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Review Paper/

Crude Oil at the Bemidji Site: 25 Years of Monitoring, Modeling, and Understanding

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Abstract

The fate of hydrocarbons in the subsurface near Bemidji, Minnesota, has been investigated by a multidisciplinary group of scientists for over a quarter century. Research at Bemidji has involved extensive investigations of multiphase flow and transport, volatilization, dissolution, geochemical interactions, microbial populations, and biodegradation with the goal of providing an improved understanding of the natural processes limiting the extent of hydrocarbon contamination. A considerable volume of oil remains in the subsurface today despite 30 years of natural attenuation and 5 years of pump-and-skim remediation. Studies at Bemidji were among the first to document the importance of anaerobic biodegradation processes for hydrocarbon removal and remediation by natural attenuation. Spatial variability of hydraulic properties was observed to influence subsurface oil and water flow, vapor diffusion, and the progression of biodegradation. Pore-scale capillary pressure-saturation hysteresis and the presence of fine-grained sediments impeded oil flow, causing entrapment and relatively large residual oil saturations. Hydrocarbon attenuation and plume extent was a function of groundwater flow, compound-specific volatilization, dissolution and biodegradation rates, and availability of electron acceptors. Simulation of hydrocarbon fate and transport affirmed concepts developed from field observations, and provided estimates of field-scale reaction rates and hydrocarbon mass balance. Long-term field studies at Bemidji have illustrated that the fate of hydrocarbons evolves with time, and a snap-shot study of a hydrocarbon plume may not provide information that is of relevance to the long-term behavior of the plume during natural attenuation.

Introduction

It has long been recognized that spills of crude oil, gasoline, aviation fuel, diesel fuel, heating oil, and other petroleum hydrocarbon fuels all pose a risk of groundwater contamination by benzene, toluene, ethylbenzene, and xylenes (BTEX) (Council on Environmental Quality 1981). Significant research efforts initiated in the 1980s (summarized by Mercer and Cohen 1990; Chapelle 1999; Cozzarelli and Baehr 2003; Oostrom et al. 2006) were devoted to understanding the processes controlling the subsurface flow, dissolution, volatilization, and biodegradation of nonaqueous phase liquid (NAPL) hydrocarbon mixtures so that effective remediation strategies could be designed. These studies ranged from laboratory experiments to field studies, and involved the development and application of complex numerical models.

By the mid-1990s, considerable evidence suggested that the extent of subsurface hydrocarbon plumes was limited by natural attenuation processes, mainly biodegradation of hydrocarbons by naturally occurring bacteria (National Research Council 1993, 2000; Wiedemeier et al. 1999). The high costs of hydrocarbon source removal and groundwater cleanup, as well as recognition of the limited effectiveness of pump and treat systems (National Research Council 1994), led the Environmental Protection Agency (EPA) to adopt guidelines for risk-based site

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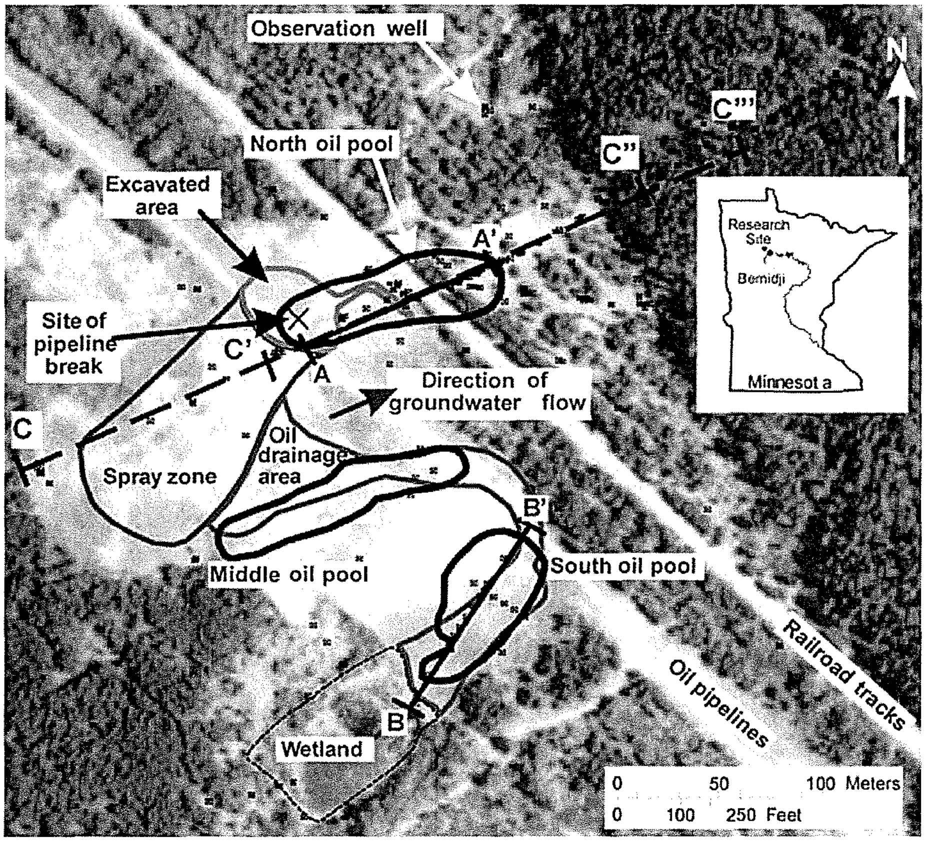

Figure 1. Aerial view of the Bemidji, Minnesota, crude-oil spill research site showing the site of the pipeline break, surface area impacted by oil spill, approximate extent of north, middle, and south oil pools floating on the water table, general direction of groundwater flow, and locations of cross sections shown in subsequent figures (modified from Delin et al. 1998; approximate extent of subsurface oil, August 1998, modified from Lakehead Pipe Line Co., written communication 1998).

assessments (EPA 1995) and the application of natural attenuation for petroleum hydrocarbons in groundwater (EPA 1997). In some cases, regulatory decisions of "no further action" (also known as site closure) were implemented at sites where groundwater benzene concentrations were dropping but did not yet meet state cleanup standards. The expectation was that natural attenuation would result in a continuing decrease in concentrations (Pelayo et al. 2008). However, a recent survey of 10 closed hydrocarbon contaminated sites in Wisconsin has shown that benzene concentrations exceed those measured at the time of site closure at five of the sites (Pelayo et al. 2008). The Wisconsin results indicate that natural attenuation of petroleum hydrocarbons can take longer than expected and that attenuation rates can change with time. Understanding the progression and evolution of natural attenuation processes, and determining the factors that control the spatial and temporal extent of a subsurface hydrocarbon plume, has been the subject of over 25 years of research at the crude-oil spill site near Bemidji, Minnesota.

On August 20, 1979, approximately 16 km northwest of Bemidji, an 86-cm diameter crude-oil pipeline burst along a seam weld, spilling about 1.7×10^6 L (10,700 barrels) of crude oil onto glacial outwash deposits (Figure 1) (Pfannkuch 1979; Hult 1984; Enbridge Energy 2008). The oil sprayed over an area of about 6500 m^2 (the spray zone) and collected in a wetland and topographic depressions where crude oil infiltrated through the unsaturated zone to the water table resulting in three subsurface oil bodies (termed the north, middle, and south oil pools, Figure 1). An estimated 1.1×10^6 L (6800 barrels) of the spilled oil was removed by pumping from surface pools and trenches, and an additional 0.2×10^6 L (1300 barrels) was removed by burning and excavation of soil. After cleanup efforts were completed in 1979 to 1980, about 0.4×10^6 L (2600 barrels) of crude oil remained in the subsurface. The NAPL oil trapped in the unsaturated zone and floating on the water table has provided a continuous source of hydrocarbon contamination. Hydrocarbon compounds have volatilized and dissolved from the oil at varying rates, changing the source composition and forming a soil vapor and groundwater plume within physically and chemically heterogeneous subsurface sediments (Figure 2). The compounds have been transported mainly by diffusion (with some advection) in the unsaturated zone, and by advection and dispersion in the saturated zone. Reactions and biodegradation have transformed the hydrocarbons to less toxic compounds,

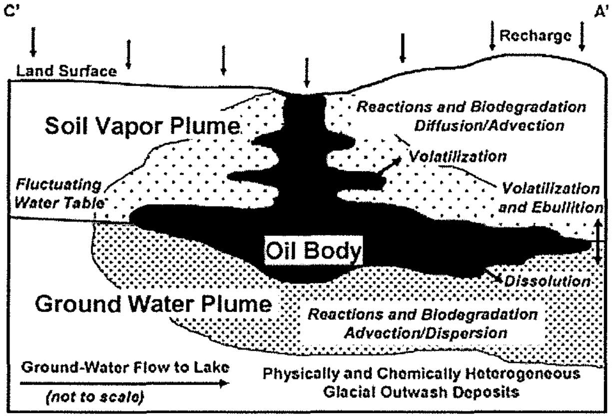

Figure 2. Generalized vertical cross section illustrating the fate and transport of spilled hydrocarbons in the subsurface (modified from Delin et al. 1998). Hydrocarbons infiltrate the subsurface as a separate oil phase, resulting in a residual oil source in the unsaturated zone and an oil body floating on the water table. Volatilization and dissolution of hydrocarbons from the oil phase produce vapor and groundwater plumes. The extent of these plumes is moderated by biodegradation and geochemical reactions that take place in a heterogeneous porous medium.

modified the subsurface redox conditions, and resulted in changes in mineral characteristics.

A long-term, interdisciplinary research project sponsored by the U.S. Geological Survey Toxic Substances Hydrology Program was established at the Bemidji site in 1983 in response to the research community's need for in situ field-scale studies of hydrocarbon fate to complement ongoing experimental and modeling efforts (Delin et al. 1998). An overview of the project with site maps and data is available at http://toxics.usgs.gov/sites/bemidji_page.html and http://mn.water.usgs.gov/projects/bemidji/. Research at this site has been oriented toward characterizing and quantifying the physical, chemical, and biological processes controlling the fate of hydrocarbons in the subsurface. From 1983 to 1999, scientists working at the site were able to study and document the extent and progression of hydrocarbon contamination under natural, undisturbed conditions. In 1999, a 5-year remediation effort focused on removing the NAPL oil source was initiated by the pipeline company in response to a mandate from the Minnesota Pollution Control Agency.

Twenty-five years of comprehensive, interdisciplinary research has made Bemidji one of the best characterized hydrocarbon spill sites in the world and has resulted in over 200 publications (complete list available at http://toxics.usgs.gov/bib/bib-bemidji.html). Research efforts at Bemidji have focused on developing and applying methods for measuring and investigating in situ properties and processes. Work at the site has ranged from characterization of microscopic-scale water-mineral interactions to plume-scale geochemical and microbial evolution, and has included testing of complex models of multiphase flow, reactive transport, and biodegradation. Investigations have involved the collection and analysis of more than 5000 samples of crude oil, water, soil, vapor, sediment, and microbes. The NAPL oil distribution and composition have been characterized and modeled to provide an understanding of the nature of the continuous hydrocarbon source. Monitoring and modeling of the geochemistry of the contaminated aquifer have elucidated the chemical and biological processes controlling the evolution and extent of the groundwater and soil vapor hydrocarbon plumes. Simulation has been used to test conceptual models, quantify properties and rates, and evaluate hydrocarbon mass balance. This paper presents an overview of Bemidji studies that have contributed to understanding the fate of hydrocarbons in the natural field setting. The approaches developed and processes studied at Bemidji are universal and can be adapted and used to evaluate other hydrocarbon spill sites.

Site Hydrogeology

The Bemidji oil spill is located in a pitted and dissected outwash plain comprised of moderately calcareous, moderately to poorly sorted sandy gravel, gravelly sand and sand with thin interbeds of silt (Franzi 1988). The average organic carbon content of these sediments was 0.09% (Baedecker et al. 1993), and the mean porosity was 0.38 (Dillard et al. 1997). At a depth of 18 to 27 m the outwash sediments are underlain by a low-permeability till layer. Local groundwater flow is to the northeast and discharges to an unnamed lake 300-m downgradient from the point of the pipeline rupture (Figure 1). Depth to the water table ranges between 0 (near the wetland) and 11 m, and water levels fluctuate as much as 0.5 m seasonally. The observed average water-table gradient was 0.0035 m/m (Essaid et al. 2003). Estimates of mean hydraulic conductivity at the north oil pool site ranged from 5.6×10^{-6} m/s (estimated from particle-size distributions, Dillard et al. 1997) to 7.0×10^{-5} m/s (calibrated model estimate, Essaid et al. 2003). Mean porosity, conductivity, and gradient estimates yield average velocity estimates that range between 0.004 and 0.056 m/day. A small-scale natural-gradient bromide tracer test conducted within the hydrocarbon plume, along a 1.6-m long flow path 57-m downgradient from the center of the oil body, yielded a mean flow velocity of 0.06 m/day and longitudinal dispersivity of 0.15 m (Essaid et al. 2003).

Mean annual temperature and precipitation at the site are 3°C and 0.58 m, respectively (National Oceanic and Atmospheric Administration 1983). Recharge rates at the site have been estimated using a water-table fluctuation method and an unsaturated zone water balance method based on time-domain-reflectometry measured soil moisture (Delin and Herkelrath 1999, 2005; Herkelrath and Delin 2001). Estimated values range from 0.1 to 0.3 m/year. The greatest recharge rates have been observed below areas of topographic lows, primarily as a result of accumulation of surface runoff in these depressions—the same depressions where spilled crude oil infiltrated to the water table.

The Oil Phase Hydrocarbon Source

Crude oil is a complex mixture of hydrocarbon compounds that volatilize into the gas phase, dissolve in water, and biodegrade at different rates. The NAPL oil distribution in the subsurface affects its contact with the water and gas phases and consequently the rates of volatilization and dissolution of hydrocarbons. Increased oil in the pore space decreases the ease with which water and air can flow past the oil and reduces the oil surface area in contact with air and water phases, reducing the transfer of hydrocarbons. Furthermore, as mass transfer of hydrocarbon components from the oil to soil gas and water progresses, and biodegradation occurs, the composition of the hydrocarbon mixture in the oil changes. These processes can be individually isolated and studied in laboratory experiments, however, in the field they occur simultaneously with complex interactions.

Oil Phase Distribution

Characterizing the subsurface oil-phase distribution is a necessary step for understanding the influence of the NAPL oil source on the vapor and groundwater plumes. Often, the only information available at a field site is the thickness of oil floating on water in an observation well, a measurement that does not correlate well with the thickness of oil in the adjacent sediments (Kemblowski and Chiang 1990). Methods to determine the subsurface distribution of oil saturation, the fraction of the pore space occupied by oil (volume of oil/volume of pore space), were developed and applied at the Bemidji site. In 1989 and 1990, cores were collected at the south and north oil pools (Figure 3) using a sampling technique that could recover relatively undisturbed core samples from both the unsaturated and saturated zones while maintaining the in situ pore-fluid distribution (Hess et al. 1992). Cores were immediately frozen and cut into 78-mm long sections. Oil and water saturations, porosity, and particle-size distribution were determined for 146 core sections aligned along a 120-m transect at the south pool (Hess et al. 1992), and 269 core sections aligned along a 90-m transect at the north pool (Dillard et al. 1997). Both transects were approximately parallel to the direction of groundwater flow.

The observed south pool oil body (Figure 3A) was more than 70 m long with, the greatest oil saturation (0.62) measured near its center in a localized zone of high oil saturations. Outside this zone there was a large area with oil saturations less than 0.20. The oil body was asymmetric and it appeared that there may have been some downgradient lateral migration of oil below the water table, possibly through zones of high permeability. The thickness of oil measured in three wells at the time of core collection did not correspond to the oil-saturation distribution in the adjacent sediments (Hess et al. 1992), illustrating that accumulated thickness in wells is a poor indicator of the actual distribution of oil in the subsurface.

The distribution of oil at the north pool site was more complex than that at the south pool site (Figure 3B). A considerable amount of oil remained in the unsaturated

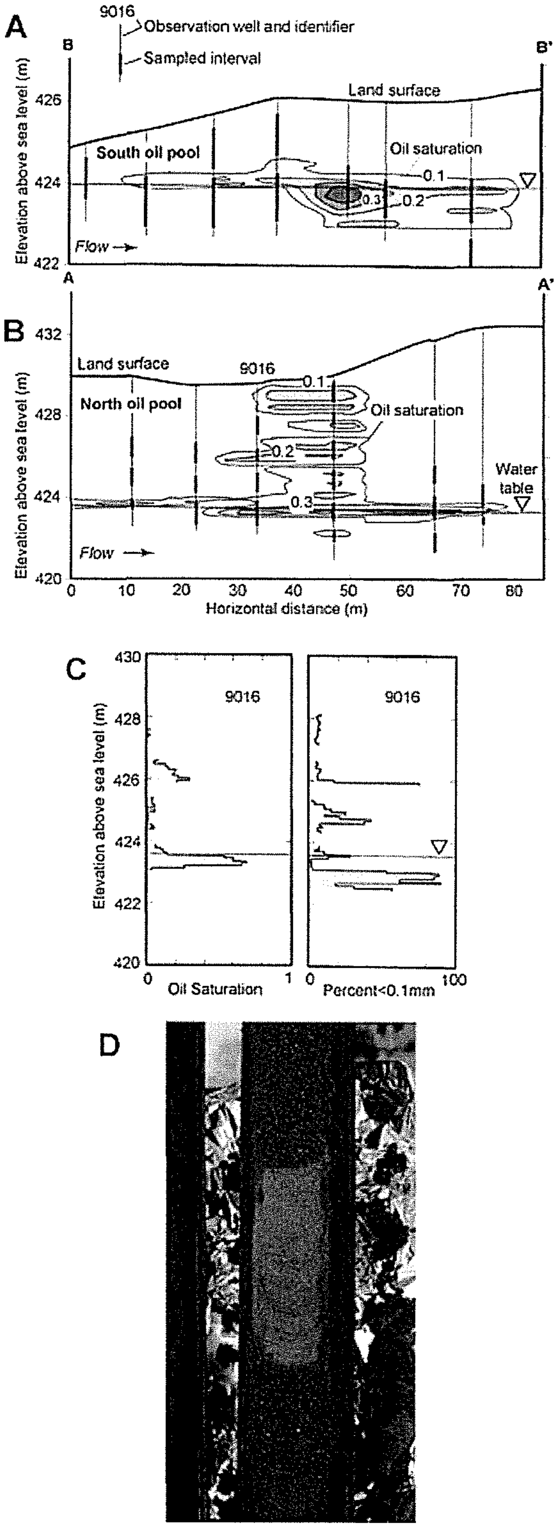

Figure 3. Oil-phase distribution at the Bemidji site (modified from Essaid et al. 1993; Dillard et al. 1997): (A) oil saturation (volume of oil/volume of pore space) distribution at the south pool; (B) oil-saturation distribution at the north pool; (C) oil saturation and percent grain size smaller than 0.1 mm at borehole 9016 showing the influence of heterogeneity on oil-phase distribution; (D) photograph of an oil core crossing the water table showing oil exclusion from a finer grained horizon.

zone where oil infiltrated following the spill. The body of oil floating on the water table was not lens shaped, but rather consisted of zones of high and low oil saturation distributed along the general direction of groundwater flow. The maximum oil saturation of 0.74 was measured in the downgradient part of the oil body. Figure 3C shows profiles of oil saturation and particle size for borehole 9016 and illustrates the influence of fine-grained layers on oil-saturation distribution. A layer containing almost 80% fines occurred in the unsaturated zone at an elevation of about 426 m. Oil saturations above this layer were greater than 0.3, even though it was more than 2 m above the water table. Apparently the fine-grained layers impeded the infiltration and redistribution of oil. The peak oil saturation was below the water table within a zone that was lacking in fines, rather than at or above the water table as buoyancy would predict. Fine-grained layers occurred above and below the zone of high oil saturation, suggesting that migration of oil near the water table was controlled by heterogeneous layering. Figure 3D is a photograph of a core collected at the water table that illustrates the effect of grain size on oil saturation. The gray zone in the center is of slightly smaller grain size and is free of oil, whereas the coarser overlying and underlying zones are heavily saturated with oil. These field data illustrate the importance of heterogeneity and capillary effects on the distribution and movement of the oil phase.

By 1990, many modeling approaches had been developed to simulate the flow of NAPL oil, however, their field applicability was untested because of a lack of field-scale and site-specific knowledge of multiphase distributions and hydraulic properties (Mercer and Cohen 1990). Observed fluid saturation and particle-size distributions at Bemidji were used in conjunction with a multiphase cross-sectional flow model of the unsaturated and saturated zone to simulate the movement of oil and water at the spill site (Essaid et al. 1993; Dillard et al. 1997). Comparisons between observed and simulated oil-saturation distributions were used as indicators of the appropriateness of using prevalent multiphase flow modeling approaches, and the relative importance of factors controlling oil flow. Spatially variable sediment hydraulic properties and constitutive relations (capillary pressure-saturation and relative permeability-saturation) were estimated from particle-size data. At the south oil pool, the general asymmetrical shape of the observed oil body was reproduced only when hysteretic capillary pressure-saturation curves with oil entrapment and representations of spatial variability of hydraulic properties were incorporated into the model (Essaid et al. 1993). The small-scale details of the observed subsurface oil distribution were not reproduced in the simulations due to uncertainty in spatial correlations, hydraulic properties, and constitutive relations estimated from particle-size distributions.

Analysis of the permeability distribution estimated from particle-size data from the north oil pool site suggested that fine-grained layers were more predominant than at the south pool site. Permeability was distributed bimodal lognormally with two population distributions corresponding to two predominant lithologies: a coarse glacial outwash deposit and fine-grained interbedded lenses. A two-step geostatistical approach was used to generate a conditioned realization of permeability representing the observed bimodal heterogeneity (Dillard et al. 1997). This permeability distribution was used to simulate flow of oil and water in the presence of air along the north pool transect for the 1979 to 1990 period. Inclusion of bimodal aquifer heterogeneity was needed to reproduce the observed entrapment of oil in the unsaturated zone and the irregular shape of the oil body. When bimodal heterogeneity was included, pore-scale capillary pressure-saturation hysteresis did not have to be incorporated into the model because a large-scale hysteretic effect was produced by the presence of low-permeability fine-grained lenses that impeded oil flow.

The field observations and modeling indicate that subsurface oil-phase flow is very sensitive to porous media heterogeneity. Oil tends to occur at higher saturations and to be more mobile in the coarser-grained higher-permeability sediments. Pore-scale capillary pressure-saturation hysteresis and the presence of fine-grained sediments can impede oil flow, causing entrapment and relatively large residual oil saturations. Realistic simulated oil distributions were obtained only when the effects of heterogeneity on capillary pressure-saturation and relative permeability-saturation constitutive relations were represented. However, there is still considerable uncertainty in estimating these constitutive relations for NAPLs, especially in the case of three-phase oil relative permeability (Dillard et al. 1997). Inclusion of the observed 0.5-m water-table fluctuations in the south and north pool models did not significantly improve the correspondence between simulated and observed oil-saturation distributions, suggesting that spatial variability was a stronger influence on oil flow and/or there was limited oil-phase mobility.

Remediation at oil spill sites often targets removal of the NAPL oil phase in order to minimize the hydrocarbon source. The Bemidji remediation effort initiated in 1999 focused on removing sufficient NAPL oil so that it would only occur as a sheen on the water-table surface. Oil was recovered by inducing depressions in the water table by pumping from beneath the north, middle, and south oil pools, with removal of inflowing oil by skimming. Efficacy of oil removal by pump-and-skim remediation depends on oil mobility and flow to the pumped well. Herkelrath (1999) made a prediction of oil removal at the north pool based on oil saturations measured in cores. This analysis indicated that about 25% of the oil was recoverable assuming a residual oil saturation of 0.2 based on observed oil-saturation distributions (Figure 3). The remediation from 1999 to 2004 resulted in the removal of about 1.14×10^5 L of crude oil from the north, middle, and south oil pools (Enbridge Energy 2008), or about 27% of the oil that remained following the initial remediation in 1979 to 1980. Although the renewed remediation decreased oil thickness in the immediate vicinity of remediation wells, average oil thicknesses measured in wells at the north pool (0.6 m) and south pool (0.3 m) were unaffected. In one observation well located about 5 m from a remediation well at the north pool, oil thickness decreased twice briefly but rebounded to preremediation levels shortly thereafter. These results, together with ongoing analyses, suggest that oil-phase recovery is challenging, and that considerable volumes of mobile and entrapped oil may still remain in the subsurface at spill sites in spite of significant remediation efforts.

Oil Phase Composition

The composition of subsurface oil at the Bemidji site has changed over time due to volatilization, dissolution, and biodegradation. In 1987, Eganhouse et al. (1993) measured the molecular composition of oil samples obtained from the pipeline and locations spanning the length of the north pool oil body. The composition of the oil body samples was dominated by saturated hydrocarbons (58% to 61%), with aromatics representing most of the remainder (33% to 36% of total oil). The dominant hydrocarbons were normal alkanes (C_{6-32}). Eganhouse et al. (1996) showed that the oil near the upgradient edge of the oil body was depleted of the more soluble aromatic hydrocarbons such as benzene and toluene as compared with the downgradient edge of the oil body. Eganhouse et al. (1996) also observed that concentrations of hydrocarbons in groundwater flowing beneath the oil increased as the water flowed from the upgradient to the downgradient edge of the oil, approaching the effective solubility limit. These results suggested that the upgradient portion of the oil body had undergone more hydrocarbon dissolution than the downgradient portion because of the continuous inflow of groundwater with low hydrocarbon concentrations from the area upgradient of the oil body. As this water flowed past the oil body and hydrocarbon concentrations increased, the mass transfer of soluble components from the oil to the water phase decreased.

Landon and Hult (1996) collected 31 oil samples from wells at various locations within the oil body during 1988 to 1989. They characterized the physical and chemical characteristics of the oil samples, compared them to relatively unaltered oil (Landon 1993), and determined the mass loss from the oil phase. Changes in physical properties of the oil samples indicated that the rate of mass loss ranged from 0% to 1.25% per year. In the oil samples with the greatest mass loss, the alkanes accounted for about 80% of the loss and aromatic compounds accounted for the other 20%. In the less altered oil samples, aromatic compounds accounted for nearly all of the loss of mass. Landon and Hult (1996) concluded that oil mass was being lost primarily by volatilization of low chain-length alkanes in the highly altered oil samples, and dissolution of aromatics in the least altered samples.

Bekins et al. (2005a) examined the composition of the NAPL oil present in core samples 25 years after the spill. They observed that substantial biodegradation of the *n*-alkane fraction in the oil had occurred under methanogenic conditions and that methanogenic biodegradation first depleted the $\geq C_{18}$ *n*−alkanes (Figure 4A), the reverse of the aerobic biodegradation progression (Peters and Moldowan, 1993). The degree of alkane depletion (degradation state) varied with position in the oil body (Figure 4B). The least degraded oil occurred near the land surface, because of extremely low moisture conditions, and at the downgradient end of the oil body. Enhanced methanogenic biodegradation occurred where there was increased groundwater recharge. Recharge rates over twice the average value occur in a topographic low above the upgradient end of the oil body (Delin and Herkelrath 2005). The increased biodegradation below the high recharge zone could not be explained by recharge transport of favorable anaerobic electron acceptors because it was observed that all electron acceptors, except carbon dioxide (CO_2), were consumed in the vadose zone before the recharge reached the floating oil (Bekins et al. 2005a). Moreover, enhanced dissolution could not be the cause, because the degradation affected highly insoluble alkanes and was not correlated with oil saturation and water relative permeability. Bekins et al. (2005a) concluded that the most likely explanation for the variation in alkane degradation states was enhanced methanogenic biodegradation caused by recharge-facilitated transport of microbial growth nutrients from the land surface, in particular dissolved phosphate, believed to be the nutrient limiting microbial growth (Rogers et al. 1998).

These studies of the NAPL oil source at Bemidji have shown that the oil phase is slowly evolving with time as hydrocarbon components are lost through mass transfer to water and soil gas, and biodegradation. The oil-phase loss of relatively soluble components (e.g., BTEX) is sensitive to factors controlling dissolution, such as water concentrations and flow rates. Relatively volatile components (e.g., short chain-length alkanes) can be rapidly lost through volatilization under favorable conditions. Alkanes are also lost from the oil body by methanogenic degradation. Bekins et al. (2005a) pointed out that hydrologic conditions at a site can control oil degradation rates, and that techniques for dating a spill on the basis of the degree of degradation may yield very different results depending on where the sample was collected. In addition, techniques to identify spilled product based on fingerprinting may provide misleading results when methanogenic conditions are present, because the fingerprint of the degraded product in such cases differs from the expected pattern under aerobic conditions (Hostettler et al. 2007, 2008).

The Groundwater Hydrocarbon Plume

By the mid-1980s it was recognized that hydrocarbons could be effectively degraded by naturally occurring indigenous microbial populations (Wilson et al. 1986).

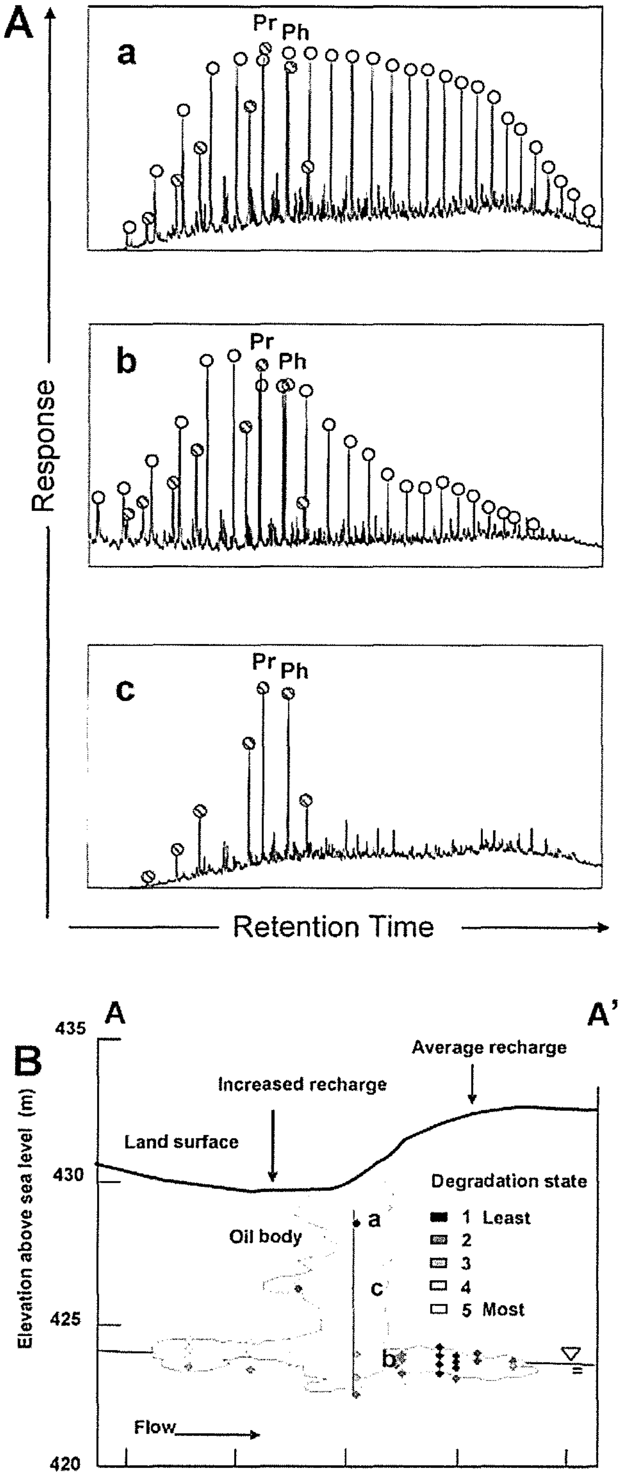

Figure 4. Evaluation of oil-phase degradation (from Bekins et al. 2005a): (A) ion chromatograms for oil samples with varying degrees of degradation (open circles are *n*-alkanes, black circles are isoprenoids) (a) relative undegraded sample with *n*-alkane concentrations greater than isoprenoids, (b) somewhat degraded sample showing selective removal of higher order *n*-alkanes and (c) highly degraded sample with *n*-alkanes completely degraded; (B) vertical cross section through north pool oil body showing relative degree of oil degradation for samples collected from 1999 to 2003.

Aerobic degradation of BTEX was accepted as an effective biodegradation process, and the potential of anaerobic degradation was just being documented (Wilson and Rees 1985). Studies initiated at Bemidji since 1984 have provided concrete evidence of the importance of anaerobic degradation for limiting the extent of hydrocarbon plumes, and significant insight into the succession of redox processes, microbial populations, and geochemical interactions. Hydrocarbon components dissolving from the oil phase have undergone different rates of transport and biodegradation. Within the plume, biologically mediated geochemical reactions have resulted in mineral alteration.

Geochemical Evolution of the Plume

Early characterization of the groundwater hydrocarbon plume (Baedecker et al. 1989, 1993; Bennett et al. 1993) identified five distinct geochemical zones below the water table (Figure 5). Zone 1 consisted of oxygenated uncontaminated native groundwater very low in nitrate, ammonia, and sulfate. Zone 2, below the spray zone, was characterized by reduced oxygen concentrations and the presence of refractory high-molecular-weight hydrocarbons transported from oil residues on the land surface. Zone 3, beneath and immediately downgradient from the separate phase oil body, was anoxic with high concentrations of hydrocarbons, dissolved manganese and iron, and methane. In addition, nitrate and ammonia concentrations were slightly higher than in background water possibly because of nitrogen-containing compounds in the oil and/or infiltration of fertilizer used at the land surface to promote tree growth following the spill. In Zone 4, there was a transition from anoxic conditions to fully oxygenated conditions, with a corresponding rapid decrease in hydrocarbon concentrations as a result of aerobic biodegradation. Zone 5 consisted of oxygenated water downgradient from the oil body with slightly elevated concentrations of dissolved inorganic and organic constituents. The relatively stable extent of the plume, when compared to groundwater flow rates, led to the conclusion that migration of the plume was being limited by natural attenuation processes, including both aerobic and anaerobic biodegradation.

Temporal changes in the plume were observed by measuring dissolved organic carbon (DOC), dissolved oxygen (DO), dissolved manganese (Mn^{2+}) and dissolved ferrous iron (Fe^{2+}), and methane (CH_4) concentrations in samples collected from water-table wells from 1986 to 1992 (Baedecker et al. 1993; Bennett et al. 1993; Eganhouse et al. 1993). DOC was split into two operationally defined fractions (Baedecker et al. 1993): volatile dissolved organic carbon (VDOC) and nonvolatile dissolved organic carbon (NVDOC). VDOC is composed primarily of benzene, alkylbenzenes, and low-molecular-weight alkanes and alicyclics, excluding methane. NVDOC is composed mainly of polysaccharides, humic and fulvic acids, low-molecular-weight organic acids, minor C_{15-28} alkanes, and polyaromatic hydrocarbons (Eganhouse et al. 1993). Figure 6 shows the temporal evolution of concentrations at a well located in the anoxic zone about 40-m

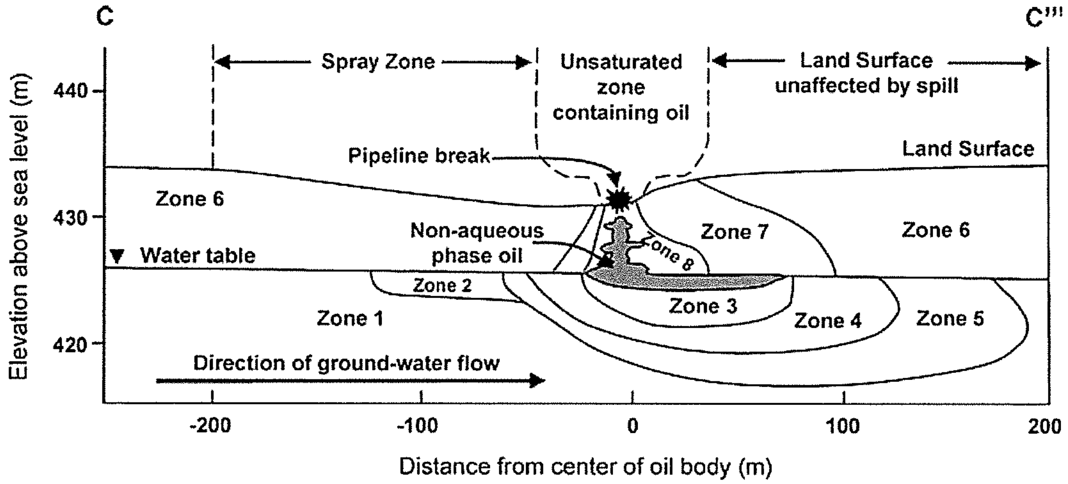

Figure 5. Subsurface geochemical zones identified at the north oil pool site (modified from Baedecker et al. 1993 and Delin et al. 1998). Zones are described in the accompanying text.

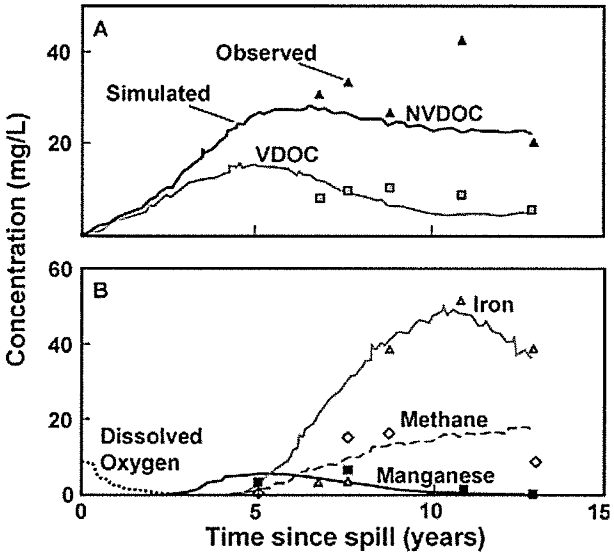

Figure 6. Observed (symbols) and simulated (lines) concentrations approximately 40-m downgradient from the center of the oil body, in the anoxic zone of the groundwater plume showing progression of terminal electron-accepting processes from aerobic degradation to manganese reduction, iron reduction, and methanogenesis: (A) volatile and nonvolatile dissolved organic carbon (VDOC and NVDOC, respectively); (B) dissolved oxygen, manganese (Mn^{2+}), iron (Fe^{2+}), and methane (modified from Essaid et al. 1995).

downgradient from the center of the oil body. VDOC and NVDOC concentrations reached relatively steady concentrations. Mn^{2+} increased, peaking in 1987, and then decreased, suggesting that the manganese available for reduction was being depleted. Fe^{2+} concentrations began to increase following the drop in Mn^{2+} and peaked in 1990. Methane concentration began to increase at about the same time as Fe^{2+} and leveled off in 1987. This sequence suggested that anaerobic (in addition to aerobic) biodegradation processes were limiting plume migration and expansion with sequential use of terminal electron acceptors that progressed from manganese reduction, to iron reduction, to methanogenesis. The trends in Fe^{2+}, Mn^{2+}, and CH_4 concentrations, and the isotopically heavier inorganic carbon, indicated that part of the plume became more reducing with time, and that the processes attenuating organic material were continuously evolving (Baedecker et al. 1993).

Further evidence of the importance of anaerobic biodegradation was obtained from anoxic laboratory microcosm experiments that showed benzene and alkylbenzene degradation concurrent with increased aqueous Fe^{2+} and Mn^{2+} concentrations indicating hydrocarbon biodegradation coupled with Fe and Mn reduction (Baedecker et al. 1993). In addition, Cozzarelli et al. (1994) investigated the geochemical evolution of low-molecular-weight organic acids in groundwater downgradient from the oil body over a 5-year period (1986 to 1990). Organic acids represent metabolic intermediates of crude-oil biodegradation and are structurally related to hydrocarbon precursors (Cozzarelli et al. 1990, 1994; Thorn and Aiken 1998). The concentrations of organic acids increased as microbial alteration of hydrocarbons progressed. The organic-acid pool changed in composition and concentration as biodegradation processes shifted from iron reduction to methanogenesis. Laboratory microcosm experiments conducted by Cozzarelli et al. (1994) supported the hypothesis that organic acids observed in the groundwater originated from microbial biodegradation of aromatic hydrocarbons under anoxic conditions.

Additional geochemical evidence of anaerobic biodegradation of hydrocarbons was provided by methane isotopic composition and sediment-associated iron. Revesz et al. (1995) found that carbon and hydrogen isotopic ratios of CH_4, and carbon isotopic fractionation between CH_4 and DOC, supported the hypothesis of CH_4 production by anaerobic breakdown of acetate (fermentation) as opposed to production by CO_2 reduction. Furthermore, there appeared to be minimal oxidation of dissolved CH_4

along the flow path downgradient from the oil body. Tuccillo et al. (1999) found that the average HCl-extractable ferric iron (Fe^{3+})concentration in the sediments closest to the oil body was up to 30% less than background values as a result of Fe^{3+} reduction to Fe^{2+}. Fe^{2+} concentrations in sediments within the anoxic zone were as much as four times those in the background sediments, suggesting mineral incorporation of Fe^{2+}. This hypothesis was also supported by scanning electron microscopy (SEM) detection of authigenic ferroan calcite. At the transition zone from anoxic to oxic conditions there was a 70% increase in total extractable Fe, indicating reoxidation and precipitation of Fe mobilized from sediment in the anoxic plume. SEM confirmed abundant Fe^{3+} oxyhydroxides at the anoxic/oxic boundary. Zachara et al. (2004), however, identified significant ion-exchangeable Fe^{2+} in the sediments but relatively thin Fe-containing particle coatings on carbonate fragments suggesting minor precipitation of ferroan calcite in regions of the aquifer with elevated dissolved Fe^{2+} concentrations. Further work is needed to elucidate the processes causing the complex cycling of iron driven by biodegradation and redox conditions.

As anaerobic biodegradation of DOC in the Bemidji plume became well documented, researchers began to compare and contrast the behavior of individual hydrocarbon components in the anoxic zone. Eganhouse et al. (1996) compared concentrations of a range of monoaromatic hydrocarbons in oil and groundwater samples collected within the north pool anoxic zone. Immediately downgradient from the oil body, certain aromatic hydrocarbons (such as benzene) were at aqueous concentrations near those expected of an oil-water system at equilibrium, and these concentrations exhibited relatively little variation over a 9-month period (8% to 20%). Other compounds (such as toluene) had aqueous concentrations significantly below the equilibrium-predicted value, and their concentrations showed considerably more temporal variation (20% to 130%). As the dissolved hydrocarbons moved through the anoxic zone of the groundwater plume, concentrations of more persistent compounds, such as benzene, decreased slowly, whereas concentrations of readily biodegradable compounds such as toluene decreased rapidly (Figure 7). This suggested that the volatile hydrocarbon composition of anoxic groundwater near the oil body was controlled by a balance between dissolution and removal rates, with only the most persistent compounds reaching equilibrium with the oil phase. The extent of downgradient transport of individual dissolved hydrocarbons through the anoxic zone was not due to differences in sorption, but was controlled by structure-specific biodegradation rates. Compounds more resistant to anaerobic biodegradation extended farther downgradient from the oil body.

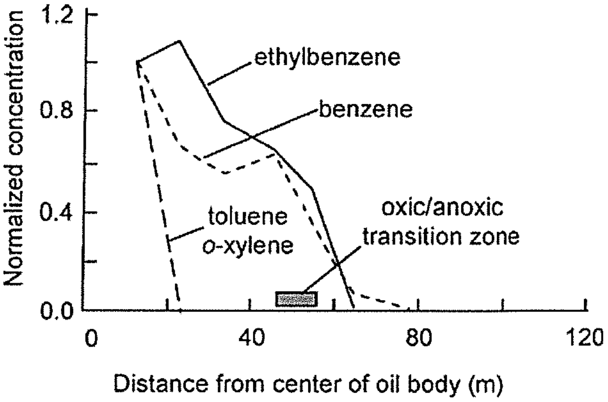

Figure 7. Groundwater concentrations of selected alkylbenzene compounds at the north pool, showing the effect of selective structure-dependent biodegradation of hydrocarbon compounds on persistence in the plume (modified from Eganhouse et al. 1996).

Early work at Bemidji (Baedecker et al. 1993) concluded that the hydrocarbon plume had reached a relatively steady state. However, continued monitoring has documented changes in the extent of the anoxic plume caused by evolving redox conditions. In the mid-1990s, Murphy and Herkelrath (1996) developed a sample-freezing drive shoe designed to operate with a wire-line piston core barrel. This technique improved the ability to obtain cores with intact fluid and sediment distributions, facilitating centimeter-scale sampling of hydrocarbon concentrations (Cozzarelli et al. 2001) and microbial population distributions (Bekins et al. 2001). Cozzarelli et al. (2001) compared concentration distributions obtained from detailed sampling of porewater drained from aquifer cores with plume-scale concentrations determined by sampling from an observation well network along the centerline of the plume. The small-scale data showed that the hydrocarbon plume was growing slowly as sediment iron oxides were depleted and the aquifer evolved from iron reducing to methanogenic conditions. Some hydrocarbons, such as *ortho*-xylene, did not appear to be moving downgradient on the basis of observation well data, but actually were migrating in thin layers of the aquifer where iron oxides were depleted and methanogenic conditions existed. The plume-scale observation well data showed that the downgradient extent of the benzene plume did not change between 1992 and 1995 as shown by the location of the 0.05 mg/L BTEX concentration contours in Figure 8. However, during this period the zone of maximum concentrations of benzene spread within the anoxic plume. Thus, subtle concentration changes in the anoxic zone may indicate depletion of electron acceptors and the potential for future plume growth.

The slow growth of the Bemidji plume contrasts markedly with the rapid growth of another well-studied BTEX plume at Laurel Bay Exchange field site, Beaufort, South Carolina (Landmeyer et al. 1996). Chapelle et al. (2002) noted that the Laurel Bay aquifer sediments contained low concentrations of Fe^{3+} and that the redox state of the contaminated aquifer evolved rapidly to methanogenic conditions. At both the Bemidji and Laurel Bay sites, biodegradation of benzene and ethylbenzene under methanogenic conditions was limited, resulting in migration of those compounds once sediment Fe^{3+} was

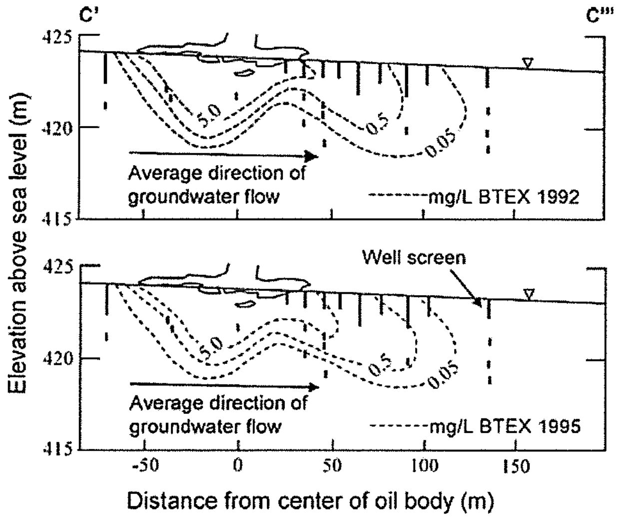

Figure 8. BTEX concentrations measured in wells (screened intervals shown as bars) in the groundwater plume for 1992 and 1995 showing that the extent of BTEX has remained relatively constant. However, the high concentration area in the core of the plume expanded as Fe^{3+} became depleted and conditions changed from iron reducing to methanogenic (from Cozzarelli et al. 2001).

depleted. However, the Bemidji benzene plume grew at only one sixth the rate of the Laurel Bay plume, due mainly to greater Fe^{3+} availability. Using data from the two sites, Bekins et al. (2005b) derived a method to relate expansion rates of benzene and ethylbenzene plumes to variations in sediment Fe^{3+} concentrations. Benzene front migration is retarded relative to groundwater velocity by a factor that depends on the concentrations of hydrocarbon and bioavailable sediment Fe^{3+}.

Long-term monitoring of plume-scale hydrocarbon concentrations and aqueous geochemistry has provided a well-documented field example of the evolution of natural attenuation processes. The Bemidji findings have influenced recommended approaches and protocols for evaluating natural attenuation at hydrocarbon spill sites (National Research Council 2000). Approaches developed at Bemidji for characterization of small-scale variations in chemistry have shown that shifts in biodegradation processes that impact the future extent of the plume may occur before changes can be detected in observation well concentrations.

Microbiology of the Plume

Concurrent with studies documenting geochemical evidence of biodegradation were efforts to characterize the microbial populations and processes responsible for aerobic and anaerobic biodegradation of hydrocarbons, as well as enhanced mineral-water interactions. Studies at Bemidji have documented bacterial colonization on rock surfaces resulting in enhanced quartz (SiO_2) dissolution, identified bacteria responsible for iron reduction, and characterized the spatial and temporal distributions of microbial populations.

Early studies of the inorganic geochemistry of the anoxic zone (Bennett and Siegel 1987; Bennett 1991; Hiebert and Bennett 1992; Bennett et al. 1993) observed SiO_2 concentrations that were an order of magnitude greater than expected equilibrium concentration with respect to quartz. This suggested that organic acid-SiO_2 complexes in the organic-rich anoxic zone were enhancing the dissolution of quartz and silicate minerals. SEM studies of sand grain surfaces in this zone showed etching of quartz and feldspar surfaces not observed on grain surfaces in the adjacent aerobic and uncontaminated zones. Hiebert and Bennett (1992) conducted in situ microcosm experiments in the anoxic plume to examine the effect of bacterial biodegradation processes on rock alteration. Their results suggested that the rate of dissolution of quartz and aluminosilicate minerals was greatly accelerated in the contaminated waters beneath the oil, probably due to the presence of surface-adhering bacteria and high concentrations of organic acids formed by the bacteria during hydrocarbon metabolism (Hiebert and Bennett 1992; Bennett et al. 1993). Expanded in situ microcosm studies of mineral surface colonization have shown that microorganisms tend to colonize surfaces that provide required electron acceptors and growth nutrients, such as iron present in goethite and phosphorous present in apatite (Bennett et al. 2000; Roberts 2004; Rogers and Bennett 2004; Mauck and Roberts 2007).

Studies at Bemidji were among the first field efforts that documented microbial evidence of anaerobic degradation of hydrocarbon compounds (Chapelle 1999; Cozzarelli and Baehr 2003). Lovley et al. (1989) demonstrated that Fe^{3+} could be an important electron acceptor for microbial oxidation of aromatic compounds in anaerobic groundwater by isolating a pure culture of the Fe^{3+}-reducing bacterium *Geobacter metallireducens* capable of obtaining energy for growth by oxidizing benzoate, toluene, phenol, or *p*-cresol, with Fe^{3+} as the sole electron acceptor. Culturing studies and molecular techniques for analyzing Fe^{3+}-reducing populations in the anaerobic groundwater plume have shown that *Geobacter* species were enriched in sediments where poorly crystalline Fe^{3+} was available and biodegradation was fastest (Anderson et al. 1998; Rooney-Varga et al. 1999; Anderson and Lovley 1999; Lovley and Anderson 2000). Anderson and Lovley (2000) also showed that the alkane hexadecane was degraded under methanogenic conditions in Bemidji sediments.

Bekins et al. (1999) used the most probable number (MPN) method to characterize the spatial distribution (in water and sediment) of six physiologic types in the anaerobic portion of the hydrocarbon plume: aerobes, denitrifiers, iron reducers, heterotrophic fermenters, sulfate-reducers, and methanogens (Figure 9A). Iron reducers formed the bulk of the microbial population in the anoxic zone of the plume. Areas evolving from iron reducing to methanogenic conditions were clearly delineated based on microbial populations, and generally occupied 25% to 50% of the plume thickness. Lower microbial numbers were observed below the water table than in the

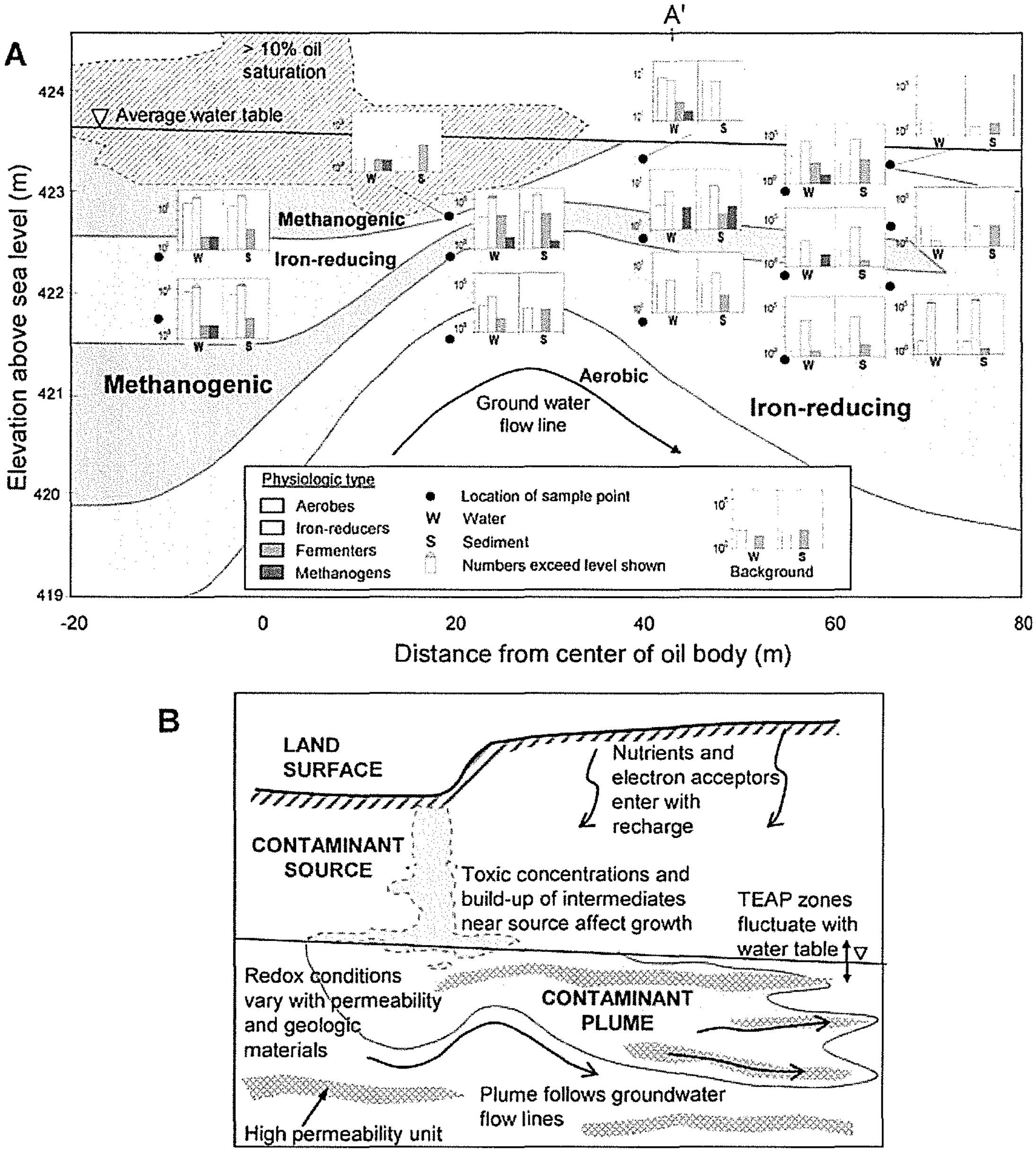

Figure 9. The influence of subsurface hydrologic and geochemical conditions on microbial populations in the hydrocarbon plume: (A) distributions of aerobes, iron reducers, methanogens, and heterotrophic fermenters in water and sediment within the north pool anaerobic plume (from Bekins et al. 1999); (B) conceptual model illustrating the complex interactions of recharge, water-table fluctuations, sediment heterogeneity, and geochemistry that influence microbial population growth (from Haack and Bekins 2000).

unsaturated zone, suggesting that nutrient limitations may be limiting growth in the saturated zone. Finally, the data indicated that an average of 15% of the total population was suspended, rather than attached to the solid substrate.

Haack and Bekins (2000) emphasized the importance of hydrogeological conditions on the evolution of terminal electron-accepting process (TEAP) zones and microbial populations (Figure 9B). Bekins et al. (2001) analyzed the microbial populations together with permeability, pore-water chemistry, NAPL oil content, and extractable sediment iron in the anoxic plume. Microbial data defined zones that had progressed from iron-reduction to methanogenesis as Fe^{3+} was depleted. These zones contained lower numbers of iron reducers, increased numbers of fermenters, and detectable methanogens. Methanogenic conditions existed both in the zone containing NAPL oil, and below the oil body in high permeability zones. High contaminant flux, either through local dissolution from the oil phase or increased advective transport through high permeability layers, played a key role in controlling first occurrence of methanogenic conditions. Other factors included the sediment iron content and proximity to the water table. Twenty years after the oil spill, a laterally continuous methanogenic zone had developed along a narrow horizon extending from the source area to 50 to 60 m downgradient of the oil body.

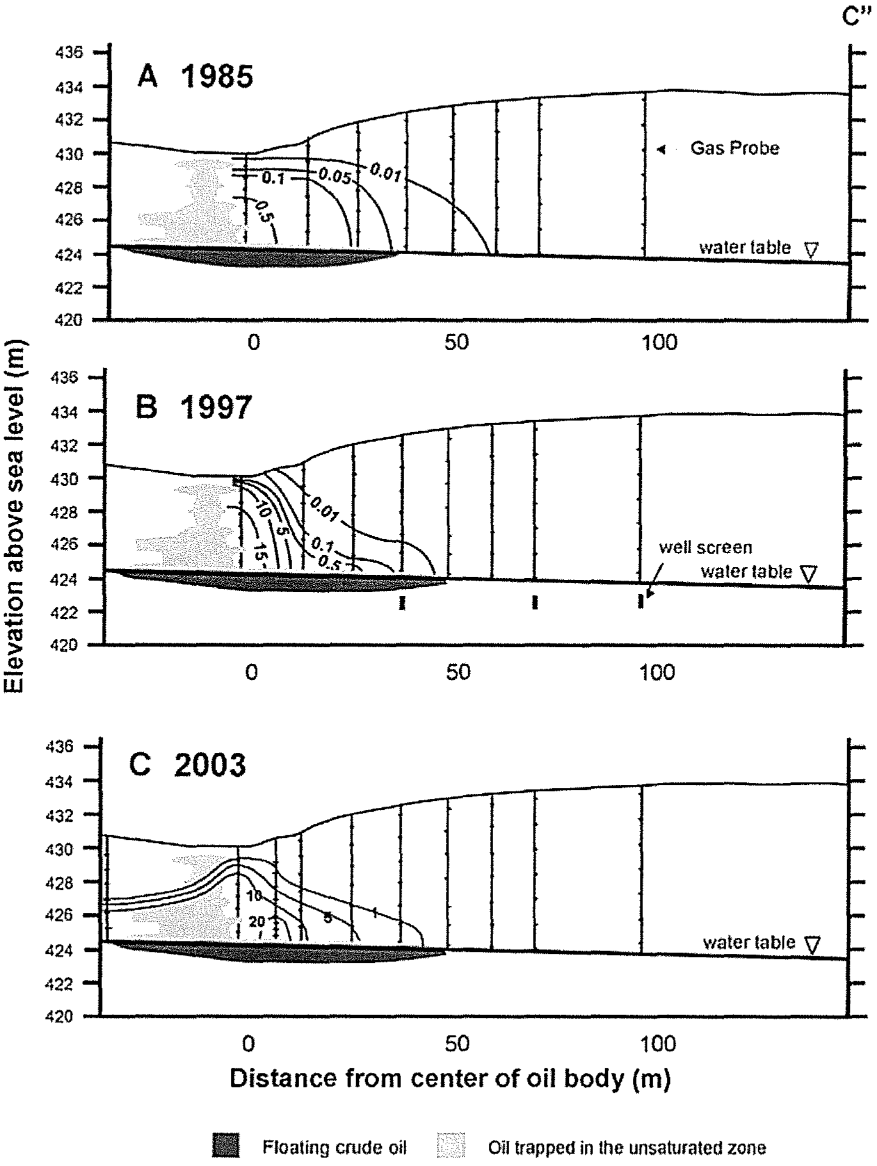

Figure 10. Unsaturated zone methane gas concentrations showing the increase with time as the plume became more methanogenic: (A) 1985 (modified from Hult and Grabbe 1988); (B) 1997 (from Chaplin et al. 2000); and (C) 2003 (modified from Amos et al. 2005).

The studies of microbial populations at Bemidji helped confirm that microbially mediated reactions and anaerobic biodegradation were responsible for the natural attenuation of hydrocarbons and observed plume geochemistry. The distribution and evolution of populations in a hydrocarbon plume are influenced by sediment properties, hydrologic conditions, and availability of electron acceptors and growth nutrients.

The Unsaturated Zone Vapor Plume

Volatile hydrocarbon compounds and biodegradation end-products are transferred from the NAPL oil and groundwater plume to the gas phase in the unsaturated zone. Understanding the factors controlling gas phase hydrocarbon transport is important for evaluating mass loss during natural attenuation and has relevance to the use of soil gas analysis as a field screening tool for NAPL contamination. Many techniques have been used to characterize unsaturated zone gas transport and biodegradation at the Bemidji site.

Mercer and Cohen (1990) cautioned that soil gas analysis could provide misleading results because unsaturated zone hydrocarbon gas concentrations were very sensitive to subsurface heterogeneity. Baehr and Hult (1991) documented the influence of heterogeneity when conducting pneumatic pump tests at Bemidji to estimate air-phase permeability, air-filled porosity and diffusion constants. They were able to characterize a thin silt horizon that separated the unsaturated zone into an upper and lower zone, with a sharp contrast in air permeability and moisture content above and below the silt lens. They illustrated that there was little air flow (and consequently little gas transport) across this interface.

Observation of unsaturated zone gas concentrations (hydrocarbon, oxygen [O_2], CO_2, and CH_4) at the north oil pool in 1997 was used to identify three geochemical zones shown in Figure 5 (Delin et al. 1998). The outer Zone 6 had near atmospheric concentrations of O_2. Zone 7, a transition zone, was defined by lower concentrations of O_2 (10% to 20%), hydrocarbon concentrations less than 1 part per million (ppm), and higher concentrations of CO_2 (0% to 10%) and CH_4 (0% to 10%). The inner Zone 8, immediately above the oil body, had the lowest concentrations of O_2 (0% to 2%) and contained the highest concentrations of CO_2 (>10%), CH_4 (>10%), and hydrocarbon (>1 ppm). Thus, the unsaturated zone vapor plume mirrored the saturated zone groundwater plume, suggesting a similar core of anaerobic degradation near the NAPL oil source. Hult and Grabbe (1988), Chaplin et al. (2002), and Amos et al. (2005) measured unsaturated zone CH_4, CO_2, and O_2 gas concentrations in 1985, 1997, and 2003, respectively. Their work showed that the vapor-phase plume above the oil body and adjacent to the oil trapped in the unsaturated zone has progressively become more anaerobic, with increasing methane concentrations (Figure 10), affirming the conceptual model of a vapor plume evolving from iron reducing to methanogenic conditions. In addition, Chaplin et al. (2002) observed that the hydrocarbon gases detected in the unsaturated zone in 1985 consisted mainly of C_{2-5} alkanes and smaller concentrations of aromatic compounds (benzene, cyclohexane, toluene, and methyl-cyclohexane). By 1997, hydrocarbon gas concentrations had decreased considerably and consisted mainly of C_{2-5} alkanes and methane with smaller concentrations of aromatic compounds (benzene, alylbenzenes, and toluene), suggesting that hydrocarbon loss by volatilization was decreasing with time, and that methanogenesis was increasing with time.

In addition to the volatilization of hydrocarbons from the oil phase, there is exchange of gases between the groundwater plume and the unsaturated zone. Revesz et al. (1995) observed that argon (Ar) and dissolved nitrogen (N_2) concentrations in the hydrocarbon plume were 25 times lower than background values and concluded that gas exsolution was removing dissolved CH_4 and gases from the groundwater. Isotopic evidence indicated that CH_4 was partly oxidized to CO_2 as it diffused upward through the unsaturated zone. Amos et al. (2005) used dissolved and vapor-phase gas data to study the processes controlling production, consumption and transport of methane in the subsurface. They found that regions of Ar and N_2 depletion and enrichment in the unsaturated zone were indicative of methanogenic and methanotrophic zones, respectively, and that reaction-induced advection, in addition to gas phase diffusion, was an important gas transport process at the site. In the saturated zone, the concentrations of dissolved Ar and N_2 were significantly lower in the methanogenic source region, implying that methane gas bubble formation and ebullition also removed the nonreactive Ar and N_2 gases. The Ar, N_2, and CH_4 gas concentrations returned to near background levels approximately 100-m downgradient of the oil source, significantly less than the distance predicted by advection rates, suggesting that the physical processes acting to attenuate the Ar and N_2 plumes must also be acting to attenuate the CH_4 plume. Finally, Amos et al. (2005) observed a slight depletion of N_2 relative to Ar near the oil body, suggesting nitrogen fixation by microbial activity.

Vapor concentrations in the unsaturated zone above the oil body have evolved with time due to volatile hydrocarbon depletion and TEAP progression to methanogenesis. Isotopes and inert gases have been shown to be useful markers for understanding the processes controlling gas transport and fate in the unsaturated zone.

Hydrocarbon Fate Modeling

Geochemical and transport models are effective tools for integrating field observations, testing hypotheses, determining the relative importance of simultaneously occurring processes, as well as quantifying reaction rates and system mass balance. The comprehensive, long-term field data set collected at Bemidji has provided an opportunity to test and refine modeling approaches. Efforts to model the fate of hydrocarbons in the Bemidji plume have become progressively more complex, providing increased insight into processes affecting the long-term fate of the groundwater and vapor plumes.

In the first modeling effort at the Bemidji site, Baedecker et al. (1993) used the geochemical mass-balance model NETPATH (Plummer et al. 1991) to deduce geochemical reactions occurring as groundwater flowed along a 40-m path in the anaerobic zone. The major reactions needed to reproduce the observed field geochemistry were dissolution of manganese and iron oxides, precipitation of siderite and a ferroan calcite, oxidation and reduction of total dissolved organic carbon (TDOC), and outgassing of CH_4 and CO_2. These results confirmed the conceptual model developed for the anaerobic Bemidji plume and described in the section above on geochemical evolution of the plume.

Essaid et al. (1995) modeled the evolution of the groundwater hydrocarbon plume and sequential use of terminal electron acceptors using the multispecies solute-transport and biodegradation model BIOMOC (Essaid and Bekins 1997). Relatively complex representations of sequential biodegradation processes, including aerobic biodegradation, manganese reduction, iron reduction, and methanogenesis with microbial growth and decay of three populations (aerobes, Mn/Fe reducers, and methanogens), were represented by multiple Monod kinetics with nutrient limitation. Simultaneous growth of Mn/Fe reducers and methanogens had to be allowed in the model to match observed concentrations. The source of hydrocarbon was represented by two operationally defined degradable dissolved fractions, VDOC and NVDOC, which entered the aquifer with recharge in the vicinity of the oil body. Model parameter estimates were constrained by published

Monod kinetic parameters, theoretical cell yield estimates, and field biomass measurements and reaction stoichiometries. Despite considerable uncertainty in model parameter estimates, the simulations reproduced the general features of the observed groundwater concentrations (Figure 6) and the measured bacterial concentrations. Simulating the hydrocarbon plume made it possible to quantify the fate of the hydrocarbons. Model results indicated that 46% of the TDOC introduced into the aquifer was degraded: 66% of the VDOC and 39% of the NVDOC. Aerobic biodegradation accounted for 40% of the TDOC degraded and anaerobic processes accounted for the remaining 60%. Thus, the model results confirmed that anaerobic biodegradation was a very important process for natural attenuation of hydrocarbons.

In a subsequent modeling study, Essaid et al. (2003) considered dissolution from the oil body, transport, and biodegradation of BTEX compounds in the saturated zone. The studies of Eganhouse et al. (1993, 1996) had illustrated that individual hydrocarbon compounds dissolved and degraded at different rates (Figure 7). The goal of this modeling study was to estimate compound-specific BTEX field anaerobic biodegradation rates, the field-scale dissolution rate, BTEX removal from the oil body by dissolution, BTEX removal from the groundwater plume by aerobic and anaerobic biodegradation, and the influence of biodegradation on dissolution. The basic conceptual model included rate-controlled dissolution of BTEX from a stationary oil phase, first-order anaerobic degradation of dissolved BTEX, and a fixed rapid first-order rate of aerobic degradation of dissolved BTEX. Simplified representations of biodegradation and dissolution processes, involving as few parameters as possible, were used to facilitate inverse modeling. BIOMOC was used in conjunction with the universal inverse modeling code UCODE (Poeter and Hill 1998) to fit the extensive historical data from 1986 to 1997. BTEX concentrations in the oil and BTEX and DO concentrations in groundwater were simulated (Figure 11A). The estimated field-scale anaerobic biodegradation rates for toluene and *o*-xylene (0.2 and 0.03 d^{-1}, respectively) were greater than the dissolution rate coefficient (0.007 d^{-1}) resulting in limited plume extent. However, the estimated anaerobic biodegradation rates for benzene, ethylbenzene, and *m*, *p*-xylene (0.0007 d^{-1}, 0.0007 d^{-1}, and 0.002 d^{-1}, respectively) were less than the dissolution rate coefficient resulting in plumes that extended into the aerobic zone of the aquifer. The calibrated model was used to determine the BTEX mass balance in the groundwater plume (Figure 11B). Anaerobic biodegradation removed 77% of the total BTEX that dissolved into the water phase and aerobic biodegradation removed 17% (Figure 11B). However, estimated anaerobic biodegradation of individual dissolved hydrocarbon compounds ranged from a low of 51% for ethylbenzene to a high of 98% for toluene. Compounds that underwent less anaerobic degradation migrated downgradient to the oxic zone of the aquifer and consequently underwent greater aerobic degradation. These results were in good agreement with the mass-balance predictions of Essaid et al. (1995) confirming the importance of anaerobic biodegradation during natural attenuation, and illustrating that the relative importance of anaerobic processes was compound specific.

The model of Essaid et al. (2003) was also used to examine evolution of BTEX composition in the NAPL oil source. The degree of removal of BTEX from oil was influenced by oil saturation and rates of dissolution and biodegradation. BTEX removal was greatest in the low oil saturation fringes of the oil body where the interaction between flowing water and oil was the greatest (Figure 12). As expected, dissolution from the oil was greater for compounds with large effective solubility, such as benzene. However, toluene, with less than half of the effective solubility of benzene, experienced almost the same amount of dissolution from the oil (Figure 12). The rapid biodegradation of dissolved of toluene reduced water-phase toluene concentrations in contact with the oil, increasing the concentration gradient and enhancing dissolution. Loss from the oil body was minor for compounds having low solubility and small biodegradation rate (such as ethylbenzene). All BTEX compounds still had significant fractions remaining in the oil body after a simulation of 18 years of dissolution, potentially providing a long-term source of contamination.

Essaid et al. (2003) also explored an alternative iron-reduction conceptual model that modified the first-order anaerobic biodegradation process for benzene to be dependent on solid phase Fe^{3+} concentration, decreasing as ferric iron was depleted. The iron-reduction model produced plume behavior that was similar to that observed by Cozzarelli et al. (2001) and Bekins et al. (2001). The overall extent of the benzene plume was similar for both the basic (described above) and iron-reduction models (Figure 13). However, the simulated high concentration zone in the center of the plume (near the oil body) migrated downgradient in the iron-reduction case, as was observed in the groundwater plume (Figure 8), illustrating that depletion of Fe^{3+} in the anoxic zone could result in an increase in concentration with time.

Curtis (2003) developed a thermodynamically based reactive transport model with mineral dissolution and precipitation for geochemical conditions similar to those observed at Bemidji. He compared the common approach of simulating reactions of multiple TEAPs with an irreversible Monod rate law to reactive transport simulations where reactions were subject to the requirement that the Gibbs free energy of reaction (ΔG) be less than zero (or a threshold value). The order of preference of TEAPs is commonly assumed to be aerobic biodegradation, denitrification, Mn reduction, Fe reduction, sulfate reduction, and finally methanogenesis. This order of preference is based on standard geochemical conditions that may be very different from field conditions. The Monod method involves use of empirical inhibition constants to achieve sequential TEAPs and estimation of many parameters. Curtis (2003) performed simulations using a single

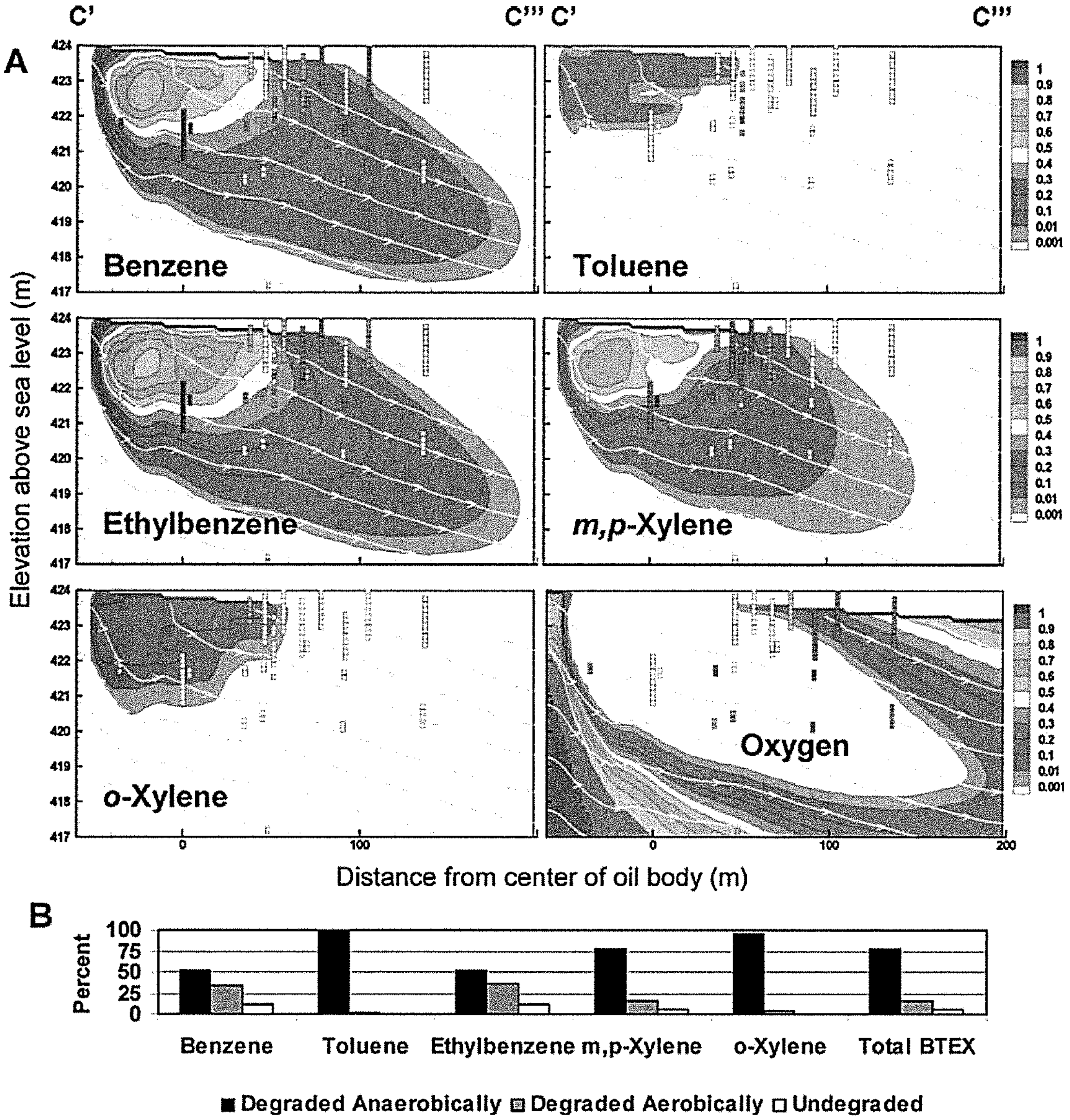

Figure 11. (A) The 1993 distribution of observed (boxes) and simulated (contours) BTEX and oxygen normalized concentrations showing that hydrocarbons with anaerobic degradation rates greater than their dissolution rate have limited plume extent (toluene and *o*-xylene), whereas compounds with anaerobic degradation rates less than their dissolution rate have plumes that extend to the aerobic zone (benzene and ethylbenzene); (B) model-predicted removal of dissolved BTEX by anaerobic and aerobic biodegradation (modified from Essaid et al. 2003).

organic substrate that was slowly and completely fermented to CO_2 and H_2. The hydrogen was then oxidized by the TEAPs with O_2, FeOOH, SO_4, and CO_2 as the terminal electron acceptors. Simulations using the Monod approach forced reduction of both FeOOH and CO_2 to proceed even when ΔG was positive, violating thermodynamics. This resulted in over prediction of FeOOH reduced to Fe^{2+} and large errors in pH. Curtis' (2003) alternate approach required a minimum number of reaction parameters and honored the governing thermodynamic constraints. Using H_2 as an intermediate was effective and efficient, allowing a fit to be obtained with only three reaction parameters. Applying this approach to Bemidji (Curtis et al. 1999) reproduced the observed pH buffering by methanogenesis, precipitation of authigenic mineral phases, parallel terminal electron acceptor use, and methane gas bubble formation.

Chaplin et al. (2002) determined unsaturated zone biodegradation mass removal rates by calibrating the gas transport model R-UNSAT (Lahvis and Bear 1997), using UCODE (Poeter and Hill 1998), to the observed O_2, CO_2, and CH_4 gas-concentration data. Reaction stoichiometry was used to convert O_2 and CO_2 gas-flux estimates to rates of aerobic biodegradation and convert CH_4 gas-flux estimates to rates of methanogenesis. Model results indicated that 3% of total volatile hydrocarbons diffusing upward from the floating oil were biodegraded in the bottom meter of the unsaturated zone in 1985. This increased to 52% by 1997, with methanogenesis responsible for approximately half of the removal. Chaplin et al. (2002)

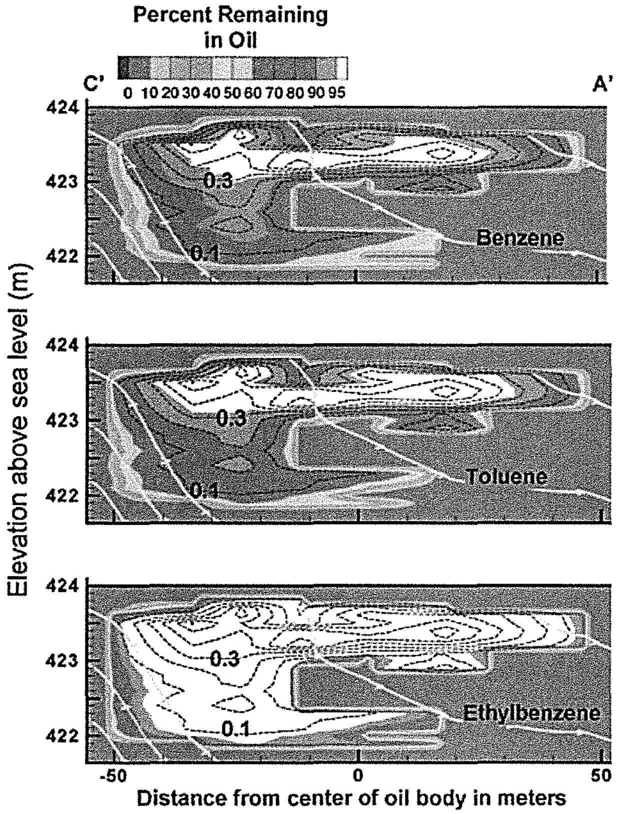

Figure 12. Simulated percent of benzene, toluene, and ethylbenzene remaining in the oil phase (relative to the initial amount in the oil body) after 18 years of dissolution and biodegradation. Dashed contours represent oil saturation and gray lines represent flow paths (from Essaid et al. 2003).

concluded that volatilization was the primary mechanism for hydrocarbon removal in early stages of plume evolution, but that biodegradation became dominant in later stages as concentrations of volatile hydrocarbons in the oil decreased and microbial populations evolved.

Amos et al. (2005) provided field evidence that CH_4 and CO_2 production in the hydrocarbon plume formed gas bubbles, affecting groundwater chemistry and potentially solute transport. Amos and Mayer (2006) modified the unsaturated/saturated zone reactive transport code MIN3P (Mayer et al. 2002) to include the formation and collapse of gas bubbles in addition to kinetically controlled redox and mineral dissolution/precipitation reactions, equilibrium hydrolysis, aqueous complexation, ion exchange and surface complexation reactions. They examined processes related to gas bubbles and gas transport in the methanogenic hydrocarbon plume. Their simulations reproduced the observed depletion of the nonreactive gases N_2 and Ar where gas bubbles formed. They concluded that reduced permeability in the hydrocarbon source zone, caused by the formation of methane gas bubbles, and dissolution of low methane concentration bubbles entrapped during water-table fluctuations combine to reduce dissolved CH_4 concentrations in the anoxic plume.

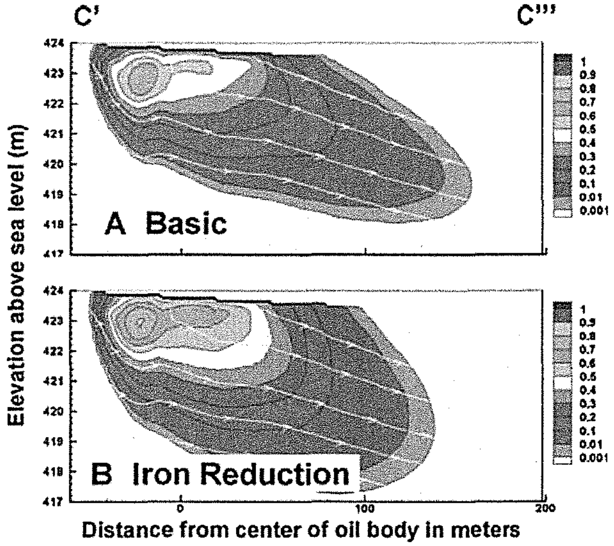

Figure 13. Predicted groundwater benzene concentration 50 years after the spill for the case of (A) a first-order anaerobic benzene biodegradation rate that is uniform in time and (B) a first-order anaerobic biodegradation rate that becomes zero when Fe^{3+} is depleted (from Essaid et al. 2003). The latter case reproduces the observed downgradient migration of the central high hydrocarbon concentration zone (see Figure 8).

Model development and application has been an important complement to the field analysis at Bemidji, affirming conceptual models developed from field and experimental observations. Models have progressively incorporated more complex processes and have provided a means to quantify mass removal and biodegradation rates. These modeling approaches have universal application to studies at other hydrocarbon contaminated sites.

Conclusions and Lessons Learned

In summarizing the status of NAPL knowledge at the end of the 1980s, Mercer and Cohen (1990) identified many limitations in the research community's understanding of subsurface NAPL behavior. Their recommendations for future research included: improved methods to measure in situ saturation; improved understanding of field constitutive relations (such as relative permeability functions); improved understanding of in situ volatilization and dissolution; studies of the influence of spatial variability on NAPL migration and recovery; and ongoing research at field sites to assess remediation strategies. They also pointed out that although many sophisticated models were available to simulate the flow of NAPL, they were mainly used in a conceptual mode because of the lack of chemical and site-specific data. Twenty-five years of study at the Bemidji crude-oil spill site has contributed significant knowledge in all of these areas.

Research at Bemidji has involved extensive investigations of multiphase flow and transport, volatilization, dissolution, geochemical interactions, microbial populations, and biodegradation. The challenge of understanding and predicting the fate of hydrocarbons in the field is that these processes occur simultaneously, interact with one another, and are influenced by subsurface flow rates. For example, oil present in the pore space reduces water flow and consequently reduces hydrocarbon dissolution. The feedback between groundwater flow, dissolution, and biodegradation influences the hydrocarbon plume extent. Also, the amount of nutrient rich recharge can impact biodegradation rates. Research at the Bemidji site has involved detailed monitoring and interpretation of field observations coupled with laboratory experiments and numerical process-oriented models of varying complexity. This combined approach has been used to synthesize and integrate field observations and develop a comprehensive understanding of the long-term fate of oil in the subsurface.

Early observations of groundwater geochemistry at Bemidji were among the first to document the importance of anaerobic processes for hydrocarbon removal and plume migration control (Baedecker et al. 1993; Eganhouse et al. 1993; Bennett et al. 1993). Aerobic biodegradation was known to be an effective hydrocarbon removal process. However, detailed characterization (Cozzarelli et al. 1990, 1994) and modeling (Essaid et al. 1995, 2003) of the Bemidji hydrocarbon plume illustrated that significant removal of hydrocarbons was also occurring in the central anaerobic core of the plume. Sequential use of terminal electron acceptors was observed (Baedecker et al. 1993; Bekins et al. 1999), coupled with selective structure-dependent biodegradation of hydrocarbon compounds (Eganhouse et al. 1996). Anaerobic biodegradation evolved from manganese reduction to iron reduction as manganese oxides were depleted. Iron reduction was shown to be very effective at hydrocarbon removal. When Fe^{+3} became depleted, methanogenesis became the predominant anaerobic biodegradation process. Methanogenic biodegradation was not as effective at removing hydrocarbon compounds as iron reduction, and consequent increases in hydrocarbon concentrations were observed in the core of the plume (Bekins et al. 2001; Cozzarelli et al. 2001). Certain BTEX compounds (such as toluene and *o*-xylene) were readily biodegraded and were not transported great distances in the plume. Benzene and ethylbenzene were more persistent. These findings illustrated that removal processes evolve with time, and estimates of removal rates made early in the life of a hydrocarbon plume may not be representative of future removal rates due to exhaustion of electron acceptors and/or nutrients. This must be kept in mind when evaluating the efficacy of natural attenuation as a remediation alternative at contaminated sites (Bekins et al. 2005b).

Spatial variability of hydraulic properties was found to be an important control on NAPL fate. The glacial outwash deposits at the Bemidji site consist primarily of moderately to poorly sorted sandy gravel, gravely sand, and sand with thin interbeds of fine sand and silt (Franzi 1988). The finer grained layers, although a small fraction of the subsurface deposits, have exerted an important influence on oil-phase flow. Observed and simulated oil-saturation distributions have illustrated that oil infiltration and redistribution are often controlled by grain-size heterogeneity due to its effect on pore size distributions and capillary phenomena (Hess et al. 1992; Essaid et al. 1993; Dillard et al. 1997). Where oil was entrapped above fine-grained layers that impeded downward movement, unsaturated zone oil saturations were still nearly 30% 20 years after the spill. Oil distributions in the saturated zone showed that the shape of the oil body floating on the water table was complex, and not lens shaped as would be expected in a uniform porous medium. Multiphase modeling studies showed that heterogeneity had to be included to reproduce this complexity (Essaid et al. 1993; Dillard et al. 1997). Modeling studies also showed that the oil flow was hysteretic, with infiltration and drainage following different characteristic curves. However, when the presence of the fine-grained layers was well characterized and explicitly represented in the multiphase flow model, hysteretic behavior could be reproduced simply through the effect of heterogeneity, without hysteretic characteristic curves.

Heterogeneity in hydraulic conductivity also influenced subsurface vapor diffusion, water flow, and the progression of biodegradation. Unsaturated zone air pump tests in an uncontaminated area showed that a thin low-permeability horizon could isolate air flow above and below it (Baehr and Hult 1991). Further studies of vapor-phase concentration above the oil body revealed a fine-grained horizon above which oxygen concentrations increased rapidly and below which there was a sharp gradient in methane concentrations (Amos et al. 2005). In the saturated zone, increased flow and mass transport rates in more conductive zones led to more rapid depletion of Fe^{2+} and more rapid evolution to methanogenic conditions (Haack and Bekins 2000; Bekins et al. 2001). Subsequently, BTEX compounds that degraded more slowly under methanogenic conditions were observed to increase in concentration and advance downgradient (Cozzarelli et al. 2001).

Considerable volumes of NAPL oil still remain in the subsurface despite 30 years of volatilization, dissolution, and biodegradation, and 5 years of pump-and-skim remediation (Herkelrath 1999; Enbridge Energy 2008). Concurrent with hydrocarbon plume evolution, the crude-oil source was evolving as hydrocarbon compounds degraded and dissolved at different rates (Landon 1993; Landon and Hult 1996; Eganhouse et al. 1996). Changes in the oil source are best described by examining two categories of hydrocarbon compounds: the relatively soluble aromatic fraction (including BTEX) and the relatively insoluble fraction (alkanes). For the soluble aromatic fraction, field data indicated that the upgradient part of the oil body underwent more dissolution than the downgradient end (Eganhouse et al. 1996). The inflow of relatively low hydrocarbon concentration groundwater created a concentration gradient across the oil-water interface driving dissolution of the soluble hydrocarbons. As water flowed downgradient past the oil body, hydrocarbon concentration increased and dissolution decreased. Modeling of dissolution and biodegradation processes has illustrated that dissolution is greatest where oil saturations are lower because of the greater flow of water through these zones (Essaid et al. 2003). Models results also have also shown that compounds with high effective solubilities (such as benzene) and/or large biodegradation rates (such as toluene) were depleted in the oil body more than other hydrocarbon compounds. Biodegradation in the water phase reduced hydrocarbon concentrations adjacent to the oil body, and consequently enhanced dissolution. The model results suggested that considerable BTEX still remained in the oil body 18 years after the spill.

The degree of depletion of the insoluble alkane fraction in the oil body (degradation state) did not depend on oil saturation, indicating that it was not caused by dissolution but instead was a result of methanogenic oil biodegradation (Bekins et al. 2005a). Alkane depletion was much higher in the area below a local topographic low where focused flow (Delin and Herkelrath 1999, 2005) has resulted in increased groundwater recharge and nutrient transport. Vastly different observed degradation states for the same starting oil composition from a single spill event invalidates use of degradation state to estimate the timing of a spill (Bekins et al. 2005a). Vapor-phase data indicate that methanogenic biodegradation was occurring in the oil body by 1987 and is the dominant degradation process today (Hult and Grabbe 1988; Revesz et al. 1995; Chaplin et al. 2002; Amos et al. 2005). Under methanogenic conditions the longer chain *n*-alkanes and alkyl side chains are depleted first, creating a fingerprint which can mimic a lighter fuel. This phenomenon was also observed at a diesel spill site in Mandan, North Dakota (Hostettler et al. 2007, 2008). Fingerprinting techniques used to identify the starting composition of spilled product must account for this degradation pattern and be based on other components of hydrocarbon fuels.

Detailed information from the Bemidji site has made it possible to develop increasingly complex models of the fate and transport of hydrocarbons in the groundwater plume. Geochemical mass-balance modeling (Baedecker et al. 1993) supported the hypothesis of anaerobic biodegradation of hydrocarbons in conjunction with dissolution of manganese and iron oxides, and outgassing of CH_4 and CO_2. Modeling of multispecies transport with sequential biodegradation represented by Monod kinetics showed that anaerobic processes removed more than half of the dissolved BTEX, and that iron reduction and methanogenesis had to occur concurrently to match observed plume concentrations (Essaid et al. 1995). Subsequent modeling based on thermodynamic constraints proved that this could be happening in the field (Curtis 2003). Inverse modeling with simple first-order biodegradation rates reproduced the general features of the plume, but failed to capture the subtle changes in the plume as it evolved from primarily iron reducing to methanogenic conditions (Essaid et al. 2003). Incorporating a switch from iron reducing to methanogenic conditions after the depletion of Fe^{3+} produced a simulated plume that reproduced the observed downgradient migration of the central high hydrocarbon concentration zone (Essaid et al. 2003). Reactive transport modeling including the effects of gas bubble formation and collapse has shown that outgassing and oxidation of methane has been an important process, and that bubble formation has impeded water flow (Amos and Mayer 2006).

Natural attenuation has been demonstrated to be an effective remediation strategy for many spills (Wiedemeier et al. 1999). However, transport and fate of hydrocarbons in the subsurface is a spatially and temporally complex problem. The persistent nature of the oil-phase hydrocarbon source and the long time frame for natural attenuation observed at Bemidji is not unique. Long-term field monitoring and process-oriented modeling at Bemidji has illustrated that hydrocarbon fate is compound specific and continually evolving with time. Thus, a snap-shot study of a hydrocarbon plume may not provide information that is of relevance to the long-term behavior of the plume under natural attenuation. Natural and induced changes in the oil source, redox conditions, microbial populations, recharge and flow rates will result in changes in plume extent. Ongoing research at the Bemidji crude-oil spill site continues to focus on providing insights and methods that will help us to understand and predict the evolution and fate of subsurface hydrocarbon plumes.

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