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Abstract The time frame for natural attenuation of crude oil contamination in the subsurface has been studied for the last 27 years at a spill site located near Bemidji, Minnesota, USA. Data from the groundwater contaminant plume show that dissolved benzene concentrations adjacent to the oil decreased by 50% between 1993 and 2007. To assess how this decrease is related to benzene concentrations in the crude oil, samples of oil were bailed from floating oil in five wells and analysed for volatile components. Compared to reference oil collected from the pipeline in 1984, benzene concentrations in the well located farthest downgradient in the oil have decreased an average of 50%. Benzene and ethylbenzene depletion are linearly correlated with oil saturation in the pore space suggesting that dissolution is the primary removal mechanism and biodegradation within the oil body is insignificant.

Key words petroleum; benzene; methanogenic; biodegradation

INTRODUCTION

Monitored natural attenuation (MNA) has been widely adopted in the USA for remediation and risk-based management of petroleum hydrocarbon contamination in groundwater (EPA, 1995). In some cases site closure decisions were based on a trend of declining concentrations, even though aqueous concentrations exceeded the regulatory limit, and light non-aqueous phase liquid (LNAPL) was present (e.g. Evanson *et al.*, 2009). A recent study by the state of Wisconsin, USA, of Leaking Underground Fuel Tank (LUFT) sites closed during 1999–2000 showed that contamination is persisting longer than expected. In five of 10 sites studied in detail, benzene concentrations were higher than at site closure and five of the 10 sites had longer benzene plumes (Evanson *et al.*, 2009). Given the widespread adoption of MNA and the Wisconsin results, studies are needed to assess the attenuation timeframe and long-term fate of petroleum hydrocarbon plumes when LNAPL source remains in the subsurface.

Processes controlling the timeframe of natural attenuation of crude oil in the subsurface are the subject of an ongoing 27-year study of a spill site near Bemidji, Minnesota, USA (Fig. 1). The site was contaminated by a 1979 pipeline rupture resulting in subsurface infiltration of over 400 000 L in three main areas. The spilled oil composition is ~60% saturated hydrocarbons with aromatics representing much of the remainder (Eganhouse *et al.*, 1993). The most abundant hydrocarbons are the C-6 to C-32 *n*-alkanes (33–36%). In 1983 the site was selected for long-term research by the US Geological Survey (USGS) Toxics Substance Hydrology Program. The largest oil body at the water table is called the “north pool” and has been the focus of most studies at the site (Essaid *et al.*, 2010). The north pool is 1–2 m thick and spans an area of ~100 × 25 m (Fig. 1) with peak oil saturations of 30–65% of the pore space (Fig. 2). In this paper we report on changes in the contaminant plume and LNAPL composition that have occurred in the north pool oil body since the 1979 spill.

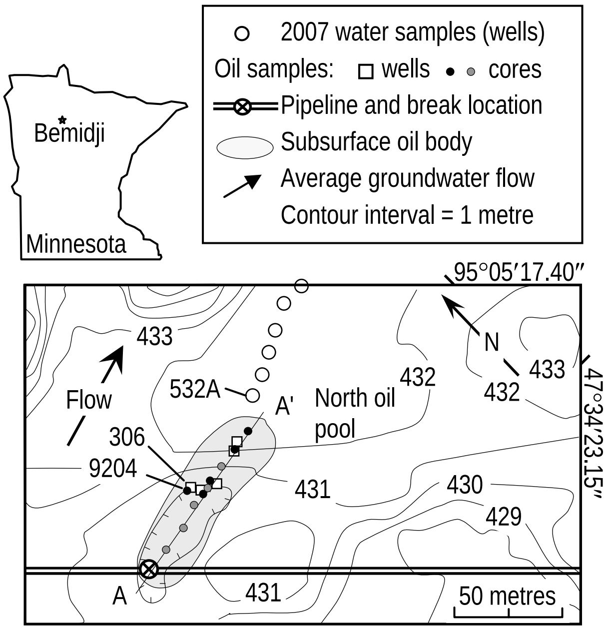

Fig. 1 Topographic map showing the north pool oil body with section line and cores (grey dots) used for Fig. 2, wells for water samples used for Fig. 3, and wells for oil samples (white squares) and cores for oil saturations (black dots) used for Fig. 4.

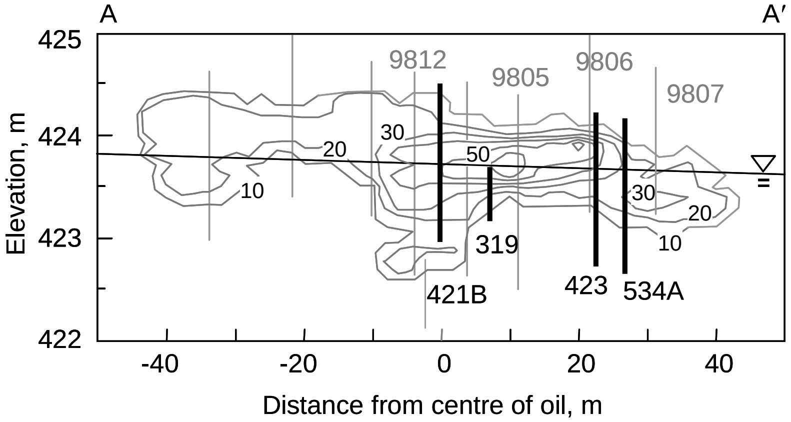

Fig. 2 Contour plot of percent oil saturation in pore space of Bemidji north oil pool in 1998 along A–A′ in Fig. 1. Light grey lines are cores used for saturation determinations. Heavy black lines are screen locations of four wells in Fig. 1 sampled for oil. Well 306 is located outside the line of section. Oil saturation for this location is given in Table 1.

SAMPLING AND METHODS

The groundwater monitoring wells in Fig. 1 were sampled in 2007 and analysed for benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations by the USGS

National Water Quality Laboratory using heated purge and trap, gas chromatography / mass spectrometry. Concentrations were also measured in 1993 in the same wells using methods described by Cozzarelli *et al.* (2001).

In 2008, oil samples were bailed with disposable bailers from five wells in the oil body (Fig. 1). These samples were analysed for 21 volatile hydrocarbons, including BTEX, naphthalenes, and C-6 to C-12 *n*-alkanes. Volatile components were separated from the oil by solid-phase microextraction and analysed by gas chromatography / mass spectrometry (SPME-GC/MS) (for detailed methods see Drennan *et al.*, 2010).

Pore space oil saturations in the north pool were determined from cores collected in 1998 and 1992 from the locations (dots) shown in Figs 1 and 2. These cores were analysed for soil and water saturation using the methods of Hess *et al.* (1992). In each core, saturations were determined for 7.5 cm sub-sections. These data were used to produce the Fig. 2 contour plot of oil saturation in the north pool.

Table 1 Oil volatile data, closest core, and peak oil saturation.

Sample	Benzene Year collected		Ethylbenzene		Closest core[2]	Peak oil saturation
	1987–89[3]	2008	1987–89[3]	2008		
306	59%	7%	134%	47%	9204	0.08
421B	92%	38%	117%	111%	9812	0.43
534A	83%	41%	93%	92%	9806 & 9807	0.45
319	98%	61%	108%	121%	9805	0.54
423	55%	56%	97%	109%	9806	0.62
Pipeline[1]	2.25		1.57		–	–

[1] Oil sample collected from pipeline in 1984, units are milligrams per gram oil.

[2] Year the core was collected is given by the first two digits of core number. Saturation for 534A value is interpolated between two cores given.

[3] Values are percentages of pipeline value. Wells 306, 319, 423 sampled 1989, wells 421B, 534A sampled in 1987.

RESULTS

Figure 3 shows benzene data from 1993 and 2007 in the groundwater contaminant plume from the north pool. In the 45-m well (532A; Fig. 1) located closest to the oil, concentrations dropped from 4.6 mg/L to 2.1 mg/L or 55% during this 14-year period. Concentrations in the next two sampled wells were also lower by 33–67% (Fig. 3). Beyond 75 m concentrations were higher, which is consistent with previously observed growth of the plume as sediment Fe(III) sources are depleted (Cozzarelli *et al.*, 2001). The drop in benzene concentrations observed in 2007 was greater than that observed in any of the four sampling years from 1987 to 1993 during which concentrations at the 45-m well (532A) averaged 4.4 ± 0.41 mg/L (n = 4). In contrast, a similar decrease was not observed for ethylbenzene, which was 0.26 mg/L in 2007 *versus* 0.24 ± 0.01 mg/L from 1987 to 1995.

The decrease in concentrations of benzene relative to ethylbenzene in the plume also occurred in the crude oil source. Figure 4 and Table 1 show the results of SPME/GC-MS analyses of oil samples from five wells normalized to a sample collected from the oil pipeline in 1984. For ethylbenzene the relative concentration

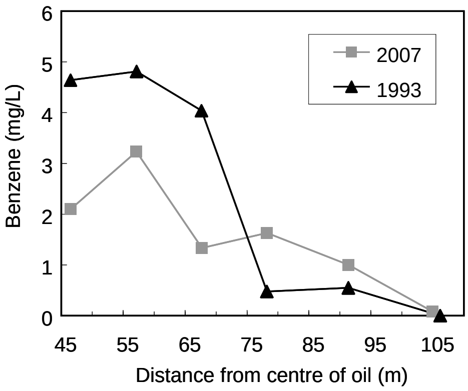

Fig. 3 Concentrations of benzene in the groundwater plume from the north oil pool showing decreases between 1993 and 2007. Locations of wells for water samples are shown in Fig. 1.

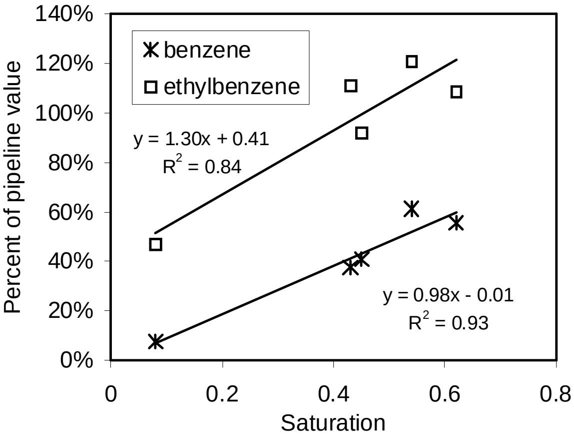

Fig. 4 Concentrations of benzene and ethylbenzene in the five oil samples from wells *vs* oil saturation in pore space of closest core. Concentrations are normalized to the reference sample collected from the pipeline in 1984.

varies from 45 to 120%. Values greater than 100% are possible because the subsurface oil body is depleted in other compounds, increasing the relative concentration of ethylbenzene. Table 1 gives the concentrations of ethylbenzene in samples of oil collected in 1987 and 2008 from the most downgradient well in the oil 534A (Fig. 2). Comparing 2008 to 1987 (Table 1) shows that the ethylbenzene has not changed much, consistent with the constant concentrations observed in the groundwater monitoring well closest to the oil (532A, Fig. 1).

Benzene is more depleted, which is expected given its higher effective solubility in the groundwater contacting the oil (Eganhouse *et al.*, 1996). Comparing 1987 and 2008 for the oil from well 534A shows that benzene decreased by 50%, in good agreement with the 55% decrease in groundwater concentrations (Fig. 3). The plot in Fig. 4 also shows that depletion of benzene and ethylbenzene is proportional to oil saturation in the pore space (R^2 = 0.93 and 0.84, respectively). A relationship between saturation and depletion is expected when dissolution is the primary mechanism for removal because saturation affects the relative permeability of water and thus the flux of groundwater past the oil.

Results of simulations by Essaid *et al.* (2003) of benzene dissolution from the north pool oil yielded a similar relation between oil saturation and benzene depletion. The strong relation in Fig. 4 suggests that dissolution rather than biodegradation controls removal of benzene and ethylbenzene in the oil body. The microbial population in the oil body is dominantly methanogenic (Bekins *et al.*, 2005) and results from other sites indicate that methanogenesis is unreliable for degradation of benzene and ethylbenzene (NRC, 2000).

CONCLUSIONS

A combined dataset of groundwater and oil concentrations shows that an observed decrease in benzene in the groundwater plume is due to depletion of benzene in the oil during the 31 years since the spill. In contrast, ethylbenzene has not decreased as much in either the oil or the plume, which is consistent with its lower effective solubility. Both compounds are depleted in proportion to the oil saturation suggesting that dissolution is the primary removal mechanism and biodegradation is insignificant under the methanogenic conditions.

REFERENCES

Bekins, B. A., Hostettler, F. D., Herkelrath, W. N., Delin, G. N., Warren, E. &Essaid, H. I. (2005) Progression of methanogenic degradation of crude oil in the subsurface. *Environ. Geosci.* **12**(2), 139–152.

Cozzarelli, I. M., Bekins, B. A., Baedecker, M. J., Aiken, G. R., Eganhouse, R. P. & Tuccillo, M. E. (2001) Progression of natural attenuation processes at a crude-oil spill site I. Geochemical evolution of the plume. *J. Contaminant Hydrol.* **53**, 369–385.

Drennan, D. M., Bekins, B. A., Warren, E., Cozzarelli, I. M., Baedecker, M. J., Herkelrath, W. N. & Delin, G. N. (2010) Fate and transport of petroleum hydrocarbons in the subsurface near Cass Lake, Minnesota. *US Geol. Survey Scientific Investigations Report 2010–5085*.

Eganhouse, R. P., Baedecker, M. J., Cozzarelli, I. M., Aiken, G. R., Thorn, K. A. & Dorsey, T. F. (1993) Crude oil in a shallow sand and gravel aquifer-II. Organic geochemistry. *Appl. Geochem.* **8**, 551–567.

Eganhouse, R. P., Dorsey, T. F., Phinney, C. S. & Westcott, A. M. (1996) Processes affecting the fate of monoaromatic hydrocarbons in an aquifer contaminated by crude oil. *Environ. Sci. Technol.* **30**(11), 3304–3312.

EPA (1995) Use of Risk-Based Decision-Making in UST Corrective Action Programs. 9200.4-17, EPA, Office of Solid Waste and Emergency Response, Washington, DC, USA.

Essaid, H. I., Bekins, B. A., Herkelrath, W. N. & Delin, G. N. (2010) Crude oil at the Bemidji Site: 25 years of monitoring, modeling, and understanding. *Ground Water* doi:10.1111/j.1745-6584.2009.00654.x.

Essaid, H.I. Cozzarelli, I. M., Eganhouse, R. P., Herkelrath, W. N., Bekins, B. A. & Delin, G. N. (2003) Inverse modeling of BTEX dissolution and biodegradation at the Bemidji, MN crude-oil spill site. *J. Contaminant Hydrol.* **67**, 269–299.

Evanson, T. A., Pelayo, A. M. & Bahr, J. M. (2009) Wisconsin closure protocol study: a retrospective study of LUST site closures between 1999 and 2000, Wisconsin Department of Natural Resources, PUB-RR-805.

Hess, K. M., Herkelrath, W. N. & Essaid, H. I. (1992) Determination of subsurface fluid contents at a crude-oil spill site. *J. Contaminant Hydrol.* **10**, 75–96.

NRC (2000) *Natural Attenuation for Groundwater Remediation*. National Academy Press, Washington, DC, USA.