

Investigating the Potential for Colloid- and Organic Matter-Facilitated Transport of Polycyclic Aromatic Hydrocarbons in Crude Oil-Contaminated Ground Water

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ABSTRACT

The potential for colloid- and organic matter-facilitated transport of polycyclic aromatic hydrocarbons (PAHs) was investigated at a crude oil-contaminated field site near Bemidji, Minnesota. Field tests focused on sampling and characterization of the ground water colloids and assessment of the partitioning of PAHs to the colloids. The colloids were mostly iron-rich spheres of 100-300 nm diameter. Their concentration reached a maximum of about 2×10^{10} particles per liter (0.75 NTU) at a distance 50 m down-gradient from the oil spill and decreased with distance to a background concentration of about 7×10^8 particles per liter at a distance of 140 m. During well purging, stable colloid concentrations decreased slightly with increasing pumping rate. Fluorescence quenching experiments revealed that partitioning of perylene to organic matter in the unaltered ground water was significant. Laboratory tests examined the effect of ferrous iron, present in high concentrations near the oil spill, on the partitioning of phenanthrene to aliphatic and aromatic carboxylic acids typical of crude oil degradation and hydrophobic acid fractions of natural organic matter. Ferrous iron increased the partitioning of phenanthrene to the organic acids by 11 to 250%, with the largest increase occurring for aromatic carboxylic acids. The data suggest that ferrous iron increased the partition coefficient by causing aggregation of the organic acids.

INTRODUCTION

Colloids, both organic and inorganic, have been implicated in the transport of metals, radionuclides, and certain ionizable organic pesticides in laboratory and field tests (Jury and others, 1986; Buddemeier and Hunt, 1988; Amrhein and others, 1993; de Jonge and others, 1998). Laboratory tests also indicate that colloids facilitate the transport of hydrophobic organic compounds (Vinten and others, 1983; Magee and others, 1991; Dunnivant and others, 1992); however, colloid-facilitated transport of hydrophobic organic compounds has only infrequently been observed in the field (Villholth, in press). To assess the potential for colloid-facilitated transport of hydrophobic organic compounds in the field, we examined the association of colloids and polycyclic aromatic

hydrocarbons (PAHs) in a crude oil-contaminated ground water at Bemidji, Minnesota.

The Bemidji site was considered a good candidate for detecting colloid-facilitated transport of hydrophobic organic compounds. Phenanthrene and fluorene, two PAHs in the crude oil, were measured in the ground water down-gradient of the oil spill at concentrations 26% and 300% greater than concentration estimates based on equilibrium between the crude oil and the surrounding water (Aiken and others, 1991). The transport distances for phenanthrene and fluorene also exceed expectations based on two-phase transport estimates (Hawley, 1995). These observations suggest sorption of the PAHs to a third phase -- a mobile colloid phase.

We suspected that organic and inorganic colloids would be abundant near the oil spill. The dissolved organic matter concentration of the

ground water increased to 50 mg C L⁻¹ adjacent to the oil spill. Degradation of the oil produced an anoxic plume of ground water and high ferrous iron concentration. These conditions have been associated with colloid mobilization in iron oxide-coated sediments (Ryan and Gschwend, 1990; 1992).

Our investigation included both field and laboratory components. In the field, we tested the dependence of the stable colloid concentration on the pumping rate and characterized the colloids collected in the samples. Using the field samples, we measured the partitioning of perylene, a five-ring PAH, to the colloids at *in situ* concentrations. In the laboratory, we tested the effect of ferrous iron on the partitioning of phenanthrene, a three-ring PAH, to different types of organic matter ranging from high molecular weight aliphatic and aromatic carboxylic acids to isolated fractions of natural organic matter.

MATERIALS AND METHODS

In this section, we describe the field site, the methods of sampling the ground water, the measurement of partition coefficients by fluorescence quenching, and the measurement of partition coefficients by solubility enhancement in the presence and absence of ferrous iron.

Field Site

The field tests were conducted at the U.S. Geological Survey Toxic Substances Hydrology research site at Bemidji, Minnesota. In August 1979, a pipeline near Bemidji burst and sprayed light crude oil on the ground surface. After cleanup, an estimated 400,000 L of oil remained in the unsaturated zone of the soil perched in a lens on the water table (Hult, 1987). Since the spill, the oil body has migrated about 30 m down-gradient and oil dissolution and degradation products have traveled at least 200 m down-gradient (Hult, 1989).

The saturated sediment at the site is a calcareous silty sand deposited as glacial moraine and outwash. The sand and silt fraction is composed of quartz, feldspar, dolomite, calcite, hornblende, and ilmenite. The clay fraction (<1%) is composed of kaolinite, smectite, and chlorite

(Bennett and others, 1993). Ground water flow is advancing at a rate of about 0.08 m d⁻¹ (Baedecker and others, 1993).

The supply of oil degradation products to the ground water has created five distinct zones of ground water chemistry (Baedecker and others, 1993) (fig. 1). Near the oil body, dissolved oxygen decreases to zero from near saturation, dissolved organic matter increases to 50 mg C L⁻¹ from 2 mg C L⁻¹, and ferrous iron increases to about 1 mM from micromolar levels.

Ground Water Sampling

Ground water was sampled from five monitoring wells aligned with the axis of ground water flow past the oil body (fig. 1) in July 1995. These wells provided samples from the uncontaminated background zone, near the oil body, and down-gradient of the oil body. The sampling apparatus and procedures were designed to minimize suspension of colloids by pumping and preserve sample chemistry.

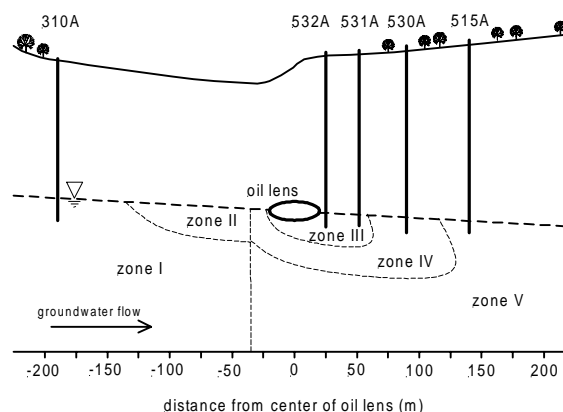


Figure 1. Locations of the monitoring wells sampled in this investigation shown with oil body and geochemical zones of contamination designated by Baedecker and others (1993). The ground water zones have the following characteristics: (I) native uncontaminated ground water, oxic; (II) high organic and inorganic carbon, sub-oxic; (III) high hydrocarbons, Mn²⁺, Fe²⁺, methane, anoxic; (IV) transition zone between III and V, sub-oxic; and (V) slightly elevated benzene, toluene, ethylbenzene, and xylenes, oxic. The water table depth ranges from 8 to 9 m for the wells shown.

Ground water was removed from the wells using a positive-displacement gear-driven pump made of stainless steel and Teflon. The pumping zone was partially isolated by a packer inflated with argon above the pump. Aluminum and stainless steel tubing (pre-rinsed with acetone and deionized water) was used to connect the pump with the surface. A low flow rate (about 0.1 L min^{-1}) was used to minimize suspension of colloids.

In one well (532A), ground water sampling was conducted at 4 different pumping rates (0.15, 0.35, 1.1, and 1.8 L min^{-1}) on successive days to test the effect of pumping rate on colloid sampling. These pumping rates span the range commonly used in ground water sampling. After sampling at the highest pumping rate on the fourth day, the pumping rate was decreased to the medium and low rates to determine the effect on turbidity.

Flow from the pump tubing was directed to the bottom of an inverted, overflowing glass funnel for measurement of pH, specific conductance, and dissolved oxygen (colorimetric vacuum ampoules; Chemetrics, Inc.). Flow was also diverted to glass vials for frequent turbidity (Hach, model Ratio X/R) and total iron measurement (Hach, field titration) during well purging. Samples were collected when the field parameters stabilized. This purging of the wells required removal of 100 well volumes over 7 h. Ground water was collected in ground glass-stoppered bottles pre-filled with argon and contained in sealed plastic bags after allowing approximately one volume of overflow. The bottles were capped, covered with plastic caps, and stored on ice in coolers.

Colloids were sampled by collecting 20 to 60 mL of ground water in glass syringes and filtering through $0.1 \mu\text{m}$ membranes. The membranes were rinsed with 10 mL of deionized water and stored in sealed petri dishes.

Laboratory Analysis

Ground Water Chemistry

Samples were analyzed for major cations and metals (Al, Ca, Fe, K, Mg, Mn, Na, and Si) in whole and $0.1 \mu\text{m}$ -filtered samples by inductively

coupled plasma-atomic emission spectrophotometry (ICP-AES). Sample handling and filtering was conducted in an argon-filled glove box. Total and dissolved organic carbon concentrations were determined by ultrafiltration (500 molecular weight cutoff), high-temperature platinum catalyst combustion of the samples from which inorganic carbon and volatile organic carbon had been purged, and infrared detection of carbon dioxide.

Colloid Characterization

The abundance of inorganic colloids on gold-coated filters was determined by scanning electron microscopy (SEM) at 20,000 times magnification and 30 kV accelerating voltage. From 40 to 100 randomly located fields were counted. Fields with colloids too numerous to count were excluded; these fields were photographed. Elemental composition of the colloids was estimated by energy-dispersive x-ray (EDX) analysis with count times of 60 s.

Fluorescence Quenching

Fluorescence quenching (Backhus and Gschwend, 1990) was used to determine the partitioning of a probe PAH, perylene, to the organic colloids present in ground water samples examined under in situ conditions. Organic colloids were operationally defined as organic matter that did not pass through a 500 molecular weight ultrafiltration membrane.

Solubility Enhancement

Solubility enhancement experiments (e.g., Chiou and others, 1986) were performed to determine the effect of ferrous iron on the partitioning of a PAH, phenanthrene, to various types of high molecular weight organic acids. The organic acids tested included the hydrophobic acid fractions of organic matter isolated by XAD-8 resin (Aiken and others, 1992) from the site ground water and the Suwannee River and high molecular weight aliphatic and aromatic carboxylic acids (table 1). The carboxylic acids (fig. 2) were chosen to represent typical oil degradation products found at the site (Eganhouse and others, 1993). The hydrophobic acid fractions

were added at a concentration of 50 mg L⁻¹. The carboxylic acids were added at a concentration of 20 mg L⁻¹, an order of magnitude below the critical micelle concentration of any of the carboxylic acids (Mukerjee and Mysels, 1971).

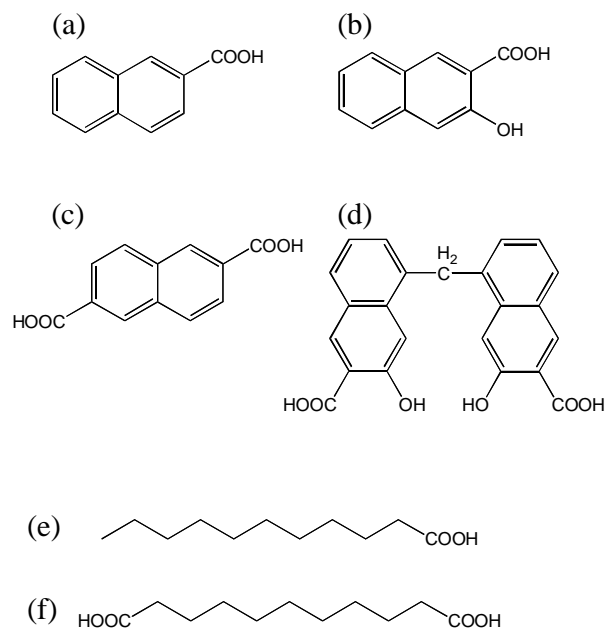


Figure 2. The aromatic and aliphatic carboxylic acids used in the solubility enhancement experiments: (a) 2-naphthoic acid, (b) 3-hydroxy-2-naphthoic acid, (c) 2,6-naphthoic acid, (d) pamoic acid, (e) undecanoic acid, and (f) 1,11-undecanedioic acid.

Ferrous iron was added as Fe₂SO₄·4H₂O at concentrations of 0.9 and 2.7 mM. The lower concentration is about 25% higher than the maximum total iron concentration measured in the contaminated Bemidji ground water. Potassium nitrate was added to control ionic strength at a concentration of 0.01 M, approximately the ionic strength of the contaminated Bemidji ground water. Phenanthrene was added in a radiolabeled form (phenanthrene-9-¹⁴C).

The phenanthrene was placed in glass centrifuge tubes with plastic caps and Teflon-lined septa. The organic acid/potassium nitrate solutions were sparged with argon to remove oxygen (<10 ppb) and added to the tubes. Sparged ferrous iron solution was spiked into the tubes and pH was adjusted to 6.5 with a sodium hydroxide solution. This pH was at least 1.5 pH units above

the pK_a values of the carboxylic acids. The headspace in the tubes was replaced with argon and sealed for 14 d (an equilibration time chosen by kinetic tests) at room temperature (20±2°C). The vials were centrifuged (1750 g, 1 h) to force the excess phenanthrene to the argon-water interface. An aliquot of the aqueous solution was withdrawn by syringe for determination of phenanthrene concentration by liquid scintillation counting. All solution preparation was performed in an argon-filled glove box. Duplicate experiments were conducted for all data reported.

Table 1. Characteristics of the hydrophobic acid fractions (XAD-8) of the natural organic matter and the carboxylic acids used in the solubility enhancement experiments. The Number-averaged molecular weight (M_n), aromaticity, carboxyl content, and oxygen/carbon (O/C) ratio are shown. Aromaticity and carboxyl content calculated for the carboxylic acids and measured by ¹³C-nuclear magnetic resonance analysis for the hydrophobic acid fractions.

organic acid	M _n (Da)	aroma- ticity (%)	carboxyl content (%)	O/C ratio
well 310A ¹ (XAD-8)	536	18	15	0.66
well 532A ² (XAD-8)	350	n.d.	n.d.	n.d.
well 530A ³ (XAD-8)	362	19	14	0.47
SR FA ⁴ (XAD-8)	826	25	21	0.71
2-naphthoic	160	91	9.1	0.24
2,6-naphthoic	204	83	17	0.44
3-hydroxy-2-naphthoic	200	91	9.1	0.36
pamoic	388	91	9.1	0.35
undecanoic	186	0	9.1	0.24
1,11-undecanedioic	216	0	18	0.48

¹Aiken and Thorn (unpublished data)

²Eganhouse and others (1993)

³Aiken (unpublished data)

⁴SR FA is Suwannee River fulvic acid (Aiken and Malcolm, 1987)

RESULTS

Pumping Rates during Sampling

Well 532A was purged at increasing pumping rates before sampling on four successive

days. Turbidity and dissolved oxygen decreased during purging, while pH and specific conductance were fairly constant (fig. 3).

The purging time required to reach a stable turbidity level decreased as the pumping rate increased (fig. 4). The stable turbidity values were highest at the lowest pumping rate. On the fourth day, when the pumping rate was decreased to medium and low rates after purging and sampling at 1.8 L min^{-1} , turbidity increased by 15 to 35% above the stable turbidity level. Only turbidity showed a significant variation as the pumping rate was increased.

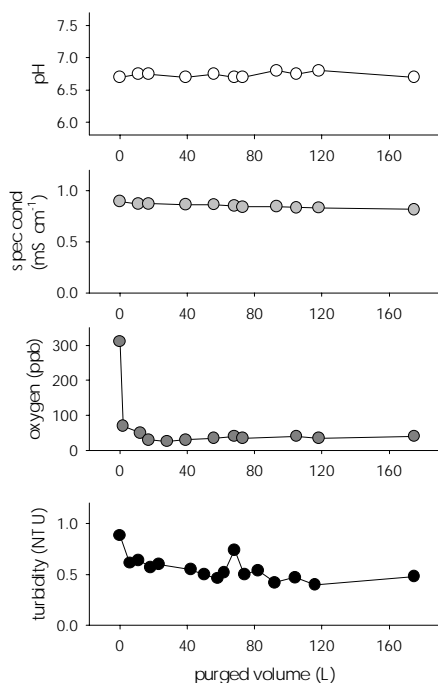


Figure 3. Changes in pH, specific conductance (spec cond), dissolved oxygen, and turbidity during the purging of well 532A at 0.35 L min^{-1} .

Ground Water Chemistry

The ground water sampling conducted during this study echoed results obtained in previous studies (Baedecker and others, 1993; Eganhouse and others, 1993) as shown in fig. 5. Near the oil body, pH decreased slightly and specific conductance roughly doubled. Dissolved oxygen decreased from near saturation to undetectable levels ($<0.1 \text{ mg L}^{-1}$). Dissolved iron

increased from undetectable levels ($<2 \mu\text{M}$) to 0.72 mM . Ground water from the background well (310A) was similar to ground water from the well most down-gradient (515A). Filtered ($0.1 \mu\text{m}$) and unfiltered ground water samples displayed no significant difference in major cation and metal concentrations. Field measurements of total iron agreed well with laboratory measurements by ICP-AES. In contrast, the organic carbon concentration of material trapped on 500 molecular weight cutoff ultrafilters ranged from 0.4 to 5.9 mg C L^{-1} (table 2).

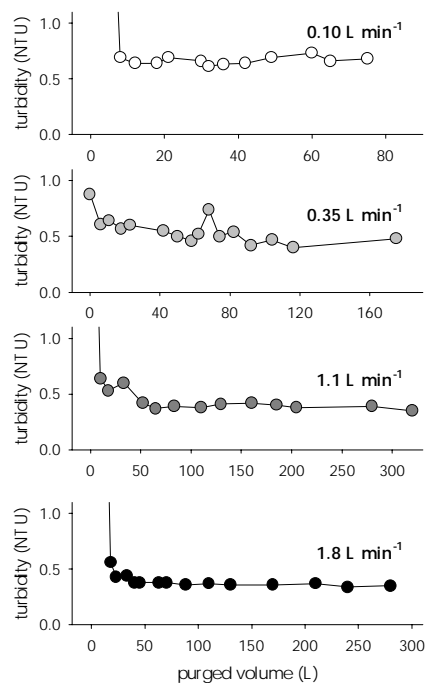


Figure 4. Changes in turbidity during purging of well 532A at four different pumping rates on four different days.

Inorganic Colloids

Turbidity measurements ranged from near zero in the background and distant downgradient wells to 0.75 NTU in the wells near the oil body (fig. 5). Estimates of particle number concentrations revealed about 30 times higher colloid concentrations in ground water near the oil body. Assuming an inorganic colloid density range of $2\text{-}4 \text{ g cm}^{-3}$, colloid mass concentrations ranged from about $1\text{-}2 \mu\text{g L}^{-1}$ in the background

ground water to about 20-40 $\mu\text{g L}^{-1}$ near the oil body. These mass concentrations are much less than the organic colloid concentration (table 2).

The inorganic colloids were roughly uniform in size (100-300 nm diameter) and shape (spherical) (fig. 6). Iron predominated the EDX scans of the colloids. Very few larger particles (approximately 1%) with elemental compositions similar to clay minerals (Al, Si, K) and organic matter (no elements above F) were also detected.

Fluorescence Quenching

The fluorescence quenching experiments showed that perylene associates significantly with the organic colloids in the ground water down-gradient from the oil body (wells 531A, 530A, and 515A; table 2). No perylene binding was observed for the background ground water (well 310A). The extent of solubility enhancement decreased with distance down-gradient of the oil body. Some of this decrease may be attributed to the decrease in colloidal organic matter concentration with distance from the oil body; however, the organic matter partition coefficient (K_{om}) also decreased slightly with distance from the oil body.

Table 2. Fluorescence quenching results for the partitioning of perylene to colloids in the Bemidji ground water. Solubility enhancement is the ratio of the apparent solubility to the predicted solubility. K_{om} is the organic matter-normalized partition coefficient.

well	distance from oil (m)	organic colloid (mg C L ⁻¹)	solubility enhancement	K_{om} (mL g ⁻¹)
310A	-190	0.4	1.0	no quench
531A	25	5.9	2.2	4.0×10^5
530A	50	3.3	1.5	3.2×10^5
515A	140	2.2	1.3	3.0×10^5

Solubility Enhancement

The results of the solubility enhancement experiments are shown in table 3. The aliphatic carboxylic acids (undecanoic and 1,11-undecanedioic acids) and pamoic acid were most effective at binding phenanthrene, but ferrous iron did not significantly improve their ability to bind

phenanthrene. The hydrophobic acid fractions and the remaining aromatic carboxylic acids were roughly equal in their ability to bind phenanthrene. At a concentration of 0.9 mM, ferrous iron somewhat improved phenanthrene binding of the hydrophobic acid fractions of the natural organic matter (11 to 55% increase in K_{om}). For the aromatic carboxylic acids (except pamoic acid), ferrous iron approximately doubled phenanthrene binding (205 to 250% increase in K_{om}).

Table 3. Solubility enhancements and organic matter-water partition coefficients (K_{om}) for phenanthrene with various organic acids in the absence and presence of ferrous iron at a concentration of 0.9 mM.

organic acid	relative solubility enhancement		K_{om} (mL g ⁻¹)	
	without Fe ²⁺	with Fe ²⁺	without Fe ²⁺	with Fe ²⁺
blank ¹	1 (±0.008)	1.03 (±0.010)	--	$10^{3.16}$
well 310A (XAD-8)	1.36 (±0.015)	1.55 (±0.017)	$10^{3.85}$	$10^{4.05}$
well 532A (XAD-8)	1.51 (±0.022)	1.62 (±0.024)	$10^{4.01}$	$10^{4.10}$
SR FA ² (XAD-8)	1.40 (±0.015)	1.45 (±0.020)	$10^{3.90}$	$10^{3.95}$
2-naphthoic	1.14 (±0.022)	1.35 (±0.028)	$10^{3.85}$	$10^{4.25}$
3-hydroxy-2-naphthoic	1.21 (±0.022)	1.44 (±0.017)	$10^{4.03}$	$10^{4.34}$
2,6-naphth-dioic	1.19 (±0.025)	1.45 (±0.010)	$10^{3.99}$	$10^{4.35}$
pamoic	1.40 (±0.008)	1.39 (±0.011)	$10^{4.30}$	$10^{4.30}$
undecanoic ³	1.44 (±0.006)	1.34 (±0.015)	$10^{4.34}$	$10^{4.24}$
1,11-undecane-dioic	1.34 (±0.008)	1.41 (±0.010)	$10^{4.23}$	$10^{4.31}$

¹The solubility enhancement caused by Fe²⁺ alone was used to correct the organic acid solubility enhancements.

²SR FA is Suwannee River fulvic acid.

³black precipitate was observed.

For the undecanoic acid, repeated trials at a ferrous iron concentration of 0.9 mM produced a black precipitate after centrifugation. We suspect that the black precipitate reduced the solution concentration of phenanthrene, resulting in a

solubility enhancement and K_{om} value lower than expected in the presence of ferrous iron. At the higher ferrous iron concentration, 2.7 mM, black precipitates were produced in all of the solutions. The solubility enhancement caused by the higher ferrous iron concentration was 1.03 ± 0.010 , the same value observed at the lower ferrous iron concentration.

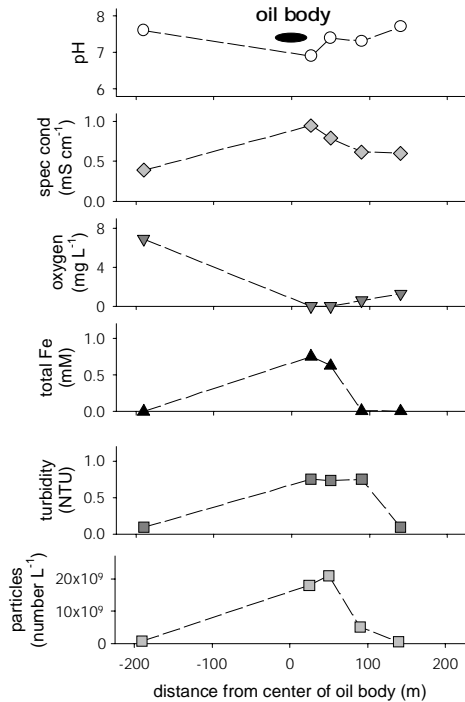


Figure 5. Variations in pH, specific conductance (spec cond), dissolved oxygen, turbidity, and particle number concentration as a function of distance from the oil body.

DISCUSSION

Pumping Rates during Sampling

Ground water sampling protocols have typically required the removal of three to five well volumes of ground water prior to sample collection. This purging of the well is meant to assure collection of ground water representative of the ground water in the formation, unaffected by the presence of the well. From this study and others (Puls and others, 1992; Backhus and

others, 1993), it is clear that turbidity is still decreasing at three to five well volumes, while parameters like pH and specific conductance have reached steady levels. At this site, as many as 100 well volumes were removed before reaching a stable turbidity level.

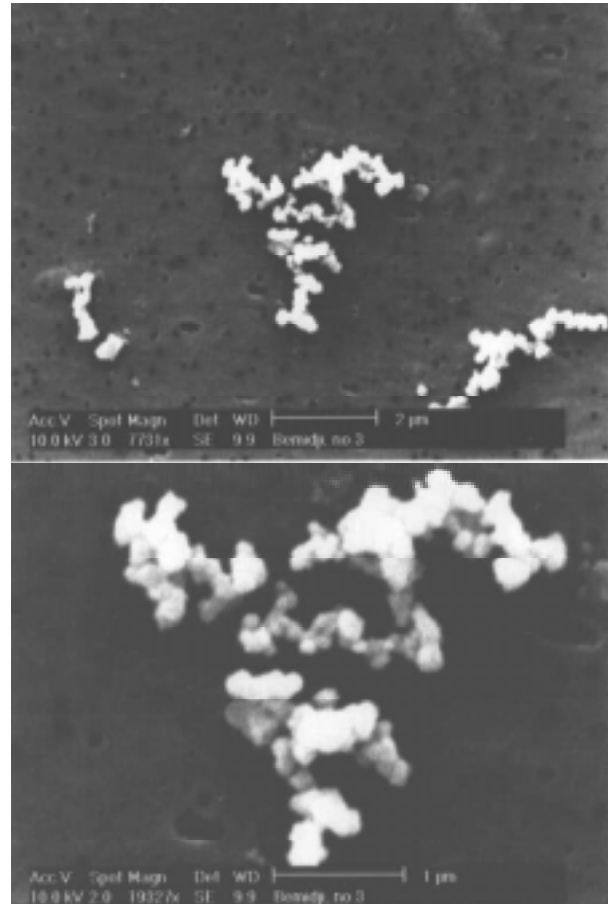


Figure 6. SEM images of colloids from well 532A (25 m down-gradient from oil body) trapped on 0.1 μm filters. Colloids are composed mostly of iron. Magnification of 7,700 times (top) and 19,000 times (bottom). Scale bars of 1 μm are shown.

Previous research on the effect of pumping rate on colloid concentrations concluded that higher pumping rates resulted in higher stable colloid concentrations (Puls and others, 1992; Backhus and others, 1993). Higher pumping rates produce greater shear on colloids attached to the framework grains. In this study, however, there was a slight decrease in the stable turbidity level as the pumping rate was increased. We suspect that the slight decrease may have resulted from depletion of the supply of colloids that could be

mobilized by shear. Note that the stable turbidity level decreased with successive tests (from low to high pumping). Inexplicably, decreases in the pumping rate after purging and sampling at a high rate also caused a decrease in the stable turbidity level. The higher stable turbidity level measured on the first day (at the lowest rate) may also be attributable to disturbance of colloids in the well. After the first day, the pump was left in the well. Puls and others (1992) observed the same effect in their studies and recommended that dedicated sampling equipment be used to more accurately sample colloids in ground water.

Colloid Mobilization and Transport

Given the significant difference between the colloid concentrations of the background well (310A) and the wells near the oil body (532A, 531A) (fig. 5), we surmise that the change in ground water chemistry caused by the oil spill is responsible for the mobilization of colloids near the oil body. A coincidence of reducing conditions and high colloid concentrations was observed by Ryan and Gschwend (1990; 1992) in Atlantic Coastal Plain sediments below an organic matter-rich swamp. At Bemidji, the degradation of oil is responsible for the onset of reducing conditions (Cozzarelli and others, 1994).

For the Atlantic Coastal Plain sediments, Ryan and Gschwend (1990; 1992) hypothesized that the mobilization of colloids (mainly clay minerals) was caused by the reductive dissolution of ferric oxyhydroxide coatings binding clay colloids to the framework grains. At Bemidji, ferric oxyhydroxides were not listed as significant components of the sediments, but ilmenite (FeTiO_3) is present in the heavy mineral fraction (Bennett and others, 1993). Ilmenite is also present in the Atlantic Coastal Plain sediments examined by Ryan and Gschwend (1992) and its weathering under oxidizing conditions released ferric iron that accumulated as oxyhydroxide coatings on grains. It is likely that the native Bemidji sediments are also coated by iron oxyhydroxides. The high concentrations of ferrous iron in the anoxic, organic carbon-rich ground water near the oil body also indicates that iron oxyhydroxide coatings must be present on the Bemidji sediments.

Despite the apparent similarity in colloid mobilization conditions, far fewer inorganic colloids were mobilized in the Bemidji ground water than in the Atlantic Coastal Plain ground waters. At Bemidji, the colloids mobilized (up to an estimated $30 \mu\text{g L}^{-1}$) are primarily small amorphous iron-rich spheres with a few clay colloids. In the Atlantic Coastal Plains sediments, the mobilized colloids (up to 60mg L^{-1}) were mainly clay minerals with a few crystalline goethite particles. The difference in colloid concentrations may be attributed to the difference in the clay content of the sediments. The clay content of the Bemidji sediments is less than 1% and the Atlantic Coastal Plain sediments contain nearly 4% clay. In addition, the relatively high ionic strength of the Bemidji ground water (estimated at approximately 10 mM near the oil body) may prevent colloid mobilization. The ionic strengths of the Atlantic Coastal Plain ground waters were about one to two orders of magnitude lower than that of the contaminated Bemidji ground water.

The morphology of the iron-rich colloids suggests that they formed by relatively rapid oxidation of ferrous iron. While it may seem likely that these colloids formed after sampling, we believe that they are present in the ground water because we assiduously avoided exposure of the samples to the atmosphere. Colloid abundance on the filters correlated well with the turbidity of the samples and turbidity was measured in the field before any significant ferrous iron oxidation could occur at the pH of these samples (6.5 to 7.0). Samples returned to the laboratory and filtered in an argon-filled glove box contained the same colloids at similar concentrations. We surmise that these colloids were formed by ferrous iron oxidation brought on by the diffusion of trace levels of oxygen ($<10 \text{ppb}$) into the Zone III and IV ground water (fig. 1). The wells sampled were screened within one meter of the water table.

Perylene Binding in Bemidji Ground Water

The fluorescence quenching experiments indicate that the oil degradation products present near the oil body enhance the apparent solubility

of perylene. The natural organic matter in the background well (310A) is not present at sufficiently high concentration to enhance perylene solubility. If the oil degradation products are mobile, they could facilitate the transport of perylene and other PAHs of similar hydrophobicity down-gradient. Given the low concentrations of inorganic colloids, it appears that the oil degradation products may be responsible for the observation of phenanthrene and fluorene concentrations above solubility at the site and the detection of these PAHs at distances down-gradient further than expected (Aiken and others, 1991).

The perylene K_{om} values measured by fluorescence quenching ($10^{5.5}$ to $10^{5.6}$ mL g⁻¹) are slightly lower than the K_{om} value predicted using the K_{om} - K_{ow} linear free energy relationship (LFER) developed by Karickhoff (1981) for PAH binding by soil organic matter. Using a K_{ow} value of $10^{6.50}$ for perylene, this LFER predicts a K_{om} value of $10^{5.85}$ mL g⁻¹. This difference may reflect a difference in the aromaticity of the organic matter responsible for perylene binding. The oil degradation products are predominantly aliphatic (Eganhouse and others, 1993) and the soil organic matter used by Karickhoff (1981) is probably more aromatic. Chin and others (1997) showed that the K_{om} values of PAHs decrease with increasing aliphatic content of the organic matter.

Phenanthrene Binding by Organic Matter

The organic matter partition coefficients for phenanthrene measured in the absence of ferrous iron compare favorably with K_{om} values estimated for aromatic hydrocarbons with K_{ow} values (Karickhoff, 1981). This LFER produces a K_{om} estimate of $10^{3.90}$ mL g⁻¹ using a K_{ow} value of $10^{4.57}$. The K_{om} values for the hydrophobic acid fractions (well 310A, SR FA) were within 10% of this estimate; however, the hydrophobic acid fraction from ground water near the oil body (well 532A) was about 30% more effective at binding phenanthrene. Given the predominance of aliphatic oil degradation products in the well 532A ground water (Eganhouse and others, 1993), we expected a lower K_{om} , similar to the effect observed for perylene binding measured by fluorescence quenching.

The binding of hydrophobic organic compounds by organic matter generally increases with the molecular weight of the organic matter (Chin and others, 1997). In contrast, we observed that the lower molecular weight carboxylic acids were at least as or more effective at binding perylene than the higher molecular weight hydrophobic acid fractions. On the basis of these differences, it appears that K_{om} increases with increasing aliphatic content and decreasing oxygen/carbon ratios. To enhance phenanthrene binding, the long hydrocarbon chains of the aliphatic carboxylic acids must provide more accessible hydrophobic surface area than the hydrophobic acid fractions.

Effect of Ferrous Iron on Phenanthrene Binding

The presence of ferrous iron alone in solution very slightly enhanced the solubility of phenanthrene. While this solubility enhancement was subtracted from the solubility enhancements caused by the organic acids as a blank correction, some association between ferrous iron and PAHs is not unexpected. Metal ions can form charge transfer complexes with pi electrons in aromatic rings (e.g., the Ag⁺-naphthalene binding constant is log K = 0.49; Smith and Martell, 1989). To check this effect, a higher concentration of ferrous iron, 2.7 mM, was added to the aqueous solution and equilibrated with phenanthrene. The solubility enhancement, however, was not significantly different than that measured at 0.9 mM ferrous iron.

The presence of ferrous iron had no significant effect on the K_{om} values for the aliphatic carboxylic acids, although the black precipitate that appeared in the undecanoic acid solution may have artificially lowered the measured K_{om} value. Ferrous iron slightly increased the K_{om} values of the hydrophobic acid fractions and roughly doubled the K_{om} values of the aromatic carboxylic acids, with the exception of pamoic acid. We surmise that ferrous iron is promoting greater association of the organic acids with each other, resulting in an effective increase in the molecular weight of the organic acids. This increase in molecular weight would provide a more hydrophobic partitioning environment and higher K_{om} values.

Bivalent cations that do not bind strongly with carboxyl groups promote the aggregation of humic substances by charge suppression. Cations that bind to carboxyl groups more strongly, like Cu^{2+} , are thought to form multiligand complexes that more effectively promote organic matter aggregation (Underdown and others, 1985). If ferrous iron behaved as Cu^{2+} did for fulvic acid, we would expect the solubility enhancement caused by ferrous iron for 3-hydroxy-2-naphthoic acid to be greater than that for 2-naphthoic acid because the 3-hydroxy-2-naphthoic acid can form a strong bidentate complex. Ferrous iron complexation constants are not available for these compounds, but we know that hydroxybenzoic acid ($\log K = 10.13$) forms much stronger copper(II) complexes than benzoic acid ($\log K = 1.76$) (Smith and Martell, 1989). Contrary to the strong multiligand aggregation hypothesis, the solubility enhancement for 2-naphthoic acid was slightly greater than that for the 3-hydroxy-2-naphthoic acid. It appears to be more likely that ferrous iron is increasing the solubility enhancement by allowing organic acid association through charge suppression.

CONCLUSIONS

The geochemical changes caused by oil degradation have mobilized a small amount of iron-rich colloids in the Bemidji ground water. The organic colloids in the contaminated ground water are capable of enhancing the solubility of very hydrophobic PAHs. Potentially, this solubility enhancement may have contributed to the transport of such PAHs over distances greater than expected (Aiken and others, 1991). The presence of high ferrous iron concentrations in the contaminated Bemidji ground water may increase the ability of the the oil degradation products to enhance the solubility of PAHs.

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