

# Processes Affecting the Fate of Monoaromatic Hydrocarbons in an Aquifer Contaminated by Crude Oil

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Crude oil spilled from a subsurface pipeline in north-central Minnesota has dissolved in the groundwater, resulting in the formation of a plume of aliphatic, aromatic, and alicyclic hydrocarbons. Comparison of paired oil and groundwater samples collected along the central axis of the residual oil body shows that the trailing edge of the oil is depleted in the more soluble aromatic hydrocarbons (e.g., benzene, toluene, etc.) when compared with the leading edge. At the same time, concentrations of monoaromatic hydrocarbons in groundwater beneath the oil increase as the water moves toward the leading edge of the oil. Immediately downgradient from the leading edge of the oil body, certain aromatic hydrocarbons (e.g., benzene) are found at concentrations near those expected of a system at equilibrium, and the concentrations exhibit little variation over time ( $\approx 8$ –20%). Other compounds (e.g., toluene) appear to be undersaturated, and their concentrations show considerably more temporal variation ( $\approx 20$ –130%). The former are persistent within the anoxic zone downgradient from the oil, whereas concentrations of the latter decrease rapidly. Together, these observations suggest that the volatile hydrocarbon composition of the anoxic groundwater near the oil body is controlled by a balance between dissolution and removal rates with only the most persistent compounds reaching saturation. Examination of the distributions of homologous series and isomeric assemblages of alkylbenzenes reveals that microbial degradation is the dominant process controlling the fate of these compounds once groundwater moves away from the oil. For all but the most persistent compounds, the distal boundary of the plume at the water table extends no more than 10–15 m downgradient from the oxic/anoxic transition zone. Thus, transport of the monoaromatic hydrocarbons is

limited by redox conditions that are tightly coupled to biological degradation processes.

## Introduction

When oil (or a refined petroleum product) comes in contact with water, a large number of compounds are found to dissolve (1). The most soluble constituents are the monoaromatic hydrocarbons (2, 3). Consequently, benzene and its alkylated derivatives are the hydrocarbons most frequently encountered in groundwater. Because the aqueous solubilities of liquid hydrocarbons decrease exponentially with increasing molar volume (or solvent cavity surface area, refs 4–6), benzene and the C<sub>1</sub>–2-benzenes, aka BTEX, tend to be the dominant monoaromatic hydrocarbons in contaminated groundwater. The higher aqueous solubilities and relatively low sediment–water partition coefficients of the BTEX compounds (7, 8) would be expected to result in greater mobilities than more highly alkylated benzenes. Several BTEX compounds are on the U.S. EPA List of Priority Pollutants and are known or suspected carcinogens. For all these reasons, the monoaromatic hydrocarbons, and in particular BTEX, are currently the subject of much interest, and considerable effort is being made to improve our understanding of processes that control their transport and fate in aquatic environments.

In this paper, we present the results of geochemical studies at a site where a crude oil spill in 1979 resulted in contamination of a sand and gravel aquifer. Data presented here reflect investigations conducted during 1985–1988 and especially 1987, the year of the most extensive sample collections. This paper focuses on processes affecting the fate of the volatile hydrocarbons (VHCs) in oil-contaminated groundwater with particular emphasis on the monoaromatic hydrocarbons. Our principle objectives were to (1) examine the effect of dissolution processes on the monoaromatic hydrocarbon composition of residual oil and groundwater, (2) determine the extent to which groundwater immediately downgradient from the oil is saturated with respect to monoaromatic hydrocarbons, and (3) establish the dominant process(es) responsible for removal of monoaromatic hydrocarbons within the anoxic zone downgradient from the oil.

## Materials and Methods

**Study Site.** In August 1979, a pipeline rupture occurred in north-central Minnesota near the town of Bemidji, causing 1670 m<sup>3</sup> of a light paraffinic crude oil to be spilled (Figure 1a). A portion of the 410 m<sup>3</sup> of crude oil unaccounted for after the cleanup effort is present as a 'body' of oil floating on the water table. The oil is irregularly distributed over

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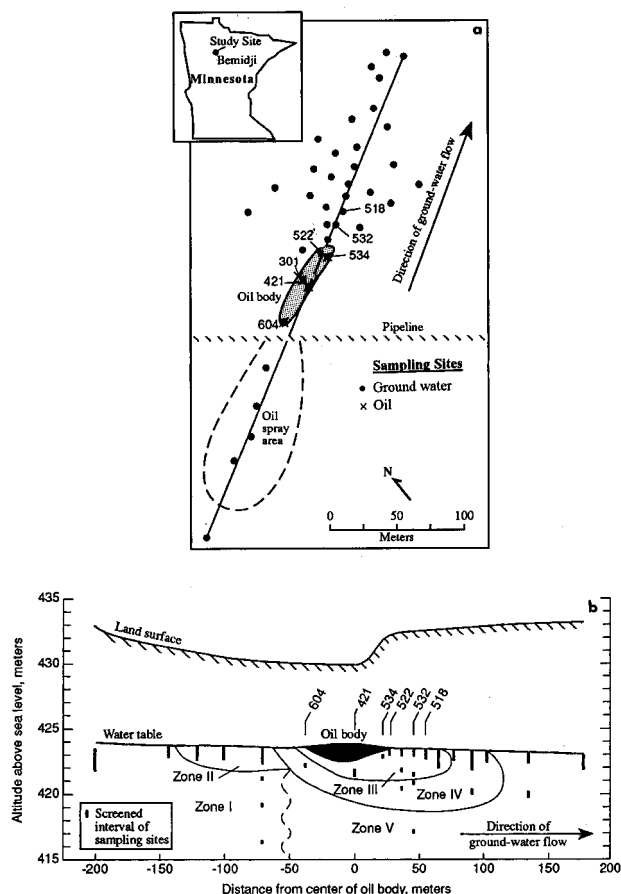


FIGURE 1. Bemidji study site: (a) plan view of site showing locations of water table wells where oil and groundwater samples were collected; (b) cross section through contaminant plume along main sampling transect showing positions of screened intervals from which groundwater samples were collected. Geochemical zonation after Baedecker *et al.* (11) based on field data collected in 1987.

a 7–8-m vertical interval of unconsolidated sediment above the water table and has spread to a length of 70–80 m in the direction of groundwater flow (9). Dissolution of soluble components of the oil in the groundwater has resulted in the formation of a plume of VHCs that extends approximately 170 m from the center of the oil body and generally parallels the direction of groundwater flow (10). The monoaromatic hydrocarbons comprise roughly 85% of the VHCs near the oil body. However, compositional changes are observed downgradient from the oil, and the shape and the size of the plume suggest that either dispersion is minimal or attenuation processes are acting to limit its migration and spread. Model calculations presented by Baedecker *et al.* (11) demonstrate that the concentration of a conservative solute would be expected to show little change over the path length described by the VHC plume. By contrast, the concentration of BTEX compounds decrease by approximately 3 orders of magnitude over the same distance.

The introduction of crude oil to this aquifer has resulted in alteration of the geochemical conditions in the groundwater and formation of distinct geochemical zones as described by Baedecker *et al.* (11). These zones reflect the dominant pathways by which metabolizable organic matter, in this case represented by soluble constituents of the oil and their byproducts, is being degraded by microorganisms. The zones, depicted in a cross section centered within the main contaminant plume in the direction of groundwater

flow (Figure 1b), correspond to the following: I, uncontaminated native groundwater; II, impacted groundwater upgradient of the oil body; III, anoxic groundwater immediately beneath and downgradient from the oil body; IV, suboxic transitional zone where anoxic groundwater from zone III mixes with more oxygenated groundwater; and V, oxygenated groundwater that approaches conditions of native groundwater. The geochemistry of the groundwater in each zone reflects that of water upgradient from it and processes (*e.g.*, sorption, dilution, degradation, dissolution, recharge, gas exchange) occurring within that zone. The reader is directed elsewhere (10–14) for more extensive discussions of the development of these geochemical zones and their evolution over time as well as the general hydrogeology and geochemistry of the site.

**Sampling and Analyses.** Details of the procedures used for the collection of residual oil and groundwater samples can be found in Eganhouse *et al.* (10). Analytical methods used for the determination of VHCs are presented in Eganhouse *et al.* (15). Groundwater samples were collected from boreholes identified in Figure 1. Positions and approximate lengths of the screened intervals are indicated in Figure 1b. Individual VHC concentrations were determined using purge-and-trap high-resolution gas chromatography (P&T-HRGC) with either flame ionization detection (FID) or mass spectrometry (MS). Oil samples were diluted with pentane and analyzed for monoaromatic hydrocarbon content using a Finnigan 4510B HRGC/quadrupole MS.

**Equilibration Experiment.** Volatile-free water (VFW; cf. ref 15) was equilibrated with each of three oil samples collected along the central axis of the oil body (604, 421, 534; cf. Figure 1a). A high oil/water ratio was chosen in order to ensure that the concentration of monoaromatic hydrocarbons in the oil phase would be reduced by no more than 1% upon attainment of equilibrium (16). Duplicate equilibrations for each oil were carried out by placing 2 mL of oil and 3 mL of VFW into 5 mL gas-tight syringes fitted with Teflon Mini-nert valves (the VFW was poisoned with  $\text{HgCl}_2$ ). The sealed syringes were maintained in the dark in a thermostated bath at  $9 \pm 0.01^\circ\text{C}$  under static conditions for a period of 35 days. At this point, the syringe was removed from the bath, and the Mini-nert valve was rinsed with VFW. The valve was then opened and flushed with a small aliquot of hydrocarbon-saturated water from the syringe after which a 1.5 mL glass vial was filled with the hydrocarbon-saturated water. The water was stored under refrigeration until it could be analyzed for monoaromatic hydrocarbons by P&T-HRGC/MS using a Finnigan Model 800A ion trap detector interfaced to a Varian 3400 HRGC and Tekmar 2016/LSC 20 Autosampler purge-and-trap system. Conditions of analysis were identical to those described in Eganhouse *et al.* (15).

## Results and Discussion

In field studies of this type, it is frequently assumed that changes in solute composition and concentration downgradient from the source are due *solely* to physical and biogeochemical processes acting to attenuate/transform the species of interest. However, temporal fluctuations in the input of these solutes can also exert an influence on downgradient variations in composition. In order to interpret the observed changes in VHC composition and concentrations downgradient from the oil body, we felt it was necessary to better characterize the source (*i.e.*, the

TABLE 1

Pearson Correlation Matrix for Alkylbenzene Concentrations in Oils<sup>a</sup>

	604 (trailing edge)	421 (center)	534 (leading edge)	301/1
604 (trailing edge)	1.000			
421 (center)	0.971	1.000		
534 (leading edge)	0.979	0.978	1.000	
301/1	0.994	0.967	0.981	1.000
301/2	0.974	0.968	0.996	0.976

<sup>a</sup>  $p < 0.001$  for all correlations.

oil) and to identify processes that could affect temporal variability in the supply of hydrocarbons to groundwater in contact with it.

**Dissolution Process: Effects on Oil Composition.** To characterize the source term, we examined the chemical homogeneity of oil in contact with groundwater. For this purpose, we collected samples of oil along the central axis of the oil body spanning its length in the direction of groundwater flow (cf. Figure 1a). Samples were obtained near the trailing edge (604), center (421), and leading edge (534) of the oil body. Oil samples were collected from these wells immediately after drilling was completed and could not have undergone weathering due to exposure (10). In addition, two samples of oil from well 301 (Figure 1a) were included in the analysis.

Table 1 presents a Pearson correlation matrix for concentrations of 22 monoaromatic hydrocarbons determined in these oil samples. The correlation coefficients exceed 0.96 (with  $p < 0.001$ ) in all cases indicating that the oil is compositionally similar regardless of location along the axis of groundwater flow. When the data for alkylbenzenes in leading edge (534) and upgradient (604, 421) oils are subjected to linear regression analysis, however, the slopes of the resulting lines are found to be greater than unity (i.e., oils upgradient from the leading edge of the oil body are depleted in some compounds). The magnitude of the difference in concentration is related to the aqueous solubility of the compound as shown in Figure 2a (cf. Table 2 for compound identification). By comparison, Henry's law constants show no relationship with the extent of depletion. This suggests that dissolution rather than volatilization is responsible for differences between the leading and trailing edge oils.

To evaluate the extent to which these differences might reflect the effects of 'water washing' during passage of groundwater beneath the oil body, we simulated the removal of 12 hydrocarbons from the 534 oil (leading edge) as a series of batch equilibrations. For purposes of this simulation, it was assumed that the composition of oil from the trailing edge (604) was initially the same as that found in oil from the leading edge in 1987 (534). Using the empirical relationship between aqueous solubility ( $S_i^w$ ) and fuel-water partition coefficient ( $K_{fw}$ ) for monoaromatic hydrocarbons developed by Cline *et al.* (17)

$$\log K_{fw} = -1.00 \log S_i^w + 0.85 \quad (1)$$

one can show that the fraction of a hydrocarbon remaining in the oil following a series of batch equilibrations with water, ( $C_{ij}/C_{i0}$ ), is given by

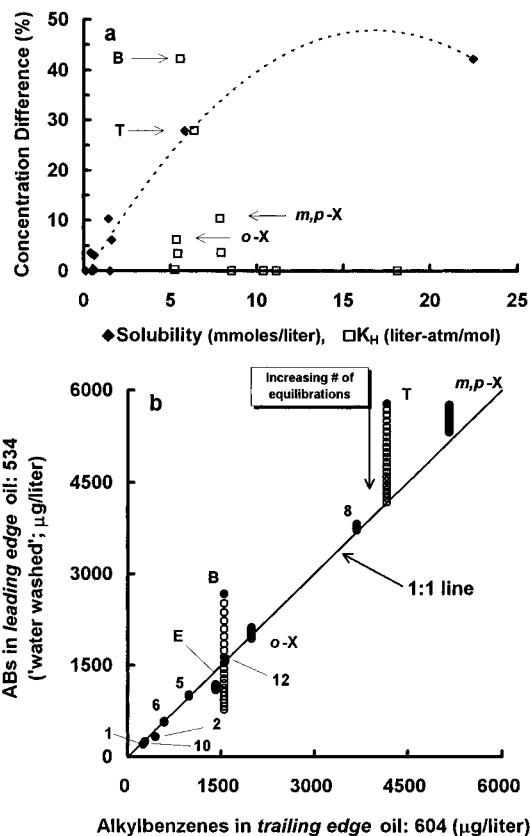


FIGURE 2. Composition of Bemidji crude oils: (a) difference in concentrations of alkylbenzenes in 534 (leading edge) and 604 (trailing edge) oils vs aqueous solubility and Henry's law constant; (b) concentrations of alkylbenzenes in simulated 'water washed' oil 534 vs oil 604. Compound identifications given in Table 2.

$$\frac{C_{ij}}{C_{i0}} = \left\{ \frac{\frac{K_{fw}}{\beta}}{\left( \frac{K_{fw}}{\beta} \right) + 1} \right\}^j \quad (2)$$

where  $K_{fw} = 10^{[0.85 - \log(S_i^w \cdot 10^6)]}$ ,  $i$  is the hydrocarbon of interest,  $j$  is the number of equilibrations,  $S_i^w$  is the aqueous solubility of hydrocarbon  $i$  at 20 °C (mol/L), and  $\beta$  is the water/oil ratio (v/v). There is no empirical basis for selecting either the water/oil ratio ( $\beta$ ) or the number of equilibrations,  $j$ , for this simulation. However, these parameters would be expected to affect the evolutionary path along which the composition of the oil changes during successive equilibrations, not the relative rates at which the alkylbenzenes would be depleted (16). As a first approximation, we used a water/oil ratio of 20 to illustrate the relationship between 'water washing' and oil composition. Figure 2b shows a scatterplot of concentrations for 12 alkylbenzenes in 'artificially water washed' oil from well 534 (leading edge) vs those in oil from well 604 (trailing edge). The solid symbols represent original compositions (untreated well 534 oil), whereas open symbols correspond to oil compositions following 20 successive equilibration steps. When these data sets are subjected to linear regression analysis with forcing through the origin, the slopes are found to decrease continuously with increasing numbers of equilibrations (from  $m = 1.17$  at  $j = 0$  to  $m = 0.987$  at  $j = 20$ ) and the correlation coefficients increase from 0.977 (untreated) to 0.990 (at  $j = 20$ ). The model can be optimized to yield a slope near unity ( $m = 1.002$ ,  $r = 0.996$  at  $j = 18$ ),

TABLE 2

## Compounds Determined in This Study

compound	identifying code <sup>a</sup>	compound	identifying code <sup>a</sup>
benzene	B	1-methyl-2-isopropylbenzene	14
toluene	T	1,3-diethylbenzene	15
<i>o</i> -xylene	<i>o</i> -X	1-methyl-3-propylbenzene	16
<i>m,p</i> -xylenes	<i>m,p</i> -X	1-methyl-4-propylbenzene	17
ethylbenzene	E	1,4-diethylbenzene	18
isopropylbenzene	1	<i>n</i> -butylbenzene	19
<i>n</i> -propylbenzene	2	1,3-dimethyl-5-ethylbenzene	21
1-methyl-3-ethylbenzene	3	1,2-diethylbenzene	20
1-methyl-4-ethylbenzene	4	1-methyl-2-propylbenzene	22
1,3,5-trimethylbenzene	5	1,4-dimethyl-2-ethylbenzene	23
1-methyl-2-ethylbenzene	6	1,3-dimethyl-4-ethylbenzene	24
1,2,4-trimethylbenzene	8	1,2-dimethyl-4-ethylbenzene	25
isobutylbenzene	9	1,3-dimethyl-2-ethylbenzene	26
sec-butylbenzene	10	1,2-dimethyl-3-ethylbenzene	27
1-methyl-3-isopropylbenzene	11	1,2,3,5-tetramethylbenzene	29
1,2,3-trimethylbenzene	12	1,2,3,4-tetramethylbenzene	30
1-methyl-4-isopropylbenzene	13		

<sup>a</sup> This code identifies compounds shown in Figures 2–6.

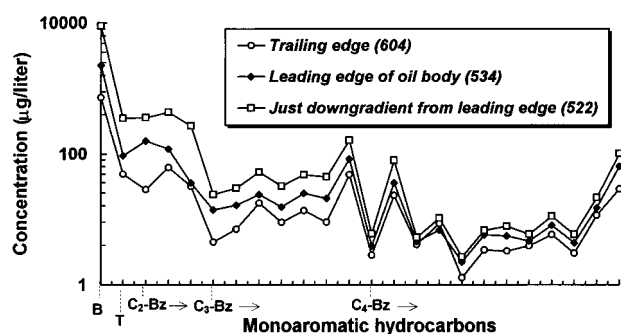


FIGURE 3. Distribution of monoaromatic hydrocarbons in ground-water beneath and downgradient from oil body.

but the important characteristic of this simulation is the progressive and systematic depletion of the more soluble (BTEX) hydrocarbons from the oil and the lack of same for the relatively insoluble alkylbenzenes. One feature to note is that each BTEX compound requires a different number of equilibrations in order to bring its initial concentration in the 534 oil to that observed in the 604 oil ( $j_{opt}$ ). This indicates that equilibrium partitioning can explain most, but not all, of the differences in oil composition. Because the value of  $j_{opt}$  appears to be inversely related to the persistence of the compound within the anoxic zone (see below), we hypothesize that  $j_{opt}$  also reflects removal processes (such as biodegradation) that are important for some compounds (e.g., toluene). In this case, removal processes would tend to move the system away from equilibrium, thereby increasing the total mass being transferred during dissolution. Notwithstanding uncertainties inherent in this preliminary computation, the results suggest that water washing of the oil body can account for most of the compositional changes observed along the groundwater flow path.

**Dissolution Process: Changes in Groundwater Composition along Axis of the Oil Body.** To further examine the dissolution process, we collected groundwater samples at the water table and beneath the oil samples described above. Figure 3 shows the distribution of monoaromatic hydrocarbons in samples from three locations (cf. Figure 1) along the axis of the oil body in the direction of groundwater flow. Well 604 was screened beneath but slightly downgradient from the trailing edge of the oil body,

whereas wells 534 and 522 were screened immediately beneath and just downgradient from the leading edge of the oil body, respectively (Figure 1b). The hydrocarbon concentration distributions, plotted on a logarithmic scale, show a high degree of correlation, and linear regression analysis of the untransformed data yields correlation coefficients of 0.998 or greater. This is consistent with observations of Burris and MacIntyre (18, 19), who found that hydrocarbon solute concentration ratios in water remain constant during the approach to equilibrium for simple three- and four-component systems. With increasing distance downgradient from the trailing edge of the oil body, all concentrations increase. Because volatile hydrocarbons have not been detected in groundwater upgradient from the oil body (10), the hydrocarbons found in these samples must be derived from the oil body via dissolution.

**State of the System: Is Ground Water in Equilibrium with the Oil?** The foregoing does little to indicate whether groundwater moving beneath the oil attains saturation with respect to the monoaromatic hydrocarbons by the time it is transported away from the oil body. To evaluate whether groundwater collected immediately downgradient of the oil body might be saturated with hydrocarbons we considered two approaches, one theoretical and the other experimental. Our purpose here is first to compare theoretical and experimental approaches and then to evaluate the field observations in the context of the latter.

The point of departure for the theoretical approach is the assumption that the Bemidji oil behaves as an ideal liquid mixture. At equilibrium, the mole fraction of a pure liquid hydrocarbon in water ( $X_{i,p}^w$ ), is given by

$$X_{i,p}^w = \frac{(\gamma_{i,p}^o X_{i,p}^o)}{\gamma_{i,p}^w} \quad (3)$$

where  $\gamma_{i,p}^o$  is the activity coefficient of pure hydrocarbon  $i$  in the organic phase (Raoult's convention),  $\gamma_{i,p}^w$  is the activity coefficient of pure hydrocarbon  $i$  in the aqueous phase, and  $X_{i,p}^o$  is the mole fraction of pure hydrocarbon  $i$  in the organic phase. Because the mole fraction and the activity coefficient of a pure hydrophobic liquid in the organic phase are both effectively unity, the aqueous



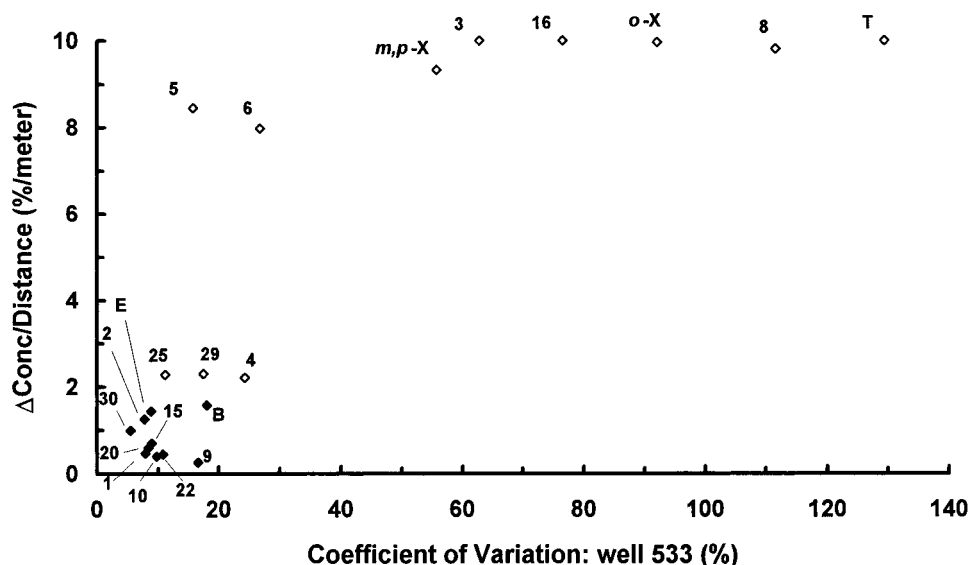


FIGURE 6. Relationship between minimum apparent disappearance rate (%/m) and temporal variability of alkylbenzene concentrations in groundwater (well 533). Compound identifications given in Table 2.

illustrated in Figure 5b which shows a plot of the (minimum) apparent disappearance rates (in units of % change in concentration/m) within the anoxic zone vs the difference between measured and equilibrium concentrations. The minimum apparent disappearance rates are calculated as the difference in concentration observed between two wells (one of which is 522), which define a trend of declining alkylbenzene abundance within the anoxic zone (cf. Figure 1b). These data show that anoxic groundwater immediately downgradient from the oil is saturated (within  $\pm 30\%$  of the equilibrium concentrations) with compounds found to be persistent under anoxic conditions within the plume. By contrast, compounds whose concentrations decrease more rapidly within the anoxic zone downgradient from the oil appear to be undersaturated ( $-30$  to  $-90\%$  of equilibrium concentrations) in groundwater from well 522.

**Temporal Variability in Groundwater Hydrocarbon Content.** Because downgradient concentration changes can be caused by temporal variations in the transfer of soluble hydrocarbons from oil to groundwater and/or time-variable recharge events, we decided to monitor the concentrations of monoaromatic hydrocarbons in groundwater just downgradient from the oil body over time. Figure 6 gives results of measurements made on samples collected at well 533 over a 9-month period from July 1988 to April 1989. Well 533 is 10 m downgradient from well 522 (abandoned in September 1987 with the appearance of oil) and was the well nearest to but downgradient from the oil at the time of monitoring study. This plot shows minimum apparent disappearance rates of monoaromatic hydrocarbons within the anoxic portion of the plume vs the coefficient of variation (CV) for concentrations of aromatic hydrocarbons measured during the monitoring study. Again, the monoaromatic hydrocarbons fall into two groups. Although there is some overlap in CVs between the two groups, those compounds showing rapidly decreasing concentrations downgradient of the oil body tend to exhibit greater fluctuations in concentration (ca. 20–129%). The more persistent species have CVs that are typically less than about 20%.

From observed compositional changes in the oil (Figure 2) and increasing concentrations of monoaromatic hydro-

carbons in groundwater along the groundwater flow path (Figure 3), it is clear that monoaromatic hydrocarbons are dissolving into groundwater as it passes beneath the oil body. The results of both the monitoring study and the comparison of theoretical predictions, equilibration studies, and field data suggest that, near the leading edge of the oil body, the concentration of a given compound is determined by a balance between its rate of dissolution and its rate of removal. Since rates of dissolution for these compounds would be expected to be nearly the same (18, 19), differences between field and equilibrium concentrations (Figure 5a) suggest that compound-specific removal processes are operative. Furthermore, the high variability of the less persistent compounds must primarily reflect temporal fluctuations in removal rates because of the very low variability seen for the most stable species ( $CV \approx 10$ –15%), which are at or near saturation in the groundwater.

**Processes Controlling Downgradient Changes in Hydrocarbon Concentrations: Distributions of Homologs and Isomeric Assemblages.** The determination of a large number of monoaromatic hydrocarbons (as compared with BTEX alone) affords an opportunity to examine the behavior of multiple homologous series and isomeric assemblages. Members of aromatic homologous series have physical properties that vary systematically with the addition of alkyl substituents or extension of an alkyl chain (24, 28). Consequently, these series can be used as probes of biogeochemical processes. Within the group of compounds we examined, there exist seven *n*-alkyl homolog series having three or more members. Because several of the compounds of interest in this study coelute under our conditions of analysis (15), we have data for only two series comprised of four or more members. These are the *n*-alkylbenzenes and the 1-methyl-2-alkylbenzenes. The abundances in groundwater of compounds representing these two series are plotted in Figure 7 as a function of distance downgradient from the center of the oil body. Concentrations have been normalized to those in groundwater collected from well 522 because this well was nearest to (but downgradient from) the leading edge of the oil body at the time of sample collection in 1987. Also shown is the approximate location of the distal boundary of the anoxic

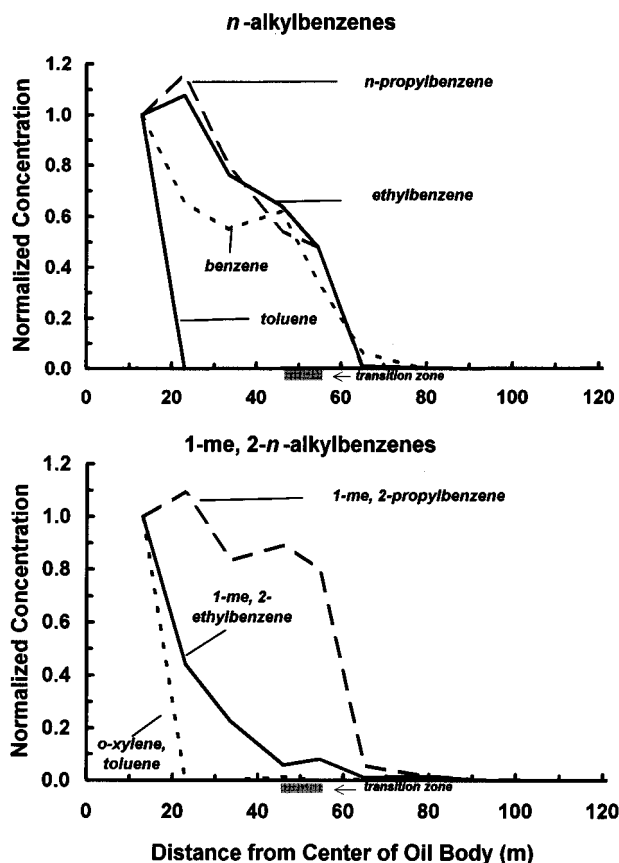


FIGURE 7. Distribution of alkylbenzene homolog series along main sampling transect (1987).

TABLE 3

Concentrations of Alkylbenzenes in Groundwater from Well 522 (1987), Log  $K_{ow}$  Values and Coefficients of Variation (CVs) Observed During Monitoring of Groundwater from Well 533 (1988–1989)

compound	concn at well 522 ( $\mu\text{g/L}$ )	log $K_{ow}^a$	CV (%)
<b>Homolog Series<sup>b</sup></b>			
benzene	9060	2.16	18.1
toluene	353	2.66	129
ethylbenzene	360	3.13	8.9
n-propylbenzene	29.7	3.71	7.8
toluene	353	2.66	129
o-xylene	269	3.25	92.0
1-methyl, 2-ethylbenzene	44.1	3.78	26.8
1-methyl, 2-propylbenzene	6.7	4.38	10.8
<b>Isomeric Assemblages<sup>c</sup></b>			
isopropylbenzene	23.8	3.89	8.0
1-methyl-4-ethylbenzene	31.8	3.90	24.4
1-methyl-3-ethylbenzene	52.2	3.88	62.8
1,2,3,4-tetramethylbenzene	100	4.30	5.5
1,2,3,5-tetramethylbenzene	21.3	4.26	17.4

<sup>a</sup> After Sherblom and Eganhouse (36). <sup>b</sup> Data refer to distributions shown in Figure 7. <sup>c</sup> Data refer to distributions shown in Figure 8.

zone at the time of sampling in 1987 (transition zone). Table 3 provides information on 'initial' concentrations at well 522, log  $K_{ow}$  values (log 1-octanol/water coefficients), and CVs determined in the monitoring study.

For all but the most rapidly removed compounds, downgradient changes in concentration exceed the degree of temporal variability of the initial concentrations for these

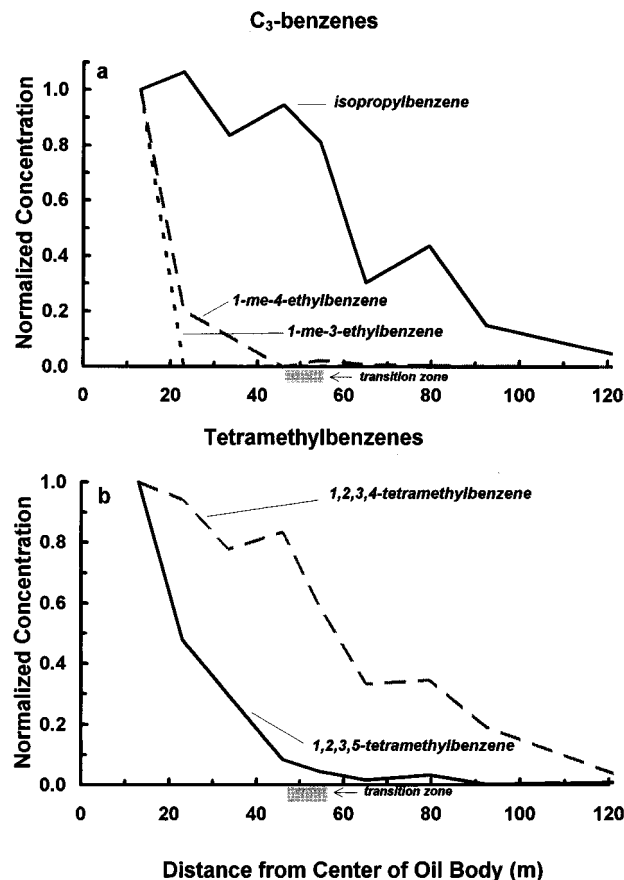


FIGURE 8. Distribution of isomeric assemblages of alkylbenzenes along main sampling transect (1987).

compounds (cf. Table 3). This indicates that these changes result from processes occurring subsequent to movement of the groundwater away from the oil body and not to temporal variations in hydrocarbon supply. If one assumes that the dominant processes controlling the transport of monoaromatic hydrocarbons at this site are physical and that sorption to aquifer solids is the principle mechanism of retardation, the expected pattern would be that compounds having shorter alkyl chains would migrate farther than those having longer alkyl chains (7, 29). As shown in Figure 7, this is clearly not the case at the Bemidji site. In fact, for the 1-methyl-2-alkylbenzene homology, the relationship appears to be exactly opposite that expected if sorption was the sole or dominant mechanism of retardation. It is unlikely that chemical degradation of these compounds is occurring under the conditions at this site. Thus, biological degradation is the most likely explanation for the large difference in trends among these homologs. In this context, it is important to note that for the most persistent species in these homologies (e.g., ethylbenzene, n-propylbenzene), the distal boundary of the plume at the water table is close to or just downgradient from (i.e., within 10–15 m of) the anoxic/oxic transition zone. This suggests that biodegradation of all but the most persistent compounds is complete before or shortly after oxygen becomes available.

Whereas an homologous series allows one to compare the behavior of compounds of known but different physical properties, isomeric assemblages are potentially more revealing because of similarities in their physical properties (e.g. refs 30 and 31). Figure 8 compares downgradient trends in the distributions of selected isomeric alkylbenzenes. In

the case of the C<sub>3</sub>-benzene isomers (Figure 8a), all of the compounds for which data are plotted have essentially identical octanol-water partition coefficients (log  $K_{ow}$  = 3.88–3.90; cf. Table 3). However, the downgradient distributions of these compounds are dramatically different. Consequently, it can be assumed that physical processes alone, including sorption to aquifer solids, cannot explain the differences in downgradient trends of these compounds. Rather, the distributions indicate that structure-specific biological degradation is the dominant process. In the particular case of isopropylbenzene and 1-methyl-4-ethylbenzene, the presumed initial concentrations are also similar (23.8 vs 31.8  $\mu\text{g/L}$ , respectively; Table 3). This further indicates that the biological availability of these compounds is not controlling their susceptibility to removal. Clearly, it is the difference in their structures. This hypothesis is further supported by data shown for selected C<sub>4</sub>-benzenes (Figures 8b). Here, trends for the tetramethylbenzenes are presented to illustrate how extremely sensitive removal rates in the anoxic zone are to compound structure. Structural differences as small as the position of a single methyl group (Figure 8b) result in large differences in apparent stability.

Anaerobic biodegradation of monoaromatic hydrocarbons has been suggested by others investigating the transport and fate of organic compounds in landfill leachate (31) and in groundwater contaminated by leaking underground storage tanks (29). Moreover, it is clear from numerous laboratory and field studies that biotransformation/mineralization of monoaromatics can occur anaerobically by a variety of terminal electron-accepting processes. The primary pathways responsible for oxidation of oil-derived hydrocarbons within the anoxic plume at the Bemidji site are methanogenesis and reduction of Fe and Mn minerals. Anaerobic biodegradation of dissolved hydrocarbons at Bemidji is supported by (in addition to evidence presented here) a variety of geochemical indicators observed in the field (11) and microcosm studies in which aquifer materials were used (32). While the specific microorganisms responsible for degradation of the monoaromatic hydrocarbons are not yet known, the present results bear similarities to those reported by other investigators studying contaminated environments with anoxic groundwater. In particular, a consistent pattern among the BTEX compounds seems to be that toluene and *o*-xylene are extremely unstable when compared with benzene and ethylbenzene. This relationship has been observed for anoxic environments where methanogenesis, sulfate reduction, and iron reduction are important metabolic pathways (30, 31, 33–35).

## Conclusions

The introduction of oil to a previously uncontaminated sand and gravel aquifer near Bemidji, MN, has resulted in the transfer of soluble hydrocarbons into the groundwater. Within the anoxic plume where biodegradation of dissolved hydrocarbons is occurring, concentrations of alkylbenzenes are determined by a balance between dissolution and removal rates. The temperature of the groundwater does not change more than about 1 °C in this aquifer. This, combined with the very low degree of variability in concentrations of the most persistent compounds (e.g., benzene, isopropylbenzene) downgradient from the oil, indicates that dissolution rates have been essentially constant over time at the site. For the most persistent compounds, rates of dissolution must therefore be sig-

nificantly greater than rates of biodegradation. The high temporal variability and undersaturation observed for the least persistent alkylbenzenes (e.g., toluene, *o*-xylene) suggest that the rate of biodegradation is an important control on the composition of groundwater in contact with and just downgradient from the oil body. This begs the question, "What controls the variation in biodegradation rate for the less persistent compounds?" One possibility is recharge. Recharge would likely introduce pulses of oxygen into groundwater upgradient from the oil. This could affect the activities and perhaps the composition of the microbial community causing them to vary over time. Once the groundwater moves downgradient from the oil, however, dissolution of the oil can no longer occur, and biological removal processes predominate. Our data suggest that either the degree of saturation or the temporal variability near the leading edge of the oil are reasonable predictors of compound persistence within the anoxic zone downgradient from the oil. Removal of almost all monoaromatic hydrocarbons is brought to completion within a short distance ( $\approx 15$  m) of the oxic/anoxic transition zone. Thus, hydrocarbon transport is effectively limited by natural biogeochemical processes.

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