

## Arsenic Cycling in Hydrocarbon Plumes: Secondary Effects of Natural Attenuation

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### Abstract

Monitored natural attenuation is widely applied as a remediation strategy at hydrocarbon spill sites. Natural attenuation relies on biodegradation of hydrocarbons coupled with reduction of electron acceptors, including solid phase ferric iron (Fe(III)). Because arsenic (As) adsorbs to Fe-hydroxides, a potential secondary effect of natural attenuation of hydrocarbons coupled with Fe(III) reduction is a release of naturally occurring As to groundwater. At a crude-oil-contaminated aquifer near Bemidji, Minnesota, anaerobic biodegradation of hydrocarbons coupled to Fe(III) reduction has been well documented. We collected groundwater samples at the site annually from 2009 to 2013 to examine if As is released to groundwater and, if so, to document relationships between As and Fe inside and outside of the dissolved hydrocarbon plume. Arsenic concentrations in groundwater in the plume reached 230 µg/L, whereas groundwater outside the plume contained less than 5 µg/L As. Combined with previous data from the Bemidji site, our results suggest that (1) naturally occurring As is associated with Fe-hydroxides present in the glacially derived aquifer sediments; (2) introduction of hydrocarbons results in reduction of Fe-hydroxides, releasing As and Fe to groundwater; (3) at the leading edge of the plume, As and Fe are removed from groundwater and retained on sediments; and (4) downgradient from the plume, patterns of As and Fe in groundwater are similar to background. We develop a conceptual model of secondary As release due to natural attenuation of hydrocarbons that can be applied to other sites where an influx of biodegradable organic carbon promotes Fe(III) reduction.

### Introduction

Arsenic (As) is a toxin and carcinogen linked to numerous forms of skin, bladder, and lung cancer (NRC 1999). Of particular concern to public health is elevated As in groundwater used for drinking water, documented in many countries worldwide, with notable examples in regions of South-East (SE) Asia (Nordstrom 2002; Smith et al. 2002). The current U.S. Environmental Protection Agency (USEPA) and World Health Organization drinking water standard for As is 10 µg/L. Recent findings document reduced child intelligence quotient associated with drinking water As concentrations of only 5 µg/L (Wasserman et al. 2014).

Owing to strong adsorption affinity, As is often associated with metal (e.g., Fe, Mn) hydroxides (Stollenwerk 2003 and references therein). Thus, soils and sediments with metal hydroxides can accumulate As, resulting in detectable As concentrations. Soils in the United States

have an average As concentration of 5.2 mg/kg (Shacklette and Boerngen 1984; Reimann et al. 2009), although not all soils and sediments contain detectable As. Glacial sediment in Minnesota, North Dakota, and South Dakota has measured As concentrations up to 56 mg/kg, with an average of less than 5 mg/kg ( $n > 2500$ ) (Kanivetsky 2000).

Although As concentrations in solids are important for predicting where As concentrations in groundwater may be elevated, an additional critical factor is the prevailing geochemistry (Smedley and Kinniburgh 2002). Increasing sediment As concentrations does not necessarily lead to increasing groundwater As concentrations (Erickson and Barnes 2005a; Thomas et al. 2008). If As is associated with Fe-hydroxides, and geochemical conditions are oxic, the hydroxide is thermodynamically stable and As remains adsorbed to the solid phase. However, if conditions become reducing due to the introduction of organic carbon, those once stable Fe-hydroxides can be microbially reduced coupled with oxidation of the organics, releasing Fe and potentially As to solution (Smedley and Kinniburgh 2002). Although there are other processes that can cause As mobilization to groundwater, including mineral dissolution and competitive desorption, this process of reductive dissolution of As-rich metal hydroxides coupled with oxidation of natural organic carbon is thought to be the dominant cause of elevated naturally occurring As concentrations in groundwater in SE Asia (e.g., McArthur et al. 2001). Elevated As

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in groundwater in glacial and alluvial aquifers in the Midwestern United States has also been attributed to reductive dissolution of Fe-hydroxides (Warner 2001; Thomas 2003; Erickson and Barnes 2005a; Erickson and Barnes 2005b; Kelly et al. 2005; Root et al. 2010).

Previous work on mobilization of naturally occurring As in groundwater resulting from introduction of anthropogenic organic carbon to aquifers includes studies of landfills (Keimowitz et al. 2005; deLemos et al. 2006; Hering et al. 2009) and sewage plumes (Stollenwerk and Coleman 2003; Kent and Fox 2004; Amirbahman et al. 2006; Pinel-Raffaitin et al. 2007). The release of As to groundwater at petroleum-impacted sites has also been suggested (e.g., Ghosh et al. 2003; Burgess and Pinto 2005; Hering et al. 2009; Brown et al. 2010), but in cases where the link has been made, the observations have been preliminary. Recently, the American Petroleum Institute published a manual on managing As at petroleum impacted sites (API 2011), which presents four case studies of sites where As in groundwater has been linked to the petroleum release. Although these studies document the existence of As at sites impacted by petroleum, there have been limited data to test hypotheses about the relationships of As with other geochemical signatures, the mechanisms of release, and the ultimate fate of As at petroleum-impacted sites. The Bemidji site in northern Minnesota is an ideal field location to examine this process, because the site has been extensively instrumented and has been monitored for organic species and redox sensitive chemical parameters for over 30 years (Essaid et al. 2011). In this study, we investigated As concentrations in

groundwater and sediment over time at the Bemidji site to examine the cycling of As in the hydrocarbon plume, thus providing insight into the potential risks associated with hydrocarbon leaks and spills.

## Field Site

A pipeline rupture occurred near Bemidji, Minnesota, in 1979, resulting in the release of approximately  $1.7 \times 10^6$  L (about 10,700 barrels) of crude oil onto a glacial outwash deposit (Baedecker et al. 1993; Essaid et al. 2011), which consists of glacially derived well sorted to poorly sorted sand and gravel with interbeds of silt (Franzi 1988; Delin and Herkelrath 2014). Crude oil sprayed on the land surface and percolated through the unsaturated zone to the water table near the rupture site resulting in three subsurface oil pools. The north pool oil body (Figure 1) has been the focus of decades of research aimed at understanding the fate of hydrocarbons in the subsurface (Essaid et al. 2011). Groundwater contamination by aromatic hydrocarbons resulted from this spill, as well as contamination of the sediments and unsaturated zone soil gas. Because of extensive biodegradation, the dissolved hydrocarbon plume is anoxic, dominated by methanogenic conditions near the subsurface oil body and transitioning to an extensive iron-reducing zone downgradient (Tuccillo et al. 1999; Bekins et al. 2001; Cozzarelli et al. 2001). Detailed discussion of the reaction processes is provided by Cozzarelli et al. (2014). Although the redox zones are identified by the dominant process, there is substantial overlap in the iron-reducing and

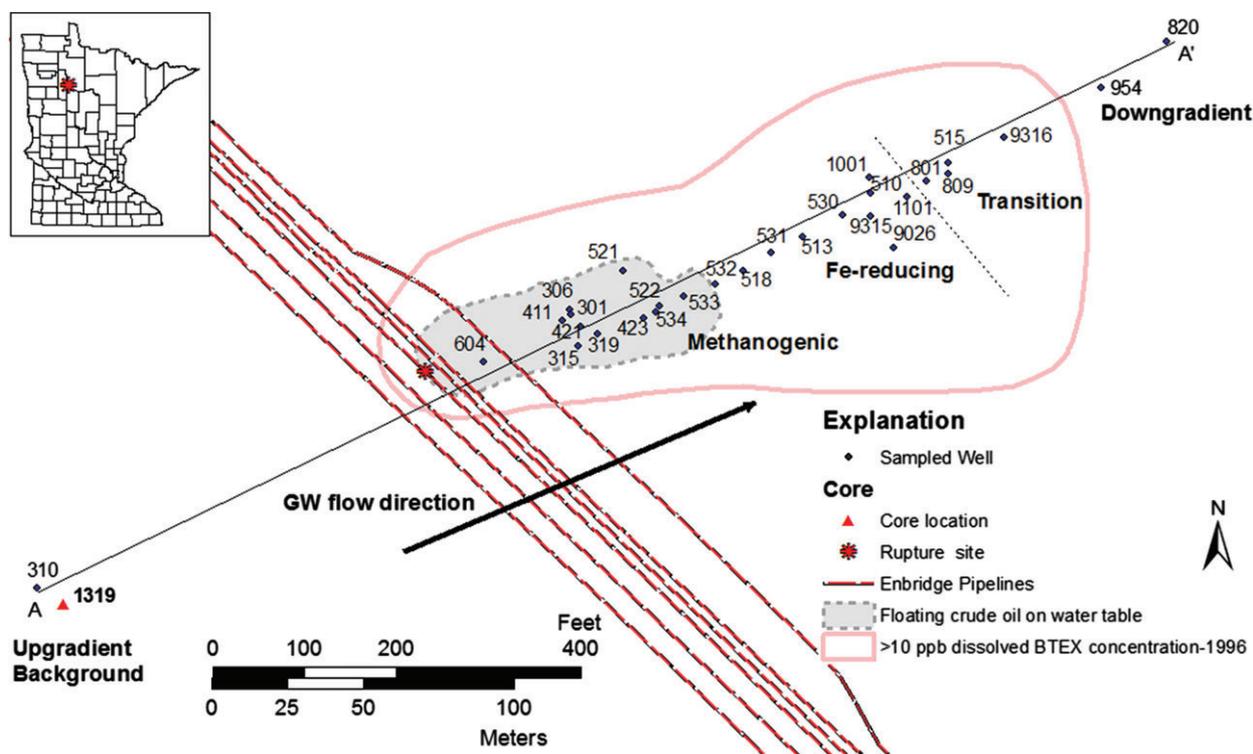
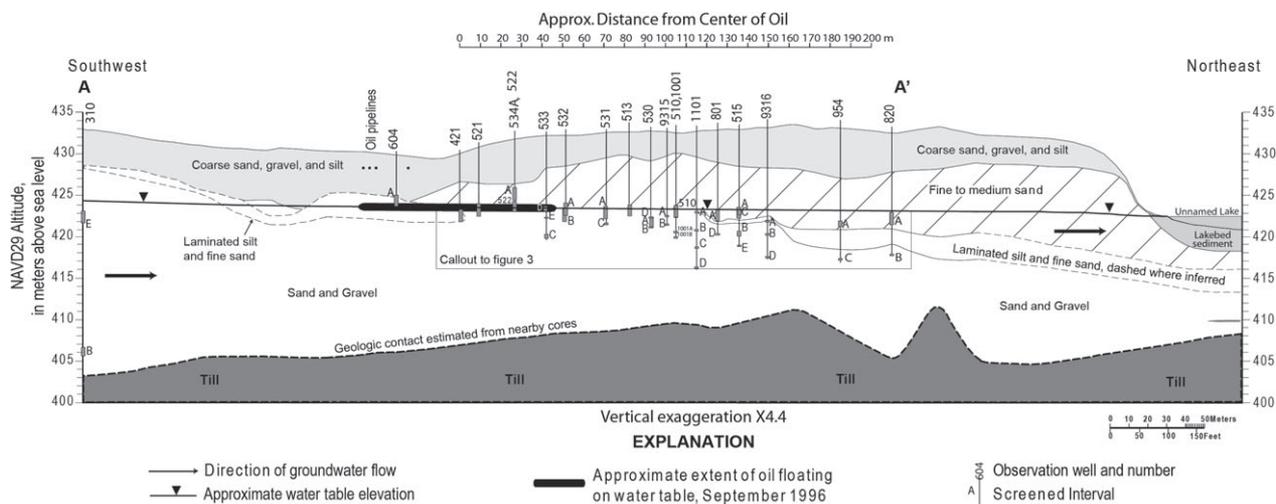


Figure 1. Map of the study site showing the approximate extent of the subsurface oil, the dissolved BTEX plume, general locations of redox zones, and locations of wells and the core sampling site.



**Figure 2.** Well locations along the plume centerline shown in Figure 1. Geologic information modified from Strobel et al. (1998) and Franzi (1988).

methanogenic zones. At the leading edge of the dissolved plume, the aquifer returns to oxic/sub-oxic conditions.

## Methods

### Groundwater Sampling and Analysis

Groundwater samples were collected annually for geochemical analyses from 2009 through 2013. Locations of wells from which groundwater was collected for this study are shown in Figures 1 and 2. For figures of the full suite of wells at the Bemidji site, see the Bemidji Crude Oil Research Site home page (<http://mn.water.usgs.gov/projects/bemidji/>). In 2009, groundwater samples were collected from wells screened adjacent to or beneath the north pool oil body by using a Teflon bailer. In 2010 through 2013, groundwater samples were collected by using a submersible Keck pump.

Dissolved oxygen (DO) was measured in flowing water directly at the pump outlet and analyzed by using a Chemetrics V-2000 portable spectrophotometer or colorimetric CHEMets visual kits (Chemetrics, Midland, Virginia). Samples collected for Fe and As analysis were filtered through 0.2  $\mu\text{m}$  Nuclepore membranes and preserved to pH less than 2 with nitric acid. Samples were stored on wet ice/refrigeration until analyzed.

For the remainder of this paper, we will use the terms “dissolved  $\text{Fe}_T$ ” and “dissolved  $\text{As}_T$ ” to represent the concentrations of  $\text{Fe(II)} + \text{Fe(III)}$  and  $\text{As(III)} + \text{As(V)}$  species, respectively, that pass through a 0.2  $\mu\text{m}$  filter. Previous work at the Bemidji site has demonstrated that dissolved  $\text{Fe}_T$  largely reflects dissolved  $\text{Fe(II)}$  (unpublished data), and thus we will use dissolved  $\text{Fe}_T$  as a proxy for dissolved  $\text{Fe(II)}$ .

The filtered, acidified samples were analyzed for dissolved  $\text{Fe}_T$  using a Perkin Elmer Optima 4300 Inductively Coupled Plasma Optical Emission Spectrometer 176 (ICP-OES; Perkin Elmer Instruments, Shelton, Connecticut), with a detection limit of 0.10 mg/L. The

dissolved  $\text{As}_T$  analyses were conducted using Perkin Elmer ELAN 9000 Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Perkin Elmer Instruments), with a detection limit for dissolved  $\text{As}_T$  of 0.1  $\mu\text{g/L}$ .

Selected groundwater samples were speciated for dissolved As [ $\text{As(III)}$ ,  $\text{As(V)}$ ] using the method of Le et al. (2000). Filtered (0.2  $\mu\text{m}$ ) samples were eluted through a 3 mL strong anion exchange (SAX) column (Supelco LC-SAX SPE; Sigma-Aldrich, St. Louis, Missouri) that had been pre-conditioned with methanol followed by a deionized water (DI) rinse. The effluent from the column contained  $\text{As(III)}$ .  $\text{As(V)}$  was retained on the column and was eluted later in the laboratory using 0.16 M nitric acid. Samples were analyzed using graphite furnace atomic adsorption spectroscopy (GFAA; Varian SpectraAA 2220Z; Perkin-Elmer, Waltham, Massachusetts) with Zeeman background correction. The detection limit for As on GFAA is 3  $\mu\text{g/L}$ .

Water for non-volatile dissolved organic carbon (NVDOC) analyses was filtered (0.2- $\mu\text{m}$  Supor filter), collected in a baked glass bottle, and acidified with hydrochloric acid to a pH of less than 2. Concentrations of NVDOC were measured by high-temperature combustion using a Shimadzu TOC-Vcsn Analyzer (Shimadzu Corporation, Kyoto, Japan). Samples for benzene analyses were collected unfiltered in prebaked amber glass bottles and preserved with hydrochloric acid to a pH of less than 2. Sample bottles were filled without headspace and preserved on wet ice/refrigeration until analyzed. Analyses were accomplished by purge and trap gas chromatography/mass spectrometry using a modification of the EPA Method 524.2 and 8260.

### Sediment Sampling, Digestion, and Analysis

In 2013, a sediment core was collected from the aquifer upgradient from the hydrocarbon spill (1319 in Figure 1) to evaluate background As and Fe in sediment. The core was collected by drilling with a hollow-stem auger to approximately two feet below the water table,

followed by driving of a piston core barrel beneath the augers to the desired depth. The bottom 10 cm of the core was frozen in situ using liquid CO<sub>2</sub> to ensure that the sediment and fluid were retained within the core liner and to maintain redox integrity of the subsurface (Murphy and Herkelrath 1996).

After collection, core ends were covered with plastic wrap and immediately capped. After description, the core was cut into smaller sections, wrapped in plastic, capped, wrapped in foil, and sealed in vacuum-sealed bags. Sections were kept frozen on site and shipped frozen with dry ice to U.S. Geological Survey (USGS). In the laboratory, sediment samples were collected at selected intervals and were dried and sieved (less than 2 mm) prior to extraction via microwave digestion with nitric acid (EPA Method 3051a). Extracts were diluted 1:10 with DI and analyzed for Fe and As by inductively coupled plasma atomic emission spectrometry (ICP-AES) (detection limits 5 and 9 µg/L, respectively). National Institute of Standards and Technology (NIST) standard reference material 2587 (trace elements in soil; As concentration 13.7 ± 2.3 mg/kg), acid blanks, and water blanks were also digested and analyzed for each microwave batch. Arsenic concentration in the NIST standard averaged 11.4 mg/kg, which reflects 80% to 100% recovery. Arsenic concentrations in acid and water blanks were below detection.

### Oil Sampling and Analysis

Crude oil collected in 1984 from the same pipeline that had ruptured and created the original spill was analyzed for As using Instrumental Neutron Activation Analysis (detection limit 5 µg/L) by Activation Laboratories.

## Results

### Groundwater

Groundwater chemical data, including DO, dissolved Fe<sub>T</sub>, dissolved As<sub>T</sub>, % As(III), NVDOC, and benzene concentrations, for 69 groundwater samples collected in 2009, 2010, 2011, 2012, and 2013 are presented in Table 1 in order of distance downgradient from the center of the north pool oil body (relative to reference well 421, Figure 1), with reported negative distances indicating upgradient from the oil body. Dissolved As<sub>T</sub> concentrations range from below detection at several locations to a maximum concentration of 230 µg/L, measured in 2010 in well 421B, which is screened just below the center of the north pool oil body. The proportion of As(III) in groundwater ranges from 80% to 92%. Dissolved Fe<sub>T</sub> concentrations range from below detection at several locations to a maximum of 167 mg/L, measured in 2010 in well 319, also screened below the oil body.

Background wells 310E and 310B are in the upgradient, uncontaminated portion of the aquifer (Figure 2). Well 310E is in the shallow, oxic zone and showed no detectable dissolved As<sub>T</sub> in 2009 or 2013. However, well 310B, which is screened in a deeper, more reduced zone

(80 µg/L DO) of the aquifer contained 2.3 µg/L of dissolved As<sub>T</sub> in 2013.

Transects of dissolved As<sub>T</sub>, dissolved Fe<sub>T</sub>, DO, and benzene concentrations in groundwater (Figure 3) show that the highest As, Fe, and benzene concentrations are present in the region of the aquifer where DO is depleted, and comparison of contours also shows a spatial similarity. Examination of the 2013 data set as a bivariate plot of dissolved As<sub>T</sub> and dissolved Fe<sub>T</sub> (Figure 4) shows a strong correlation ( $r^2 = 0.82$ ) between these two parameters.

Figure 5 shows dissolved Fe<sub>T</sub> and dissolved As<sub>T</sub> concentrations in three wells (510, 9315A, 9315B), at the downgradient edge of the Fe-reducing zone of the plume, in 2009, 2012, and 2013. Concentrations of both Fe and As in groundwater increase between 2009 and 2013 illustrating the expansion of the Fe-reducing zone over this 4-year period and underscoring the dynamic nature of the plume more than three decades after the spill.

Figure 6 compares the dissolved Fe<sub>T</sub>, dissolved As<sub>T</sub>, NVDOC, and DO in the shallow and deep zones of background aquifer near well 310 (shallow = 310E; deep = 310B) to the shallow and deep zones of the aquifer at well 533 near the edge of the oil body (shallow = 533E; deep = 533C) in 2013. These results demonstrate the vertical spatial variability of groundwater chemistry. In the background location, the shallow aquifer sample has high DO (~8000 µg/L) and less than 1 µg/L dissolved As<sub>T</sub>, whereas the deeper sample naturally contains low DO (80 µg/L) and has low, but slightly elevated dissolved As<sub>T</sub> of 2.3 µg/L. The natural NVDOC at this upgradient location is 2.4 mg/L. Near the edge of the oil body, the shallow groundwater (533E) is substantially impacted by dissolved hydrocarbons (NVDOC of 31 mg/L). This high NVDOC is associated with low DO and elevated dissolved Fe<sub>T</sub> and dissolved As<sub>T</sub> concentrations of 30.8 mg/L and 43.4 µg/L, respectively. The deep aquifer at this location (533C) is below the hydrocarbon plume and looks similar to the deep background groundwater with dissolved As<sub>T</sub> less than 1 µg/L and dissolved Fe<sub>T</sub> of 0.26 mg/L.

### Sediments

Table 2 shows Fe and As concentrations in sediment from background core 1319 (see Figure 1 for location). Arsenic concentrations in this background sediment range from 0.7 to 2.4 mg/kg; Fe concentrations range from 3874 to 7210 mg/kg. The elevation of the background core (422.5 to 423.7 m above mean sea level [AMSL]) is within the shallow zone, at the same elevation as background well 310E.

### Oil

Results from the oil analysis show that the crude oil collected from the pipeline in 1984 contained 35 µg/L of As. The potential temporal variability of As concentrations in the crude oil is unknown.

**Table 1**  
**Selected Groundwater Data Collected from the Bemidji Site (2009 to 2013)**

Well	Center Screen Elev (m AMSL)	Screen Length (m)	Year	DO (µg/L)	Dissolved Fe <sub>T</sub> (mg/L)	Dissolved As <sub>T</sub> (µg/L)	%As (III)	NVDOC (mg/L C)	Benzene (µg/L)	Dist. Well 421 (m)
310B	406.84	0.914	2013	80	0.1	2.28	n.a.	2.4	1.3	-200.54
310E	423.05	1.321	2013	7960	<0.1	<1	n.a.	1.5	bdl	-200.48
604A	424.70	1.524	2010	80	35.6	55	n.a.	40	1207.2	-34.968
411	424.12	1.524	2010	n.a.	49.8	24.9	n.a.	68	1017.4	-7.079
315	424.42	1.524	2010	40	50.8	11.1	n.a.	53	2269.3	-6.75
421B	424.25	1.524	2010	40	24.9	230	n.a.	52	2775.5	0.863
319	423.40	1.524	2010	n.a.	167	17.5	n.a.	75	n.a.	5.488
306	423.50	1.524	2010	n.a.	94	140	n.a.	72	1227.1	5.519
301A	424.03	1.524	2010	n.a.	88.2	55.2	n.a.	51	1591.4	6.935
423	422.52	1.524	2010	n.a.	38.3	76.5	n.a.	18	4681.1	20.376
521	423.80	1.524	2010	n.a.	24.8	41.1	n.a.	20	1584	22.384
534A	423.88	1.524	2010	n.a.	40	53.7	n.a.	38	4270.8	24.495
522	424.18	1.321	2010	n.a.	33	95.1	n.a.	56	4351.6	26.025
533C	420.73	0.152	2013	220	0.26	<1	n.a.	4.3	125.52	34.582
533D	423.94	0.61	2010	10	31	140	n.a.	53	2999.3	37.516
533E	422.81	0.152	2013	550	30.8	43.4	n.a.	31	2714	38.774
532B	422.32	0.152	2013	100	21.5	38.1	89.0	18	976.78	45.691
532A	423.69	1.321	2012	<10	33.5	55.6	n.a.	23	3290	46.354
518B	422.90	0.152	2013	80	28.4	58.9	88.7	24	1761	55.93
518A	423.99	1.321	2013	240	30.5	62.9	87.1	22	2241	57.087
531C	422.04	0.241	2013	330	22.8	16.7	78.5	5.9	0.72	66.703
531A	423.44	1.524	2013	140	26	45.2	91.8	14	821.5	67.573
531A	423.44	1.524	2012	<10	35.6	53.9	n.a.	24	1152	67.573
513	423.68	1.321	2013	990	34.7	37	88.6	22	1415	78.152
513	423.68	1.321	2012	n.a.	34.8	34.5	n.a.	23	1640	78.152
530B	422.11	0.152	2013	70	24.3	26.4	88.2	14	13.32	91.27
530A	422.26	1.321	2013	890	24.2	34.7	90.3	16	11.13	91.871
530D	422.91	0.152	2013	300	26.3	40.8	91.0	18	7.77	93.439
9315A	423.33	0.241	2013	230	24.8	26.3	86.4	24	615.21	101.274
9315A	423.33	0.241	2012	<10	16.2	20.3	n.a.	9.4	55.6	101.274
9315A	423.33	0.241	2009	50	7.6	15.2	n.a.	6.1	n.a.	101.274
9315B	422.22	0.241	2013	70	29.6	11.8	89.8	23	474.35	101.638
9315B	422.22	0.241	2012	<10	28.4	8.78	n.a.	15	205	101.638
9315B	422.22	0.241	2011	540	16.8	10.6	n.a.	16	n.a.	101.638
9315B	422.22	0.241	2009	75	12.1	7.21	n.a.	7.7	n.a.	101.638
510	423.83	1.321	2013	10	21	17.6	80.2	8.6	1.25	104.772
510	423.83	1.321	2012	<10	29.2	17.1	n.a.	8.4	121	104.772
510	423.83	1.321	2009	100	14	12.8	n.a.	6.7	n.a.	104.772
9026	422.69	0.152	2009	150	0.14	<1	n.a.	4.9	n.a.	106.118
1001B	420.57	0.244	2011	<10	8.46	12.6	n.a.	11	n.a.	106.283
1001A	421.27	0.244	2011	270	6.9	10.4	n.a.	5.5	n.a.	106.617
1101A	422.62	0.241	2013	250	23.3	19.6	n.a.	14	22.26	114.68
1101A	422.62	0.241	2011	240	21.3	18.5	n.a.	11	n.a.	114.68
1101B	420.51	0.241	2013	680	0.325	1.96	n.a.	3.3	bdl	115.463
1101B	420.51	0.241	2011	180	3.1	2.1	n.a.	4.5	n.a.	115.463
1101C	418.70	0.241	2011	160	0.85	0.502	n.a.	2.5	n.a.	116.362
1101D	416.59	0.241	2013	2810	0.2	<1	n.a.	3.2	bdl	117.236
1101D	416.59	0.241	2011	2990	0.095	0.128	n.a.	2.1	n.a.	117.236
801D	421.06	0.241	2009	120	0.194	2.66	n.a.	5	n.a.	123.279
801A	423.06	1.321	2013	1170	<0.1	<1	n.a.	7.7	0.53	125.457
801A	423.06	1.321	2012	<10	34.1	<1	n.a.	5.1	49.4	125.457
801A	423.06	1.321	2009	>1000	<0.1	0.99	n.a.	5.4	n.a.	125.457
515E	419.65	0.241	2013	160	0.23	2.24	n.a.	11	0.7	131.691
515C	423.61	0.54	2009	50	1.02	1.53	n.a.	4.1	n.a.	132.498
515B	420.95	0.54	2013	220	0.185	<1	n.a.	9.6	bdl	135.721
515A	423.60	1.321	2013	5870	<0.1	<1	n.a.	5.2	0.19	136.875
515A	423.60	1.321	2012	<10	0.028	<1	n.a.	3.5	3.6	136.875
9316B	421.01	0.241	2013	484	0.605	<1	n.a.	3.7	n.a.	151.859
9316D	418.01	0.152	2013	230	<0.1	1.4	n.a.	12	0.33	152.61
9316A	422.57	0.241	2013	540	0.16	1.2	n.a.	3.1	bdl	152.651
9316A	422.57	0.241	2009	130	<0.1	1.67	n.a.	2.9	n.a.	152.651
954A	422.08	0.655	2013	370	0.13	<1	n.a.	2.5	0.86	188.278
954C	417.81	0.244	2013	350	0.895	0.7	n.a.	4.3	bdl	188.848
820B	418.30	0.244	2013	1310	0.895	0.7	n.a.	3.1	bdl	210.829
820A	422.86	1.524	2013	4090	<0.1	<1	n.a.	3.5	bdl	214.942

n.a. = not analyzed; bdl = below detection.

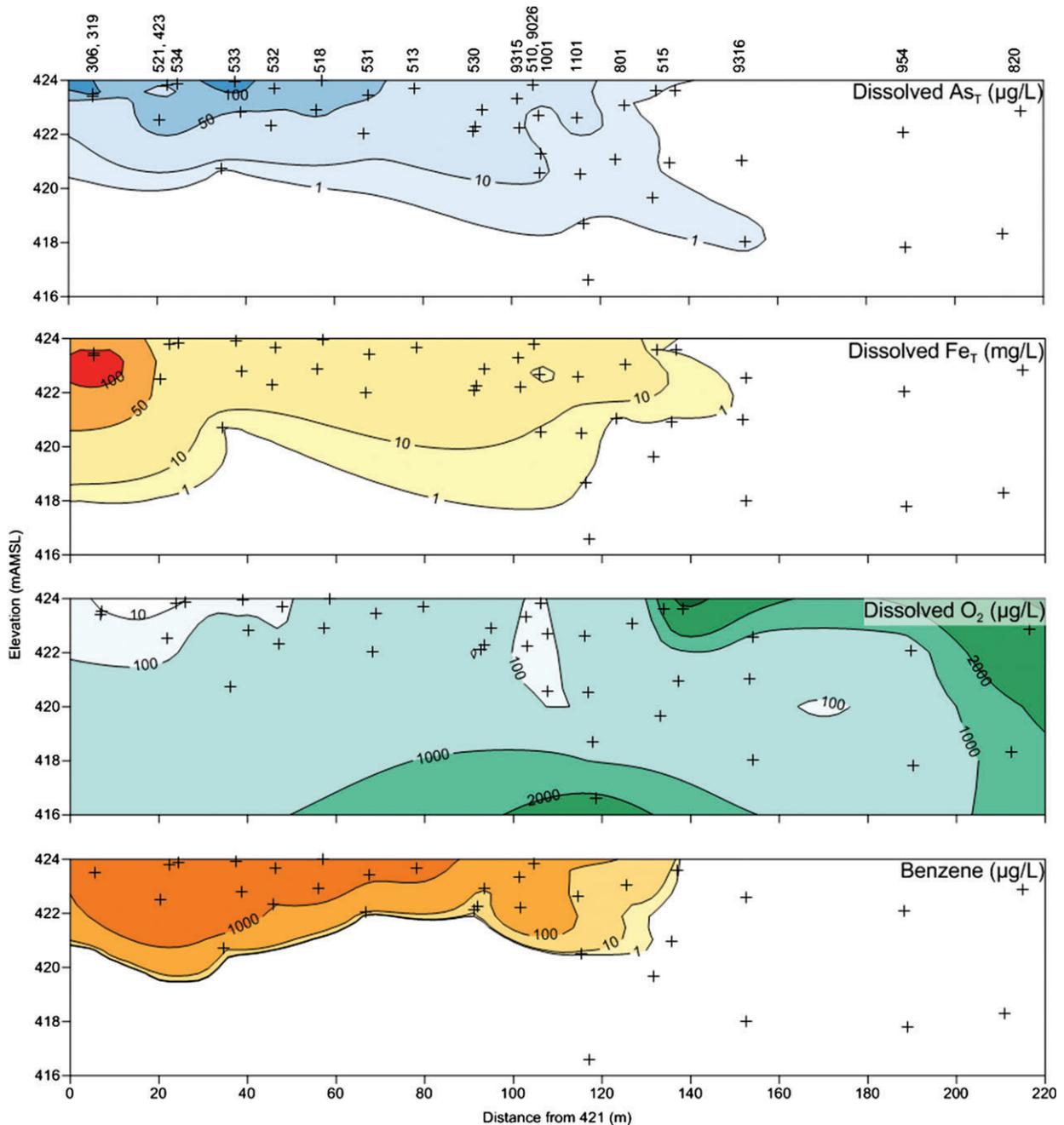


Figure 3. Transects (see Figure 2 for location and extent of the oil) of dissolved As<sub>T</sub>, Fe<sub>T</sub>, oxygen, and benzene concentrations in groundwater based on data collected from 2009 to 2013 (data shown in Table 1). Upgradient data from well 310 not shown.

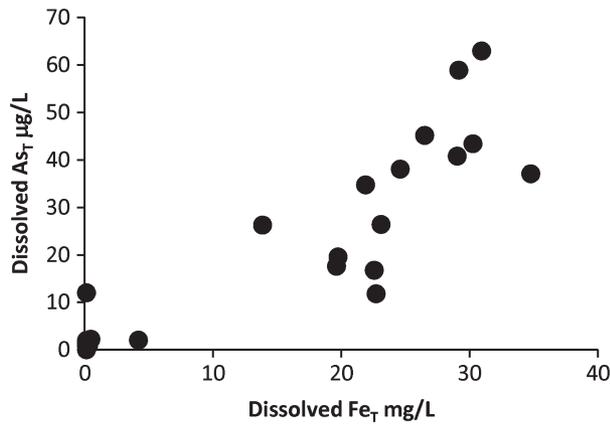
## Discussion

### Source of As in Groundwater

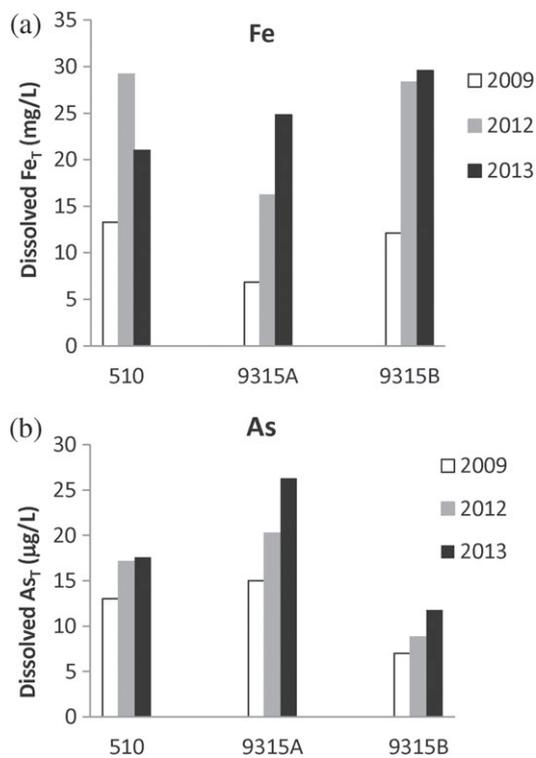
There are three potential sources of As to groundwater in the dissolved hydrocarbon plume at the Bemidji site. The first potential source is the crude oil. Oil and other fossil fuels contain As and other trace elements, with concentrations varying based on the source. Stigter et al. (2000) analyzed As and other trace elements in 23 crude oils worldwide; concentrations ranged from less than 10 to 37 µg/L. The crude oil spilled at the Bemidji site contains 35 µg/L, on the upper end of the worldwide range. If oil was the primary source of As to groundwater, then

even in pure oil, the maximum As concentration could only be 35 µg/L. In the plume, measured As concentrations reach 230 µg/L, indicating that the oil cannot be the primary source of As to groundwater.

The second potential source of As in the plume is from reduced, upgradient groundwater. Background well 310B, screened in a suboxic zone upgradient from the plume, contained 2.3 µg/L As in 2013 (Table 1; Figure 6a). Detection of low concentrations of naturally occurring As in Minnesota groundwater is common (MDH 2014). Although these results indicate that As is detectable in groundwater under naturally reducing conditions upgradient from the hydrocarbon plume, the



**Figure 4. Relationship between dissolved  $As_T$  ( $\mu\text{g/L}$ ) and dissolved  $Fe_T$  ( $\text{mg/L}$ ) concentrations in groundwater in 2013.**



**Figure 5. (a) Dissolved  $Fe_T$  ( $\text{mg/L}$ ) and (b) dissolved  $As_T$  ( $\mu\text{g/L}$ ) in three wells located in the Fe-reducing zone (see Figures 1 and 2 for location of wells) in 2009, 2012, and 2013.**

concentrations are considerably lower than those detected within the plume itself and thus cannot represent a primary source of dissolved As.

The third potential source of As to groundwater in the plume is the aquifer sediment. Results from our extractions of sediment upgradient from the plume show that As is present up to 2.4 mg/kg (Table 2). Similar glacial sediment in a previous study measured total As of 2 to 10 mg/kg, of which 0.4 to 0.8 mg/kg As was adsorbed to iron oxides (Erickson and Barnes 2005a). We can calculate the maximum amount of As released to porewater, using the following assumptions: the As

**Table 2**  
**Arsenic and Iron Data in Background Sediment (Core 1319; see Figure 1 for Location)**

Elevation (m AMSL)	Near-Total Fe (mg/kg)	Near-Total As (mg/kg)
423.7	7210	2.4
423.5	5504	1.3
423.1	3874	0.7
422.8	6800	1.2
422.5	5890	0.9

Data represent averages of triplicate digestions/analyses.

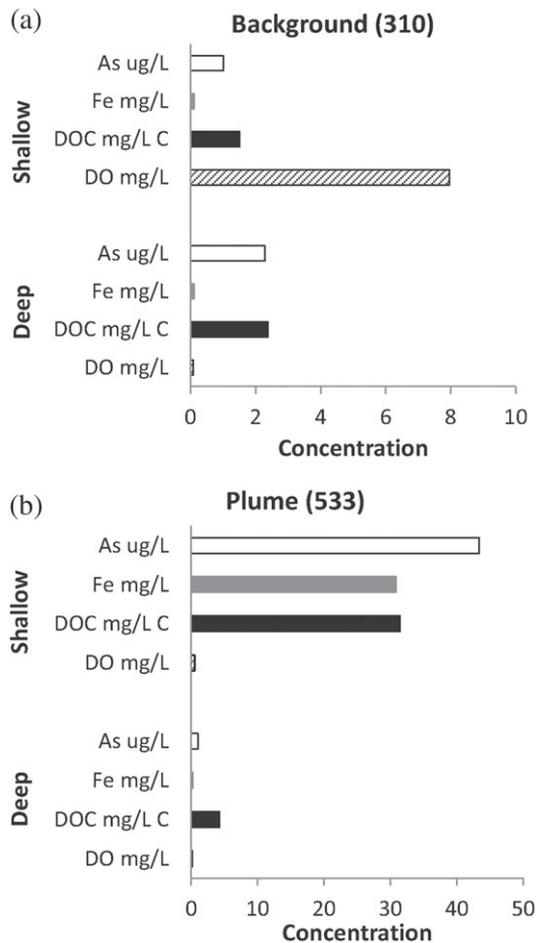
concentration in background aquifer sediment is 2.4 mg/kg ( $\mu\text{g/g}$ ), the aquifer sediment is predominantly made up of quartz, with a particle density of 2.65 g/cm<sup>3</sup>, and the aquifer has a porosity of 30%.

$$\begin{aligned} \frac{\text{mass As}}{\text{vol aquif}} &= \left( \frac{2.4 \mu\text{g As}}{\text{g sed}} \right) \left( \frac{2.65 \text{ g sed}}{\text{cm}^3 \text{ sed}} \right) \\ &= \frac{0.7 \text{ cm}^3 \text{ sed}}{\text{cm}^3 \text{ aquif}} = \frac{4.45 \mu\text{g As}}{\text{cm}^3 \text{ aquif}} \\ \frac{\text{mass As}}{\text{L gw}} &= \left( \frac{4.45 \mu\text{g As}}{\text{cm}^3 \text{ aquif}} \right) \left( \frac{1 \text{ cm}^3 \text{ aquif}}{0.3 \text{ cm}^3 \text{ gw}} \right) \\ &= \left( \frac{14.84 \mu\text{g As}}{\text{cm}^3 \text{ aquif}} \right) \left( \frac{1 \text{ cm}^3 \text{ gw}}{0.001 \text{ L gw}} \right) \\ &= \frac{14,840 \mu\text{g As}}{\text{L gw}} \end{aligned}$$

Thus, if all of the As from the background sediment was released to solution, the As concentration in groundwater would be 14,840  $\mu\text{g/L}$ . The highest measured concentration in groundwater is 230  $\mu\text{g/L}$ , which is 0.15% of the calculated maximum possible concentration. These calculations demonstrate that there is enough mass in sediment to cause the As concentrations that we measure in groundwater at the Bemidji site, and provides strong support for a sediment source of As to groundwater.

### Arsenic Cycling in the Bemidji Plume

Our spatial and temporal data demonstrate how a hydrocarbon spill can promote secondary water-quality effects, such as As release from sediments into groundwater. In this aquifer system, the background NVDOC concentrations are naturally low but can result in reduced DO and slightly elevated dissolved  $Fe_T$  and  $As_T$  in background groundwater (Figure 6a). Although detectable, the background dissolved  $As_T$  concentration is well below the 10  $\mu\text{g/L}$  USEPA drinking water standard and is typical of As concentrations in uncontaminated aquifers in the region (Erickson and Barnes 2005a). The introduction of biodegradable organic carbon, in the form of petroleum hydrocarbons, shifts the redox conditions from suboxic to strongly anoxic at the Bemidji site, resulting in release of dissolved  $Fe_T$  and  $As_T$  to groundwater. Deeper in the aquifer (Figure 6b), below the zone of high carbon



**Figure 6. Dissolved  $As_T$ , dissolved  $Fe_T$ , NVDOC, and DO concentrations in monitoring wells collected in 2013 from (a) upgradient from the crude oil spill (310; shallow = 310E; deep = 310B) and (b) downgradient from the spill near the edge of the oil body (533; shallow = 533E; deep = 533C). See Figures 1 and 2 for well locations. Benzene concentrations not shown but are presented in Table 1.**

influx, the dissolved  $Fe_T$  and  $As_T$  concentrations reflect the geochemical character of the background groundwater, demonstrating that the spatial heterogeneity of As release is closely tied to the presence of introduced carbon. These results indicate that what may be considered a natural process in this region is enhanced by an influx of a high concentration of biodegradable organic matter.

Our conceptual model for As cycling in the Bemidji plume is summarized in Figure 7. The specific zones were developed based on the background sediment chemistry, the chemistry associated with the wells shown in Table 1, and historical published data. In the oxic, upgradient zone of the aquifer (zone 4), there is negligible dissolved  $Fe_T$  and  $As_T$  in groundwater. However, sediment contains As (up to 2.4 mg/kg) which is correlated with sediment Fe (Ziegler et al. 2013). Deeper in the upgradient zone and below the dissolved hydrocarbon plume (zone 5), groundwater is naturally sub-oxic. Under these mildly reducing conditions, dissolved  $Fe_T$  and  $As_T$  are low but detectable. Under the oil body, groundwater is anoxic and contains elevated concentrations of dissolved hydrocarbons,  $Fe_T$ ,

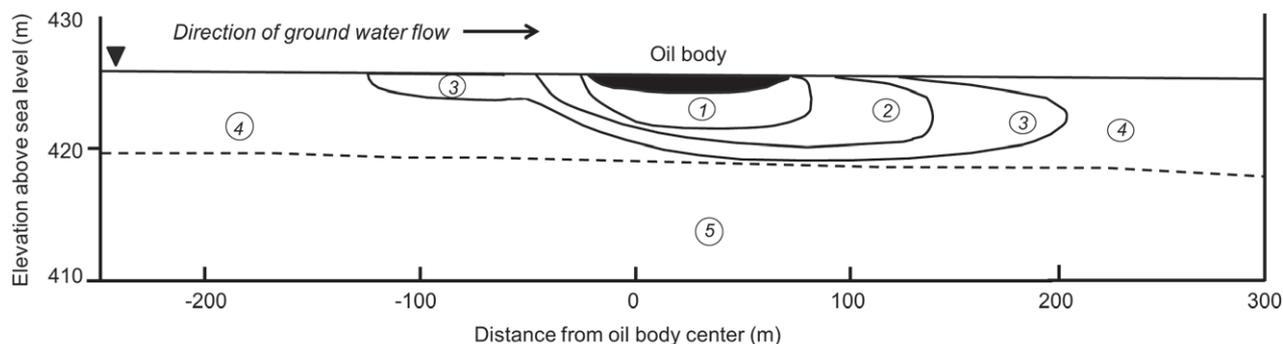
and  $As_T$  (zone 1). This zone has been identified as largely methanogenic based on previous geochemical and microbiological data (Bekins et al. 2001; Cozzarelli et al. 2001). The persistence of high dissolved  $Fe_T$  in this zone is attributed to the large reservoir of sediment Fe(II) (Ng et al. 2014). In the anoxic, Fe-reducing zone of the plume (zone 2), groundwater contains elevated concentrations of dissolved hydrocarbons, dissolved  $Fe_T$ , and  $As_T$  concentrations, but concentrations are all lower than in the methanogenic zone. At the “transition” zone (zone 3), redox conditions shift from Fe-reducing to sub-oxic. In comparison with Fe-reducing conditions, the transition zone, created by the mixing of the Fe-reducing plume with oxygen-containing groundwater at the plume fringes, has higher DO concentrations and lower dissolved  $Fe_T$  and  $As_T$  concentrations.

We hypothesize that when groundwater with elevated dissolved  $Fe_T$  and  $As_T$  from the Fe-reducing zone enters the transition zone where conditions are more oxidized, the dissolved Fe will oxidize to form Fe(III)-hydroxides in sediment and/or adsorb onto existing Fe(III)-hydroxides; the dissolved As will then adsorb to or co-precipitate with the Fe-hydroxides. Ongoing work on the sediment will examine this process in more detail. Downgradient from the plume, where the shallow aquifer returns to oxic (zone 4), DO concentrations increase, dissolved  $Fe_T$  concentrations decrease to less than 1 mg/L, and dissolved  $As_T$  concentrations are less than 1  $\mu$ g/L.

Combined with previous work at Bemidji and in similar glacial sediments, our data suggest the following:

1. Naturally occurring As is associated with Fe-hydroxides present in the glacially derived aquifer sediments at the Bemidji site;
2. Introduction of petroleum hydrocarbons shifts the aquifer redox environment due to the large influx of electron donor. This influx of carbon results in consumption of DO and, in the absence of DO, the reduction of As-bearing Fe-hydroxides;
3. Reduction of the As-bearing Fe-hydroxides releases dissolved  $Fe_T$  and  $As_T$  to groundwater;
4. At the leading edge of the plume, in a transition zone between anoxic and sub-oxic conditions, dissolved  $Fe_T$  and  $As_T$  are removed from groundwater and retained on sediments;
5. Downgradient from the plume, and beneath the plume, where conditions are sub-oxic to oxic, patterns of dissolved  $Fe_T$  and  $As_T$  in groundwater are similar to background.

In groundwater at the Bemidji site, most of the dissolved As (80% to 100%) is present as As(III), consistent with other sites where reductive dissolution is the source of As (Kim et al. 2002; Ahmed et al. 2004; van Geen et al. 2004). Although the mechanisms controlling As speciation at the site have not been fully evaluated, the dominance of As(III) is important from both toxicity and mobility perspectives. Additional work



Zone	Redox	DO $\mu\text{g/L}$	Benzene $\mu\text{g/L}$	Dissolved Fe $\text{mg/L}$	Dissolved As $\mu\text{g/L}$
1	Anoxic; methanogenic	Low (<100)	High (>1000)	High (>25)	High (> 50)
2	Anoxic; Fe-reducing	Low (<100)	Moderate (15-1000)	Moderate (1-25)	Moderate (10-50)
3	Sub-oxic; "transition"	Moderate (100-1000)	Low (5-15)	Low (0.5 – 1.0)	Low (1-10)
4	Oxic	High (>1000)	Negligible (<5)	Negligible (<0.5)	Negligible (<0.5)
5	Sub-oxic	Moderate (100-1000)	Negligible (<5)	Low (0.5 – 1.0)	Low (1-10)

**Figure 7. Conceptual model of arsenic cycling in the Bemidji plume based on general concentration ranges in the table. Note that the model is general and does not capture some of the heterogeneities observed in Figure 3.**

on As speciation in aquifer sediment within and outside of the plume is underway.

In addition to identifying these spatial patterns, it is important to recognize that the system is dynamic, and as the plume continues to evolve, these patterns will shift. Bekins et al. (2005) estimated the groundwater flow velocity in this plume at 21.9 (m/year) and demonstrated using a mathematical model that the different constituents of the plume have very different migration rates. For comparison, Bekins et al. (2005) calculated that the 5  $\mu\text{g/L}$  benzene plume had expanded at only 0.26 m/year. Our temporal data show that the zone of Fe reduction is continuing to migrate, as observed from comparing 2009 to 2012 and 2013 data from wells 510, 9315A, and 9315B (Figure 5). This dynamic evolution of redox zones is consistent with previous observations from Cozzarelli et al. (2001) who showed that the rate of downgradient movement of the high dissolved Fe(II) plume (defined by the 40 mg/L contour) was approximately 3 m/year in the 1990s. Well 510, for example, was beyond the leading edge of the dissolved Fe<sub>T</sub> plume in 1995 and had a dissolved Fe<sub>T</sub> concentration less than 0.5 mg/L (Cozzarelli et al. 2001). This steady and continual migration of the Fe-reducing zone will affect not only the locations of the Fe and As plumes in groundwater but also the location of the transition zone, which currently acts as a sink for As. Over time, when the Fe-reducing zone reaches this zone of elevated As, the As mass could be re-released to groundwater. Thus, in dynamic plumes such as the Bemidji plume, it is important to realize that what at present is a sink for As may eventually become a source of As to groundwater. An improved characterization of the Fe minerals present over time in the aquifer is crucial to understanding and predicting the long-term As mobilization profile downgradient of petroleum spills. Different Fe minerals have significantly different

capacities to capture and retain As through changing redox conditions (Muehe et al. 2013).

### Managing As in Petroleum Plumes

Development of a conceptual model includes characterizing site geology and hydrogeology, measuring the ambient As geochemistry within the plume, evaluating the distribution of petroleum compounds and redox zones, and determining potential receptors and exposure pathways (API 2011). The example presented here from the Bemidji plume follows this approach, but with a more detailed dataset than reported from other sites. Our study of the Bemidji plume shows that the 10  $\mu\text{g/L}$  benzene plume closely matches the 10  $\mu\text{g/L}$  As plume (Figure 3) and indicates that the groundwater at the site exceeds the drinking water standards for both contaminants within the area 120 to 140 m from the center of the oil body. Beyond this zone, both contaminants are below drinking water standards due to natural attenuation processes.

The long-term migration potential of As in plumes of petroleum or other readily biodegradable organic carbon requires understanding the electron donor mass and its complex interactions with aquifer solids. In a mass balance study of Fe in the Bemidji plume, Ng et al. (2014) show that oil constituents other than BTEX (benzene, toluene, ethylbenzene, xylenes) were important in controlling the development of the dissolved Fe plume. They also showed that 99.9% of the Fe(II) in the aquifer is attenuated on sediments. The relationship between this attenuated Fe(II) and As concentrations remains an open question and will be further investigated at Bemidji.

### Conclusions

In the shallow, glacial aquifer at the Bemidji site, introduction of petroleum hydrocarbons promotes

reduction of Fe(III)-hydroxides, resulting in the secondary mobilization of naturally occurring As into groundwater. Results from our field investigation reveal that although As concentrations can reach 230 µg/L in the plume, concentrations are below drinking water standards downgradient from the plume. Our results suggest that introduction of biodegradable organic carbon to aquifers with naturally occurring As should be monitored closely and over the long term, because plumes with active biodegradation are dynamic. At Bemidji, the impact of long-term shifts in electron donor reactivity and continued migration of the Fe-reducing plume will cause changes in the concentration and extent of the dissolved As plume over time. Results of this work suggest that release of trace elements such as As due to reducing conditions may be mitigated owing to adsorption of the trace elements in oxidized sediment, but that process may be reversible, giving additional support for long-term monitoring.

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