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Colloid Characterization and Colloidal Phase Partitioning of Polycyclic Aromatic Hydrocarbons in Two Creosote-Contaminated Aquifers in Denmark

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Colloidal matter inherent in the subsurface may provide a favorable phase for contaminant partitioning and furthermore act as agents for facilitated contaminant transport. The objectives of the present study were to determine the abundance and properties of intrinsically mobile colloids in the anoxic groundwater from two creosote-contaminated aquifers and to determine the in situ distribution of polycyclic aromatic hydrocarbons (PAHs) between the dissolved phase and two colloidal fractions. The experimental procedure comprising field sampling of bulk groundwater and a sequential laboratory fractionation scheme consisting of a centrifugation and an ultrafiltration step was designed and performed to maintain groundwater chemical and physical integrity. The colloids were identified as clay minerals, Fe-oxides, Fe-sulfides, and quartz particles containing significant amounts of organic carbon. The PAH partitioning to the coarse (>100 nm) colloid fraction ($\log K_{oc}$) was linearly correlated with the corresponding PAH octanol–water partitioning coefficient ($\log K_{ow}$), indicating a hydrophobic partitioning. The K_{oc} values agreed with literature information of PAH sorption to soil organic matter.

Introduction

Colloids in the form of suspended organic and inorganic matter have been recognized as ubiquitous constituents of soil and aquifer systems. The genesis of colloidal matter in the subsurface has been ascribed to hydraulic or chemical perturbations in the water phase, occurring naturally or induced by contamination plumes (1). Indications that colloids may behave as potentially mobile carriers of contaminants in laboratory experiments (2–12) have increased the effort to elucidate the mechanisms involved and the implications for contaminant transport under field conditions.

PAHs constitute a major fraction of coal tar creosote (approximately 85%, 13, 14) and hence account for a significant source of pollution at creosote-contaminated sites. In Denmark, a relatively large number of creosote waste sites from previous gas works, asphalt factories, and wood preservation industries have been identified (15). At these sites, high molecular weight PAHs have been detected in groundwater downstream of creosote contamination sources in concentrations exceeding solubilities (15). PAH concen-

trations exceeding estimates based on transport calculations assuming equilibrium sorption to the stationary aquifer material have also been reported (16). A possible but previously undocumented explanation for the observations is colloid-facilitated transport.

It is well-known that PAHs represent a group of nonionic, low solubility, similarly structured organic compounds that partition extensively with organic matter. Because the PAHs are hydrophobic by nature, the affinity of PAHs to the colloids is anticipated to increase with increasing molecular weight or K_{ow} of the PAHs and with increasing organic carbon content of the colloids. Relatively few studies have addressed the in situ partitioning of PAH to colloids in unaltered groundwater. Gounaris et al. (17) used an ultrafiltration separation technique to investigate the content of in situ PCB and PAH substances associated with different size fractions of groundwater colloids sampled from an abandoned landfill. More than two-thirds of the total amount of contaminants were found to be associated with colloids >1.3 nm.

The objective of this study was to characterize the colloid population of the groundwater in two creosote-contaminated aquifers in Denmark. Furthermore, the in situ distribution of PAHs between the dissolved and colloidal phases in the groundwater was determined. The extent of colloidal partitioning of PAHs was related to the literature-derived octanol/water partition coefficient (K_{ow}) of the compounds and to the colloidal characteristics at the two sites.

Materials and Methods

Groundwater Sampling Sites. Two sites on the Zealand island of Denmark, Collstrop (CS, latitude 55°25') and Østre Gasworks (OG, latitude 55°40') with documented creosote contamination originating from previous industrial activity (gasworks and wood preservation, gasworks, respectively), were selected for the study. Both sites are located in urban areas less than 600 m from the eastern coast with a general groundwater flow direction toward the east.

At the CS site, the focus was on the upper, unconfined aquifer consisting of a relatively homogeneous, unconsolidated postglacial marine sand layer of regional extent resting on glacial clay and silt. No remediation below ground level in the area has been performed since the cessation of industrial activity. Sampling was performed in the zone of high contamination. Based on previous monitoring (18) well B15 (Figure 1) was selected for this purpose. Furthermore, high contamination levels of trace metals (As, Cr, Zn) have previously been observed at CS.

At the OG site, the focus was on the lower, partly confined aquifer and on the downstream potential occurrence of PAH association with colloids. For this purpose, well 102A, which is approximately 200 m downstream of the industrial site, was identified as an appropriate testing well (Figure 2). A contamination plume based on analysis of BTEX (benzene, toluene, xylenes, ethyl benzene), phenol, and PAHs in wells along the transect in Figure 2 has been documented during a previous site characterization (19). The lower aquifer consists of eluvial glacial sand above a regional base of bryozo limestone. The upper, unconfined aquifer is associated with postglacial marine sand fill. Soil excavation and removal, membrane coverage, and replacement of upper soil layers and introduction of shallow subsurface drainage systems in the source area have alleviated the continued release of contaminants.

Groundwater Sampling Procedure. A prerequisite for the successful experimental evaluation of the influence of colloids on PAH phase distribution is a scheme for the sampling and

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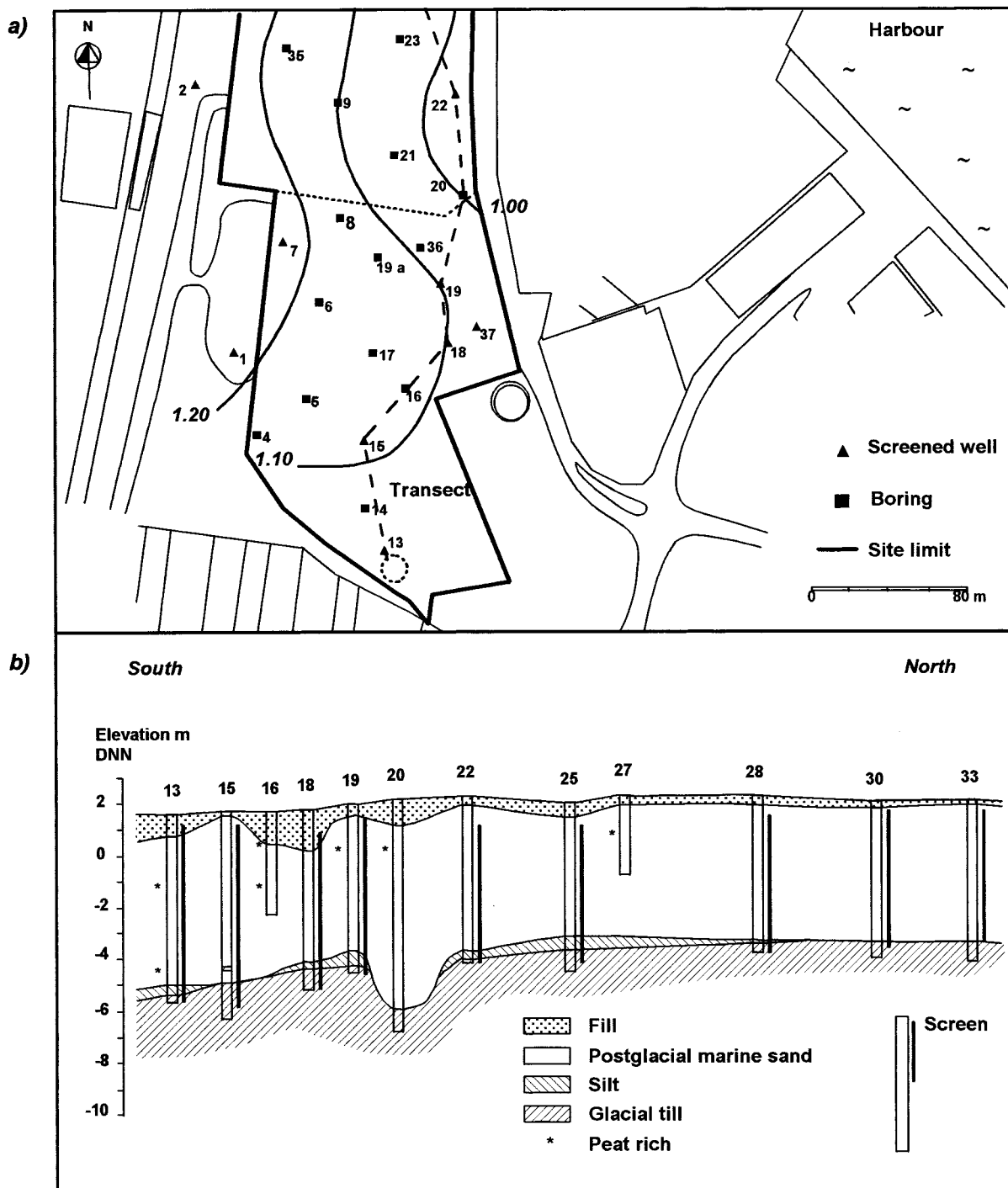


FIGURE 1. Collstrop site. (a) Map of the area, including location of wells and contour lines of the groundwater table. (b) Geological profile along the transect indicated in (a).

handling of groundwater that maintains in situ conditions with respect to chemical and colloidal characteristics. To minimize artifacts of excessive colloid release from the aquifer material during sampling and colloid generation or coagulation during transport and laboratory procedures, the method described by Backhus et al. (20) was implemented. Briefly, groundwater was pumped to the surface at a relatively low pumping rate (<0.5 L/min) in a closed system that eliminated atmospheric contact with the sampled water. The closed system allowed continuous on-line measurement of environmental parameters (pH, temperature, redox potential, specific conductivity, turbidity). To remove previous stagnant water around the pump, groundwater was withdrawn until stable levels of all environmental parameters were attained.

The environmental parameters measured during purging stabilized within one to three screen volumes purged. Because the total water-filled volume of the wells exceeded the purged volume, it is believed that due to the slow pumping rate and with the pump intake located in the middle of the screened interval, only water within the screen section and in the formation immediately adjacent to it was mobilized and sampled. Thus, water in the well below and above this section was effectively stagnant, rendering a total removal unnecessary (21, 22).

The pump used was a submersible 12 V positive displacement pump (38 mm o.d.) made of polystyrene and polyamide. A new pump was used for the sampling of each well to avoid cross contamination. Stainless steel pipe sections

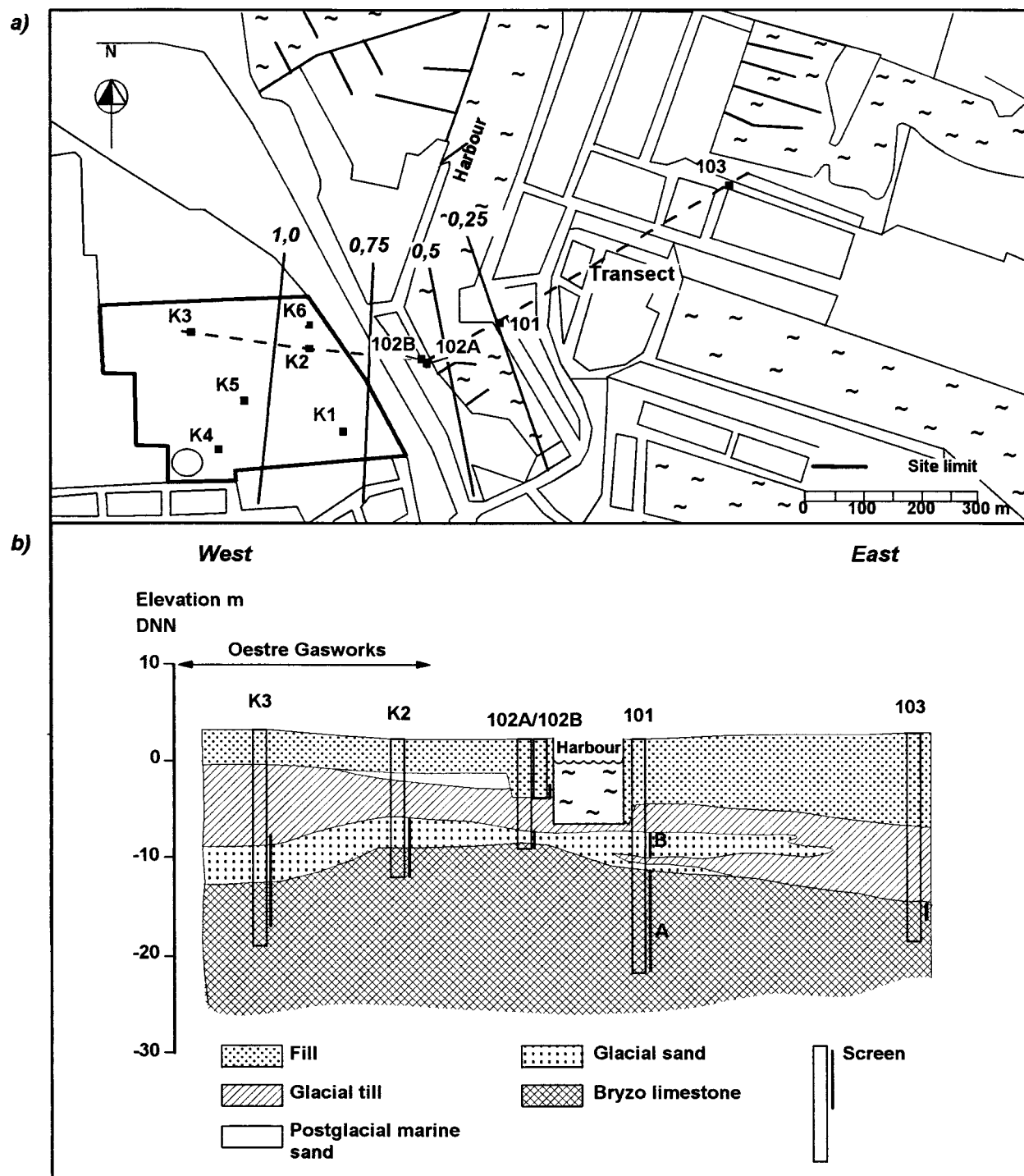


FIGURE 2. Oestre Gasworks site. (a) Map of the area, including location of wells and contour lines of the potentiometric surface in the primary aquifer. (b) Geological profile along the transect indicated in (a).

of 1–2 m (1 cm i.d.) were combined to the desired length and connected to the pump at the bottom and to the flow-through, thermally insulated chamber at the top. Connecting tubes were made of PTFE (Teflon). Turbidity was measured on a separate line (2 mm i.d. Teflon tube) that diverted a subsample (rate: 5 mL/min) to a flow-through glass cuvette (28 mL) in a Hach 2100 N turbidimeter. Periodically during purging and sampling, approximately 5 mL of groundwater directly from the flow-through chamber was sampled by self-filling ampoules (Chemetrics) for the colorimetric determination of dissolved oxygen. Approximately 16 L of groundwater was collected from each of the wells (CS-B15; OG-102A) for fractionation in the laboratory. Samples were

collected without headspace in 1 L glass bottles with glass stoppers and kept in nitrogen atmosphere ($[O_2] < 3$ ppm) during transport to the laboratory. The samples for PAH analysis were preserved by addition of extraction solution (see next section) immediately upon arrival to the laboratory. Colloid samples for scanning electron microscopy/energy-dispersive X-ray microanalysis (SEM/EDX) were collected by filtering 20 mL of groundwater sampled on-line in a glass syringe through a $0.1 \mu\text{m}$ (25 mm diameter) Millipore polycarbonate track-etched screen filter and by subsequent rinsing by filtering with 7.5 mL of Milli-Q (Millipore Inc.) water.

Laboratory Procedure. In the laboratory, the groundwater was subjected to a sequential two-step fractionation procedure. The first fractionation (yielding a >100 nm fraction) was achieved by centrifugation, controlling the temperature at 10 °C (Sorvall centrifuge, 7 min centrifugation time at 13500g). Subsequently, the isolated supernatant was ultrafiltrated using a pressurized, stirred 2 L cell (Amicon 2000C, 0.5 bar, flow rate of approximately 50 mL/min) and a 10 nm Poretics polycarbonate track-etched membrane (diameter 150 mm), yielding a 10–100 nm fraction.

To maintain and control a total mass balance of constituents in the various fractions (supernatant and remanence from centrifugation (CF), filtrate and retentate from ultrafiltration (UF) as well as the raw (unfractionated) groundwater), all fractions were subjected to the various quantitative analysis. The volume concentration ratios (6 for the CF and 2 for the UF step) were kept low to obtain concentrated, aqueous rather than solid fractions and to minimize disturbances from coagulation and clogging effects in the UF step (23). The flow rate remained constant during UF indicating that clogging was insignificant. An observed concentration increase in the remanence (relative to the supernatant) or in the retentate (relative to the filtrate) was inferred to be associated with the colloidal content of that particular analyze in the >100 nm or 10–100 nm colloidal size range, respectively. These fractions are hereafter referred to as the coarse and the fine colloidal fraction, respectively. Material in the filtrate (<10 nm) was considered dissolved. Precautions were taken to preserve the intact groundwater and the original phase distribution of PAHs between the dissolved and colloidal state. All procedures were conducted under a reducing ($N_2 + H_2$) atmosphere. A glovebox ($[O_2] < 5$ ppm) in a 15 °C climate room was used for the storage, transfer, and UF of the groundwater. For the CF of samples, N_2 gas ($[O_2] < 3$ ppm) was introduced into the rotor compartment prior to and during the process. Sorptive losses of PAHs were minimized by avoiding polymeric material during fractionation. An all-stainless steel UF unit and stainless steel containers for CF were constructed specifically for this purpose. The filter material for UF was preequilibrated with the supernatant in three steps, each time replacing the supernatant (750 mL) after 24 h. The filtration was subsequently performed with new supernatant. The necessary conditions for this process (the minimal required number of steps, and the time to reach equilibrium in each step) were determined based on separate small-scale batch experiments using ^{14}C -labeled pyrene dissolved in Milli-Q water. After three 24 h sorption steps, the accumulated sorbed amount increased by less than 17% for an initial pyrene concentration of 100 $\mu g/L$. The supernatant, being more concentrated with respect to PAHs, would act to saturate the filter material more effectively. The desorption from the filter material after the sorption procedure proved to be minimal (<6%) using two 24 h desorption steps. The CF step was implemented rather than a second UF step in order to minimize the amount of groundwater needed for the presaturation of filter material. Furthermore, the CF step removed the majority of colloidal matter and hence the subsequent UF step was facilitated because the coagulation tends to increase with increased colloid concentration (23).

The raw water and the various fractions were analyzed for the following parameters: PAH content (24 species), total solids (TS), and fixed solids (FS) which are the inorganic remnants after combustion (see later), nonvolatile organic carbon (NVOC), and major elements (Al, Fe, K, Mg, Si). In addition, the raw water (and in cases the fractions from the CS site) were analyzed for volatile organic carbon (VOC), Ca, Cl, Na, NH_4 , $NO_2 + NO_3$, PO_4 , total-S, SO_4 , and 11 trace metals.

Quantification of selected PAHs was performed with capillary gaschromatography/mass-spectrometry (single ion

monitoring) using temperature and pressure programming. Sample pretreatment included double extraction with cyclohexane (1 L sample, 50 mL solvent each time), drying of combined extracts with anhydrous sodium sulfate and concentration to 5 mL by evaporation. Recovery determination was based on internal standards of three deuterium-labeled PAHs (biphenyl D,¹⁰ pyrene D,¹⁰ dibenzo[a,h]-anthracene D¹⁴) added to the samples prior to extraction. The precision associated with the analysis was 10–15%. The detection limit ranged from 0.02 to 0.1 $\mu g/L$.

The amounts of TS and FS were determined on duplicate samples by weighing the residue of 500 mL suspension dried at 105 and 550 °C, respectively. The ambient atmosphere in the oven was continuously replaced by the addition of N_2 -gas ($[O_2] < 3$ ppm) to minimize any influence from atmospheric oxygen. NVOC was determined on duplicate 50 mL HNO_3 (Suprapur, 2 mL/L) acidified samples by IR spectrometry using a Dohrmann DC-190 infrared analyzer. VOC was determined by purging neutral samples with purified oxygen gas.

Cationic elements (including elemental S) were analyzed on acidified samples (one tenth HNO_3 Suprapur) using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) for the ions of relatively high concentration (approximately > 0.3 mg/L) and inductively coupled plasma-mass spectroscopy (ICP-MS) for the remaining trace metals (modified EPA methods 200.7 and 200.8).

The filter samples from the field were studied by SEM/EDX to determine the size, abundance, morphology and inorganic elemental composition of individual particles trapped on the filters. Filters were gold-coated (Polaron E5000) for the SEM analysis and graphite-coated (Polaron TB500) for the EDX analysis. The samples were SEM-scanned (Philips XL40) at different magnifications (500–25 000 times), and selected representative particles were analyzed by the EDX unit (Noran, Voyager 2.6), which was integrated with the SEM instrument. A software program automatically processed the signals from the backscattered electron detector. The elemental composition determined, however, is semiquantitative owing to the deviation of the particles from an ideal specimen (i.e., a medium that is flat and thick relative to the depth of electron penetration). Size resolution for the detection of individual particles was estimated to be 0.05 μm for the SEM and approximately 1 μm for the EDX. The particle counting was performed by visual inspection of a set of six or seven SEM images ($58 \times 40 \mu m$, 200 times magnification) for particles larger than approximately 100 nm.

Finally, electrophoretic mobility was determined on the bulk groundwater samples to determine the relative surface charge of the colloids present. A Zeta-meter (ZM-75, Zeta-Meter, Inc., New York) instrument was used by which a sample could be analyzed in an airtight system. The dispensing of the sample to the electrophoresis cell was performed within an N_2 -filled glovebag.

Results and Discussion

General Groundwater Chemistry. The typical temporal development of the environmental parameters recorded during purging of the sampling wells showed that turbidity, redox potential, and dissolved oxygen consistently were the parameters that displayed the largest relative change and stabilized after the longest time (data not shown). The same tendencies regarding the sensitivity of environmental parameters to indicate aquifer equilibration have been noted by other researchers (20, 24, 25). Continuous checking of parameters during the sampling of groundwater ensured that the conditions were maintained during this phase. Increasing the flow rate (by a factor of 2.5–11.0) after sampling did not change the on-line turbidity measurement indicating that

TABLE 1. Chemical Data for the Bulk Groundwater Collected from the Wells

	CS	OG		CS	OG
temp, °C	8.6	11.4	Cl, mg/L	6.7	250
pH	6.7	6.9	S ²⁻ , mg/L	3.22	1.39
redox potential, mV	-59	-153	NO ₃ + NO ₂ , mg/L	1.32	<0.04
dissolved oxygen, mg/L	0.13	0.03	PO ₄ , mg/L	12.17	1.22
specific elec. condn, mS/m	86.7	168.7	SO ₄ , mg/L	77.24	1.09
turbidity, NTU	0.7	0.9	As, µg/L	8.68	<1.0
ionic strength, mM	14.7	22.4	Ba, µg/L	37	262
alkalinity, meq/L	9.2	10.3	Cd, µg/L	0.12	<0.05
total solids, mg/L	735.3	1047.3	Co, µg/L	2.66	1.23
fixed solids, mg/L	653.8	908.8	Cr, µg/L	1.35	<0.9
NVOC, mg/L	56.7	23.5	Cu, µg/L	22.2	<1.0
VOC, mg/L	1.34	40.5	Hg, µg/L	<0.6	<0.6
Al, mg/L	0.023	0.0028	Mn, µg/L	1590	156
Ca, mg/L	139	161	Ni, µg/L	16.6	6.9
Fe, mg/L	0.56	5.93	Pb, µg/L	0.626	0.624
K, mg/L	8.21	10.9	Zn, µg/L	2790	10.3
Mg, mg/L	4.82	42.1	PAH, total, µg/L	150.26	348.60
Na, mg/L	28	106	PAH, 2-3 rings, µg/L	143.07	348.60
Si, mg/L	15.2	9.74	PAH, 4-5 rings, µg/L	7.19	0
NH ₄ , mg/L	1.43	2.26			

the aquifers were not sensitive to shear stress-induced colloid release (1, 20, 26-29) and that the stable turbidity level reflected in situ colloid concentrations. Repeated samplings in the same well within one year generated only minor changes in the indicator parameters.

The water from CS-B15 and OG-102A were similar with respect to a near-neutral pH, a high alkalinity, and high Ca concentrations (Table 1). Both aquifers were close to anoxic and were found to have high specific conductivity and ionic strength.

The content of organic matter was significantly higher in the bulk water at CS (56.7 mg/L) than at OG (23.5 mg/L) for several reasons: (1) more organic matter being introduced to CS because of its shallower depth and phreatic character and the shorter residence time of the organic matter in the aquifer before reaching the observation well, (2) higher microbial activity due to higher redox potential, giving rise to higher microbially derived organic mass, (3) previous disposal of organic-rich wastewater from the wood-preserving facility, and (4) higher content of contaminant hydrocarbons. The PAHs, which comprise a major mass fraction of creosote, contributed only 0.25% and 1.4% to the measured NVOC at respectively CS and OG, indicating that this source of organic matter is negligible. The concentration levels of individual PAH substances were generally negatively correlated with the octanol-water partitioning coefficient (log K_{ow}) (Figure 3), which is consistent with lower water solubilities for the more hydrophobic components. The observed concentrations did in no case exceed the expected water solubilities (according to Mackay et al. (30)) giving no immediate indication of PAH association with colloids or the existence of free phase droplets of creosote in the groundwater.

Abundance and Characteristics of Groundwater Colloids. The total abundance of colloids was similar in the CS (B15) and OG (102A) groundwater. Both wells contained on the order of 10⁹ particles/L and 5 mg/L of colloids, the latter measured as TS in the two colloid fractions (Table 2). The colloidal TS constituted in both cases approximately 0.5% of the TS in the bulk groundwater, indicating that the mass fraction of colloids was small. Gounaris et al. (17) found that approximately 3% of the mass of TS in groundwater was associated with colloids > 10 nm. Assuming an average particle density of 2 g/cm³ (representing an average for clay, hydrated silica, and iron oxy-hydroxide according to McCarthy and Degueudre (1)) and spherical particles, the number and mass concentrations correspond to an average particle

diameter of 900 and 1100 nm for the CS and OG water, respectively. From inspection of the SEM images, the colloidal populations (colloids retained on a 100 nm filter) were polydisperse with few large particles (>500 nm) and an abundance of smaller particles (<500 nm), indicating that an average particle diameter is likely to be smaller than the calculated and semiquantitative average owing to an underestimation of the number of smaller particles retained on the filters.

The TS in the coarse fraction (>100 nm) was larger than the content in the fine fraction (10-100 nm). The trend was the opposite for the organic carbon (NVOC) content analysis, which showed that the smaller colloids were richer in organic matter than the larger ones (Table 2). This trend has also been observed by others (17). The CS colloids had a significantly higher organic carbon mass fraction than did the OG colloids. The percentage of NVOC in the bulk groundwater associated with the colloidal fractions was no more than 0.8% (CS) and 2% (OG), suggesting that most of the organic matter was in a dissolved/macromolecular form.

The particles from both sites had negative electrophoretic mobilities (Table 2). As discussed by several researchers (26, 31-33), colloidal stability is generally enhanced by particle coating by natural organic matter. With a relatively high organic carbon content in the colloids, this phenomenon may be a significant factor in colloid stability at the two sites. Especially at the CS site, where the assemblage of minerals comprising the mobile colloid fraction was dominated by iron oxides (according to the SEM/EDX analysis), which have a positive charge at the pH of the groundwater (pH 6.7) (34), the coating of the colloidal minerals with negatively charged organic matter was likely to have decreased the surface charge of the colloids, an explanation for the observed mean negative electrophoretic mobility.

The inorganic content of the colloids was evaluated according to the elemental composition obtained by SEM/EDX analysis and the fractionation procedure. From the SEM/EDX analysis of a set of 14 single particles from each well, the average composition of major elements of the colloids was determined (Table 3). Besides O, which was the largest contributor to colloidal mass, Si and Fe were the most abundant elements. Relatively high mass of P in the CS colloids (3.2% vs 0.9%) and high S in the OG colloids (3.1% vs 0.8%) point to phosphorus and sulfur-containing species, respectively, in the two groundwaters. Despite higher total S concentration at CS (Table 1), the sulfides apparently were not precipitated at the redox potential observed. The relative

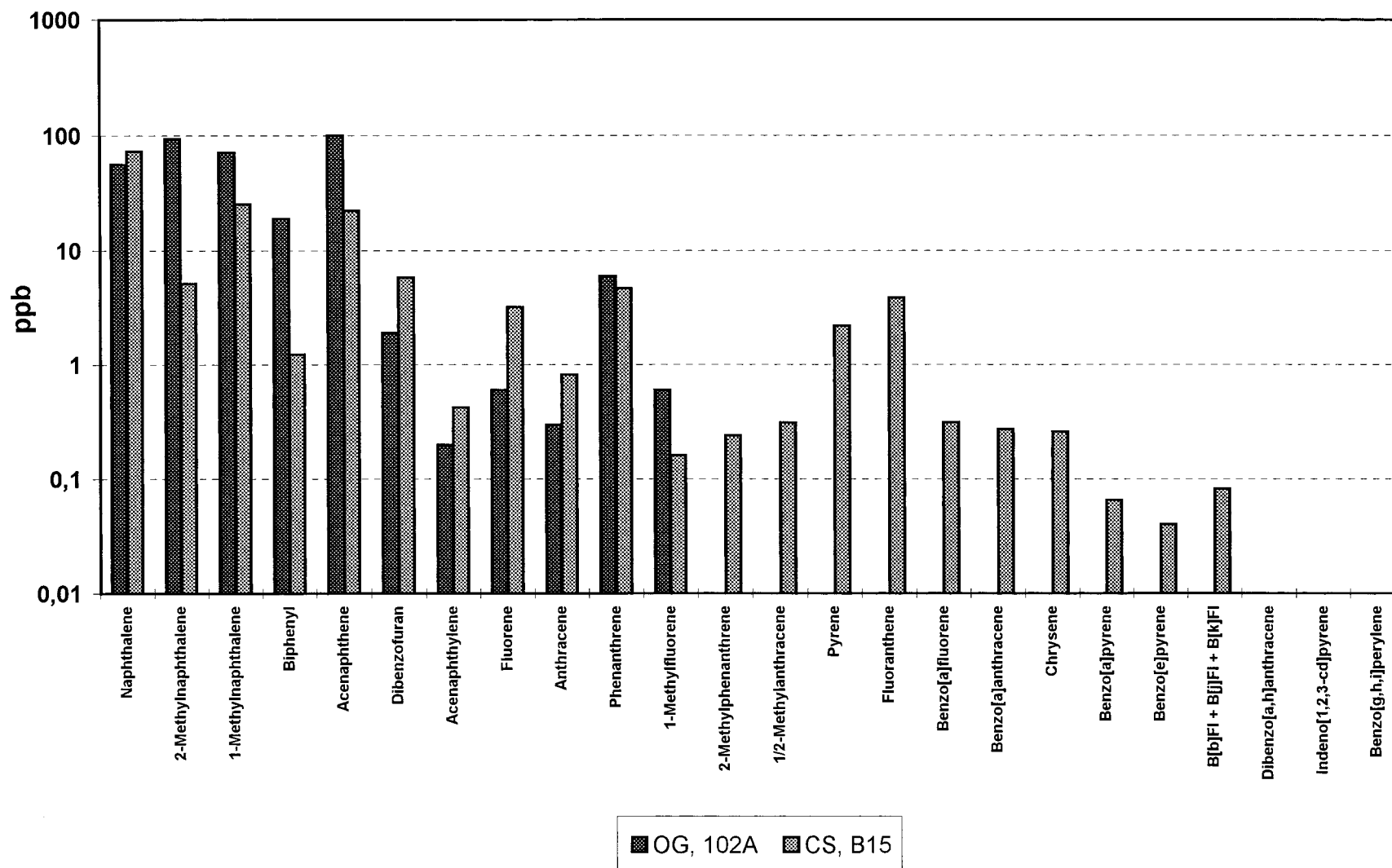


FIGURE 3. PAH concentrations in bulk groundwater at the source at Collstrop (CS-B15) and downstream at Oestre Gasworks (OG-102A).

TABLE 2. Characteristics of Groundwater Colloids from the Wells

	coarse fraction (> 100 nm)	fine fraction (10–100 nm)	total (> 10 nm)
Concentration, mg/L			
CS	2.2 ± 0.7	1.0 ± 0.9	3.2 ± 1.2
OG	3.1 ± 1.0	2.0 ± 0.9	5.1 ± 1.3
Number Concentration, part./L			
CS	> 3 × 10 ⁹		
OG	> 2 × 10 ⁹		
Organic Carbon Mass Fraction, %			
CS	16	23	18
OG	8	15	10
Electrophoretic Mobility, (μm/s)/(V/cm)			
CS			–1.2
OG			–3.2

TABLE 3. Predominant Elements from EDX Analysis of Single Particles

Collstop (W/W %)		Oestre Gasworks (W/W %)	
O	(40.0 ± 6.9)	O	(40.8 ± 7.9)
Fe	(20.7 ± 16.7)	Si	(15.8 ± 14.1)
Si	(13.8 ± 15.3)	Fe	(12.0 ± 15.6)
Al	(4.8 ± 5.5)	Na	(8.1 ± 4.7)
Ca	(3.2 ± 3.9)	Zn	(8.1 ± 7.3)
P	(3.2 ± 4.0)	Al	(4.2 ± 4.6)
Na	(2.8 ± 3.4)	S	(3.1 ± 5.5)
Cr	(2.2 ± 3.3)	Cl	(1.8 ± 2.3)
K	(1.8 ± 2.0)	Mg	(1.4 ± 2.9)
Zn	(1.8 ± 1.5)	Ca	(1.3 ± 1.0)
Ni	(1.7 ± 2.6)	P	(0.94 ± 0.74)
Mg	(1.3 ± 1.9)	Cr	(0.92 ± 2.53)
Mn	(1.2 ± 2.1)	K	(0.50 ± 0.83)
S	(0.79 ± 0.65)	Mn	(0.47 ± 0.54)
Cl	(0.55 ± 0.64)	Ti	(0.43 ± 0.47)
Ti	(0.18 ± 0.38)		

mass content of Fe in colloids is lower at OG than at CS (Table 3) despite a higher total Fe concentration in the bulk groundwater at OG (Table 1). This is presumably because the iron oxides generally are more soluble at the lower redox potential existing at OG and are only partly replaced by reduced Fe-precipitates (e.g., FeS). A higher content of Fe in the colloids at CS was supported by the sequential fractionation (results not shown).

From the SEM/EDX analysis and the calculated mass fractions for the various elements the particles could largely be identified as clay minerals (5% < Si < 42%, Al > 8%), Fe-oxides (Fe > 23%, S < 2%), Fe-sulfides (Fe > 5%, S > 2%), and quartz particles (Si > 42%). Some particles, especially the Fe-oxides/sulfides, were of a less identifiable signature, presumably because of the conglomerate nature of the particles. For the CS groundwater, clays, Fe-oxides (mixed with Ca–P and Fe–Cr–Ni) and quartz constituted 36%, 50%, and 14% of the number of particles analyzed. For the OG groundwater, clays, Fe-sulfides (mixed with Fe-oxides, Zn–S, Ca–P, and Na–Cl), and quartz were identified as 8%, 58%, and 33% of the particles analyzed.

Colloid Partitioning of PAH. A significant partitioning of PAHs with the colloidal phase could be observed at the CS site. For benzo[*b*+*j*+*k*]fluoranthene (log K_{ow} = 6.51), benz[*e*]pyrene (log K_{ow} = 6.44), benz[*a*]pyrene (log K_{ow} = 6.15), and benzo[*a*]anthracene (log K_{ow} = 5.81), the mass associated with the > 100 nm colloid fraction constituted 34.7, 12.3, 10.7, and 5.4% of their total masses, respectively. The extent of partitioning was related to the hydrophobicity of the PAHs. By plotting the calculated log K_{oc} values versus the log K_{ow}

values (Figure 4, K_{ow} values from Mackay et al. (30)), a satisfactory agreement with previously reported correlations between PAH sorption to organic matter in soil, sediment, and aquifer material and log K_{ow} (35–40) was found (log K_{oc} = 1.03 log K_{ow} + 0.724, R^2 = 0.9621, n = 7). This result indicates that the partitioning of PAH to the larger organic-matter-containing colloids at these sites may be similar to the sorption to bulk soil organic matter.

A lack of PAH partitioning for log K_{ow} < 5.7 is indicated by the experimental data (Figure 4). Rather than signifying a lower limit for PAH sorption to the colloids, which would be in contrast to the gradual decline observed from sorption to soil, the apparent cutoff most likely reflects a lower limit with respect to the sensitivity of the experimental method. This was supported by the fact that an accumulation of the less hydrophobic PAHs, though not significant, followed the same trend as for the more hydrophobic congeners (Figure 4).

Colloid partitioning was not observed at OG. The organic matter comprised a significantly smaller fraction of the colloidal mass at the OG (10%) site compared to the CS site (18%). In addition, the content of high molecular-weight PAHs was small at the downstream OG location (Figure 3), and owing to the limited sensitivity of the experimental procedure mentioned above, partitioning could not be recorded. The capacity to positively detect colloid association of PAH and hence the sensitivity of the experimental procedure is correlated to the concentration factors applied in the fractionation steps. However, while a higher concentration factor yields a better chance of recovering a significant partitioning, the risk of adverse colloid alteration processes also increases. Hence, the design of a fractionation procedure needs to balance the consideration of these two aspects.

Colloidal association of PAH was solely observed for the coarse fraction at CS (colloids > 100 nm) despite a higher organic matter content in the finer fraction, implying that there is a lower limit to the size of colloids to which PAHs may associate. Gounaris et al. (17) similarly found that colloids in the 10–100 nm fraction (containing 3% of TOC) was a considerably less favorable phase for partitioning of PAHs and PCBs than the > 100 nm (6% of TOC), while associations of the 1.3–10 nm colloids (22% of TOC) were statistically insignificant. Backhus and Gschwend (41) detected no sorption to the < 500 MW ultrafiltered fraction of groundwater freshly amended with PAH although it contained 44–88% of the TOC. The observed agreement of PAH partitioning with colloids > 100 nm and with soil organic matter in our case also indicates that PAH did not partition significantly to dissolved organic carbon (< 10 nm, 99% of TOC). If this was the case, the apparent aqueous PAH concentration would be elevated resulting in relatively lower K_{oc} values for the colloidal compared to the soil organic matter.

The results indicate that dissolved/colloidal organic phases (DOM/COM) become less favorable for PAH partitioning as the size of the sorbent phase decreases. The findings are in agreement with observations that (1) log K_{oc} values for PAH sorption to DOM/COM is positively correlated with molecular or particle size or molar volume of DOM/COM (42, 43); and (2) PAH sorption to organic phases associated with mineral colloids are higher than to the residual, unattached, dissolved organic matter, due to the preferential adsorption of higher molecular weight, relatively hydrophobic constituents of the natural organic matter to the mineral phases (44).

A distinction between natural DOM/COM and isolated fractions (e.g. humic acids) may be necessary. Whereas sorption to organic isolates of high humic and aromatic content may show a significant PAH partitioning (43, 45, 46), partitioning to unfractionated natural DOM/COM from various soils is typically much lower due to a significant content of

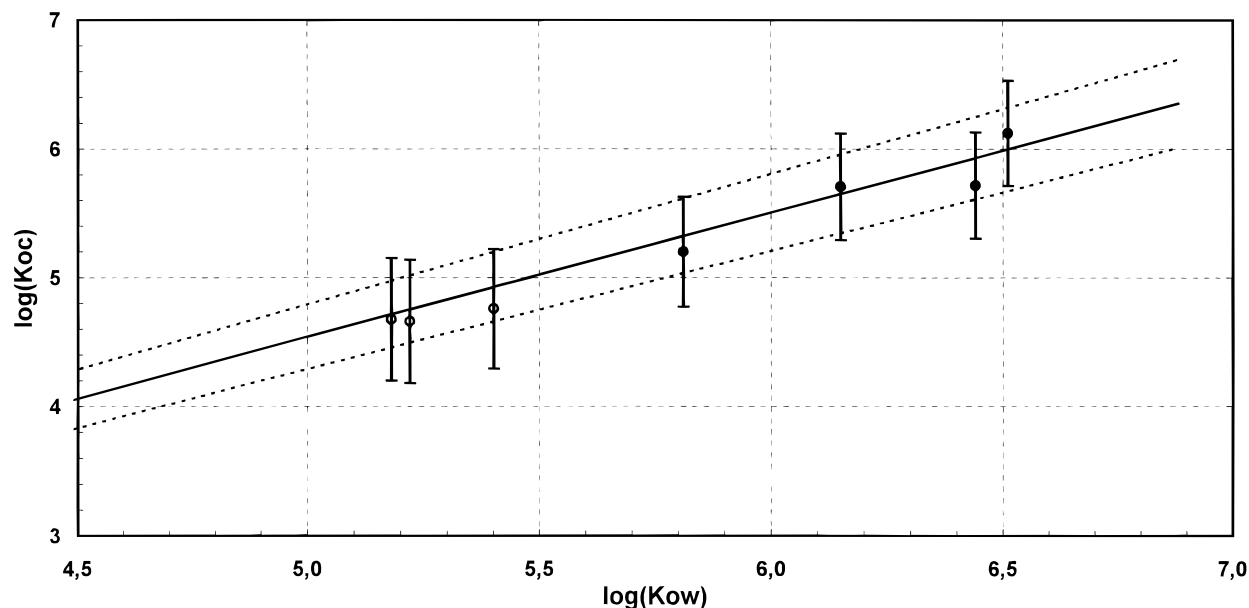


FIGURE 4. Relationship between the in situ partition coefficient $\log(K_{oc})$ and the octanol–water partition coefficient $\log(K_{ow})$ for PAHs detected in the coarse colloid fraction at Collstrop. The lines represent the literature-derived correlation and standard deviation for PAH partitioning to bulk soil/sediment. Open circles represent values that were not significant. Error bars represent one standard deviation.

hydrophilic constituents (47, 48). This discrepancy may be even more pronounced for intact groundwater which is known to generally contain higher proportions of hydrophilic constituents than soil (49). Hence, it is recommended to characterize the organic matter with respect to its proportion of hydrophobic fractions in the various size fractions of natural colloidal matter. A large fraction of naturally occurring organic matter in an operationally defined dissolved fraction in groundwater may be relatively inactive in the partitioning of PAH, with possible implications for the colloid-facilitating transport capacity of the groundwater.

Conclusions

An investigation of intrinsically mobile colloids in two creosote-contaminated anoxic groundwaters showed that colloids > 10 nm are present in significant amounts (approximately 5 mg/L) and that they are dominated by clay, Fe-oxides, Fe-sulfides, and quartz particles. The specific colloidal composition (in terms of inorganic and organic content) and surface characteristics reflect the general groundwater chemistry. A two-step fractionation procedure of the groundwater revealed that the intrinsically present PAH is partly associated with the larger colloids (> 100 nm), that the sorption is hydrophobic in nature, that it is related to the organic matter content of the colloids, and that the magnitude of the association is comparable to previously reported sorption to soil organic matter. The indicated inherent colloid partitioning of PAH suggests a potential for colloid-facilitated transport of PAH. The observed absence of PAH partitioning to colloids < 100 nm presumably indicated a weaker binding to smaller, more hydrophilic organic constituents of the groundwater. A continuous research effort is advocated that emphasizes the role of naturally occurring dissolved or small organic-rich colloids compared to that of larger complex mineral-organic colloids in partitioning and co-transporting PAH under field conditions.

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