloids and assuming no pore exclusion effects (*43*).

For a typical natural aquifer ($f_{oc} = 10^{-3}$ kg$_C$/kg), the benzo[*a*]pyrene retardation factor would decrease from about 1000 to about 100 with the magnitude of colloid-enhanced solubilization observed at this coal tar site. The resultant colloid-impacted retardation factor for benzo[*a*]pyrene is still high, but if the industrial site that was the source of this groundwater contamination had been in operation for over 100 years, as is common for many coal tar and industrial sites, sufficient time may have elapsed for benzo[*a*]pyrene to have been transported to sensitive receptors, even with a retardation factor of 100. Certainly, other colloid partition coefficients measured in other anthropogenically impacted aquifers exhibited much greater capacities to sorb HOCs than colloids sampled from pristine locations outside of the zone of contamination (*14*, *15*).

Ideally, characterization of the colloidal materials at this coal tar site would enable a water quality parameter (e.g., acid filtered organic carbon) to be used to delineate solubility enhancements as a surrogate for direct organic contaminant analysis. No bulk water quality parameters that we measured (TOC, turbidity, total or filtered Fe, Al, Si) correlated with the concentration enhancement factors of hydrophobic compounds such as benzo[*a*]pyrene for the suite of wells sampled here. Thus, knowledge of the source and composition of the groundwater colloids is required to enable predictions of spatial and temporal colloid distributions at this coal tar site and to enable predictions of their occurrence at other similar sites.

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