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ORIGINAL ARTICLE

Concentration trends and water-level fluctuations at underground storage tank sites

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Abstract Concentration trends of monitor wells utilized in monitored natural attenuation at petroleum underground storage tank sites can be used to predict achievement of regulatory standards if the data approximate a first-order decline trend. However, declining concentration trends often display seasonal and other fluctuations that complicate trend interpretation. Seasonal correlations between concentration and water-level elevation, including in-phase and inverse relationships, constitute one of the most common types of variation. The in-phase fluctuations are most common for monitor wells located in or near the source area of the release. This relationship may be the result of increased contact with the smear zone in the source area during periods of high water table. Conversely, inverse trends of water-level elevation and concentration are most common in downgradient wells beyond the limit of the source area. In a year long study of short-term fluctuations in BTEX and other parameters in a downgradient monitor well, the data suggest that the winter/spring recharge event significantly controls the concentration trends of BTEX as well as inorganic compounds in the well. Recharge and associated water table rise began in late fall and were soon followed by a slug of inorganic ions strongly influenced by road salt application. This slug of recharge diluted the concentrations of petroleum compounds and alkalinity (bicarbonate). Electron acceptors including oxygen, nitrate, and sulfate, which is a component of road salt, are also contributed to the water table during recharge. Oxygen and nitrate were not detected in the monitor well samples and were most likely consumed quickly in biodegradation reactions at the top of the contaminant plume. Sulfate peaked during winter/spring recharge and then slowly declined during the summer and fall, along with redox potential. Alkalinity (bicarbonate) increased during this period, which may represent the coupled oxidation of organic carbon to CO_2 with sulfate as the electron acceptor. BTEX concentrations peaked in the fall probably due to the lack of diluting recharge. The slow changes in concentration over the summer and fall months, interpreted to be caused by biodegradation, contrast with the rapid changes associated with dilution during the recharge event.

Keywords BTEX · UST site · Natural attenuation · Water table fluctuations · Biodegradation

Introduction

Under subtitle I of the Solid Waste Disposal Act (SWDA), owners of underground storage tanks (USTs) in the United States were required to upgrade, close, or replace all tanks. By September 2007, 474,127 confirmed releases had been reported from USTs, most of which involved petroleum fuels (USEPA 2008). Remediation of these sites can include a wide range of activities addressing both soil and groundwater contamination. In the 1990s, risk-based corrective action (RBCA), or risk-based decision making, was

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adopted as a process for defining site cleanup, or closure, in terms of the exposure pathways and risks posed by the compounds released to the subsurface (USEPA 1997a).

Under RBCA, the concentration levels, or standards, that must be achieved to close the site depend upon site specific risk criteria. The most stringent criteria are the residential risk-based screening levels.

The vast majority of UST releases include a common set of regulated constituents present in petroleum fuels. These gasoline indicator parameters (GIPs) include the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX), two trimethyl benzene isomers (1,2,4 TMB and 1,3,5 TMB), 1,2-dichloroethane and 1,2-dibromomethane, several polyaromatic hydrocarbons, and the fuel additive MTBE. The persistence and mobility of these compounds in the subsurface is highly variable. Attenuation processes that reduce concentrations include volatilization, dilution and dispersion, sorption to aquifer solids, and biodegradation.

When a release of petroleum fuel to the subsurface occurs, the liquid phase is known as a light, non-aqueous phase liquid (LNAPL) because its specific gravity is <1.0. As it moves downward under the influence of gravity, it may reach the water table as a free, separate phase (free product), but it also partitions into the solid, liquid, and vapor phases of the unsaturated zone (Kehew 2001). Partitioning varies by compound based upon properties such as vapor pressure, Henry's constant, specific gravity, solubility, and the octanol–water partitioning coefficient (log K_{ow}) (Davis 1997). Small droplets of product retained in the pores of unsaturated soils are referred to as residual phase. Partitioning into the vapor and aqueous phases continues for long periods of time from these residual phase accumulations. Biodegradation begins to reduce concentrations, although the rates vary depending on the specific compound and the geochemical environment. In the presence of oxygen, aerobic biodegradation generally results in the fastest rates (Barker et al. 1987; Davis et al. 1994). If the oxygen is consumed, anaerobic conditions become dominant and biodegradation effectiveness and rates depend upon the terminal electron accepting process (TEAP). Biodegradation of BTEX and related compounds has been shown to occur under aerobic as well anaerobic conditions utilizing various electron accepting processes, including denitrification, iron reduction, sulfate reduction, and CO_2 reduction (Barker et al. 1987; Lovley and Phillips 1988; Major et al. 1988; Lovley et al. 1989; Davis et al. 1994; Flyvberg et al. 1993; Lovley and Lonergran 1990; Haag et al. 1991; Baedecker et al. 1993; Borden et al. 1995, 1997a, b; Chapelle et al. 2003). The specific compounds benzene, toluene, ethylbenzene, and the three xylene isomers o-, m-, and p-xylene, vary significantly in their mechanisms and rates of anaerobic biodegradation (Chapelle et al. 2003; Johnson et al. 2003; Chakraborty and Coates 2004; Schreiber et al. 2004; Scow and Hicks 2005; Hu et al. 2007; Dou et al. 2008). Although benzene was traditionally considered to be particularly recalcitrant under anaerobic conditions, recent work has shown that biodegradation does occur (Johnson et al. 2003). However, the availability of the appropriate organisms and electron acceptors is much more site-specific than the other compounds.

If sufficient product is released, free product will accumulate at the water table. Compounds will slowly dissolve into the aqueous phase depending upon their solubility and other factors and move in dissolved form in the groundwater flow system. Biodegradation continues to reduce concentrations along the flow path, but anaerobic processes become dominant because of the low solubility of oxygen in water. Until recently, anaerobic biodegradation was thought to proceed in a fixed sequence of reactions controlled by the presence of electron acceptors such as nitrate, ferric iron (which occurs on the aquifer solids), sulfate, and carbon dioxide. Schreiber et al. (2004) have shown, however, that simultaneous utilization of electron acceptors yielding overlapping zones of electron accepting processes is likely in the subsurface. Microscale heterogeneity, mixing within large screened intervals of monitor wells, or other factors could explain these complexities. As the water table fluctuates vertically within the source area in response to seasonal and longer term variations in recharge, a zone of high residual phase concentration called the smear zone develops. This zone alternates between unsaturated and saturated conditions as the water table rises and falls, and if the water table lies within the smear zone, concentrations in water samples collected from monitor wells screened across the water table may include a free-phase component and therefore may overestimate dissolved concentrations in the aquifer (Zemo 2006).

Biodegradation in a petroleum plume, which is controlled by redox conditions, is subject to strong spatial and temporal gradients. McGuire et al. (2000) documented a decline in redox potential to the level of methanogenesis in fall samples from a petroleum plume when recharge was not transporting electron acceptors downward to the top of the plume, to raise the redox potential into the range of other biodegradation processes (i.e. iron reduction). Scholl et al. (2006) found a similar relationship in a landfill leachate plume. Sulfate concentrations peaked during recharge and slowly declined afterward due to sulfate reduction in the plume. Sulfate was transported as much as 1.75 m below the water table, whereas nitrate was restricted to shallower depths, probably because of more rapid reduction.

Remediation at UST sites includes active measures, such as vadose zone excavation and removal, dual phase extraction, plume capture with purge wells, soil vapor extraction, air sparging, bioremediation and in situ chemical oxidation (ISCO). When the source area is devoid of free product, there are no nearby downgradient receptors, and the dissolved plume in groundwater is stable or shrinking, however, many owners choose monitored natural attenuation (MNA) as a remedial option. Under this method, plumes are sampled at periodic intervals for GIPs and allowed to attenuate gradually. MNA can be utilized for petroleum fuel releases because of the effectiveness of biodegradation for some or all of these compounds (USEPA 1997b, 1999).

Purpose and objectives

Time series data of aqueous phase concentrations constitute the most significant basis for evaluating the behavior of a plume of contamination in routine UST investigations. Concentration values represent the aggregate effects of many variables: continued supply or depletion of compounds from the source area, partitioning of the compound into aqueous, gaseous and solid phases, biodegradation, advection, dispersion, sorption, current and past remedial measures, and water-level changes. As a result of the large number of variables, monitor well concentrations frequently fluctuate widely from sample to sample. Time series trends in concentration are extremely important, as they are used to document plume expansion, stability, or shrinkage. If MNA is being used as a remedial measure, documentation of concentration declines to the regulatory standard is critical. Fluctuations in concentration create a level of uncertainty in these trends that can delay or prevent closure of the site.

The purpose of this paper is to evaluate the effects of water-table fluctuations on concentrations and concentration trends. Here, we attempt to characterize concentration trends and explain some of the variability in these trends in terms of the hydrogeological processes associated with water-level fluctuations.

Hydrogeological setting of sites

The sites used for this analysis are typical of commercial gas station facilities at which past releases have occurred. Various remedial techniques have been utilized at these sites, including soil excavation, plume capture and treatment, soil vapor extraction, and air sparging. Currently, MNA is being used as the dominant remedial measure.

Hydrogeologically, the sites are generally similar, in that they are located in southern Michigan, a region underlain by a variable thickness of glacial drift. Contaminant plumes develop in shallow, unconfined aquifers composed of medium-to-coarse textured soils. Intergranular flow is assumed, although flow-through fractures in finer materials, such as till or glaciolacustrine sediment may occur in portions of some sites. The water table lies between 10 and 50 feet (3.1–15.2 m) below the surface at all sites. This area has a humid, temperate climate with about 40 in. (102 cm) of precipitation per year.

Monitoring at the sites selected for this analysis has generally taken place for at least 5 years and often for 10 years or more. During that time, regulatory requirements for compounds that must be measured have changed, so that some compounds may have a shorter historical record. At some sites, a suite of biodegradation indicators was measured at some point in the project. These parameters include dissolved oxygen, nitrate, sulfate, dissolved iron, and total alkalinity.

Concentration trends

The sites and monitor wells mentioned in this paper were selected from several dozen sites with a total of about 200 monitor wells. A wide range in concentration trends was observed. Most wells that were heavily impacted at the time of installation have shown significant declines in concentration as a result of active remediation and natural attenuation. When plotted against time, some wells follow exponential declines in concentration (Fig. 1). If an exponential trendline can be closely fitted to the data, natural attenuation can be approximated as a first-order process. Although biodegradation is considered to play a major part in this process, it must be kept in mind that the decay rate represented by the curve includes all possible attenuation mechanisms occurring in the aquifer. The equation that describes first-order kinetics is:

$$C = C_0 e^{-kt}, \qquad (1)$$

in which C is the concentration of the degrading compound, C_0 is the initial concentration, k (time^{-1}) is the rate constant, and t is time since concentration was at

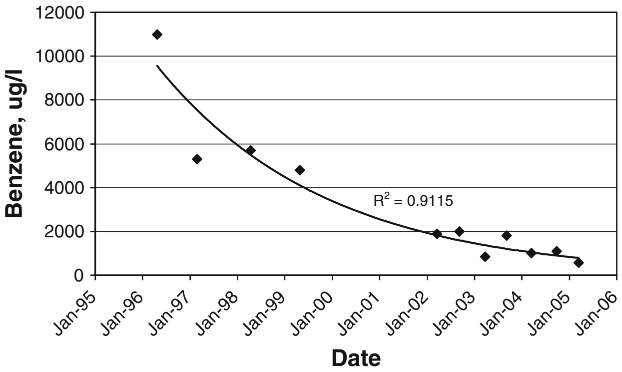


Fig. 1 Exponential decline in benzene concentration at a monitor well

the initial value. The value of C_0 can be chosen as the concentration of the first sample collected. This equation can be solved for the degradation rate by taking the natural log of both sides and solving, for k, as shown below.

$$k = -\ln(C/C_0)/t. \quad (2)$$

An estimate of the time it will take until the compound declines to the standard can be made based on the assumption of first-order kinetics (Eq. 1). The measured concentration values are plotted as ln (C/C_0) versus time (C_0 = first sample concentration) and a trendline is fitted to the data using linear regression. This line can then be extrapolated to the level of the standard for the compound of interest expressed in the same way (C/C_0) and the approximate date at which the concentration will reach this level can be predicted (Fig. 2). In Fig. 2, the extrapolation of the trendline for benzene to the regulatory standard of 5 μg/l for the data set shown in Fig. 1 predicts that benzene will reach this concentration in approximately 2023.

The assumption of first-order kinetics can be evaluated by the coefficient of determination (R^2) of the trendline. Values greater than 0.8 are rare, but reasonable predictions can still be made with values as low as 0.3. Wells that exhibit strong seasonal fluctuations in concentration will yield a lower R^2 and the reasons for these fluctuations are explored below.

The reliability of this method was tested by using data from wells that have already declined to values below their standard. Figure 3 shows benzene concentration data from a well that were plotted in the manner described above. Using data collected between 1990 and 1995, the extrapolated trendline reached the level of the standard around the beginning of 1996. The actual concentrations exceeded the standard until 1998, with only one exceedence after that. Therefore, the predicted date of compliance only slightly underestimated the actual time at which the standard was achieved. Observations at numerous sites confirm that as the concentration begins to approach the standard, seasonal fluctuations result in a period of up to several years when the concentration will alternate values above and below the standard. Once this period of fluctuation around the standard is over, the concentration will generally remain below the standard. For example, Fig. 4 in Electronic supplementary material shows a monitor well data set in which the trendline crossed the regulatory standard in early 2004. In the next 2 years, values both above and below the standard were measured.

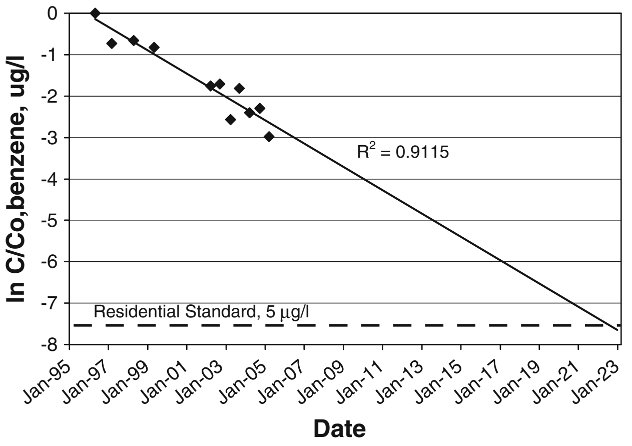


Fig. 2 Concentration of benzene in monitor well shown in Fig. 1 plotted as ln *C*/*C*o and extrapolated to level of the residential standard

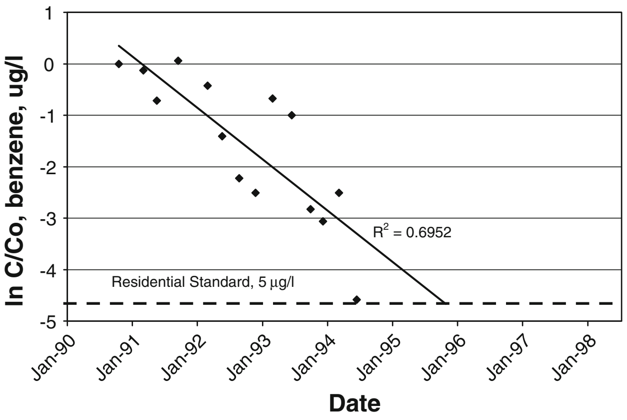


Fig. 3 Concentration trend for benzene in plotted as ln *C*/*C*o and extrapolated to the residential standard

Obviously, predictions made by this method should be considered as general guidelines only. However, when balancing the costs of additional source remediation to accelerate MNA versus continued MNA without additional remediation, trends that suggest that standards will not be reached for several decades or more may play an important role in the decision.

Water-table fluctuations and long-term concentration trends

Water tables fluctuate both seasonally and in response to longer term climatic trends. Seasonal fluctuations typically follow a regular pattern of water table rises in the winter and spring followed by drops in the summer and fall. Two general types of concentration trends produced by biannual or quarterly sampling have been observed to accompany these water-table fluctuations. In one type, rises and falls in concentration are in phase with longer term fluctuations in the water table (Fig. 5). This relationship is more likely to occur for monitor wells installed in the source area of the release. In the second type of pattern, water-table fluctuations are out of phase with concentration changes and, in fact, are inversely correlated with concentrations of GIPs.

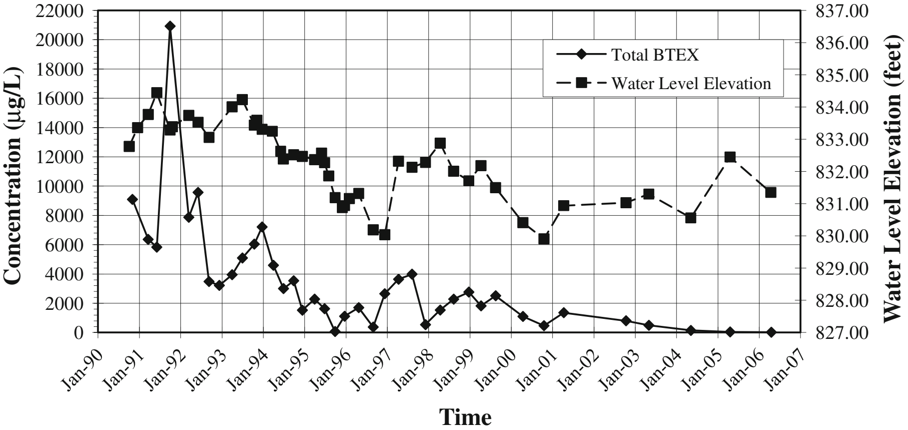


Fig. 5 Plot of total BTEX concentrations and water-level elevation for a well in a source area. For most of the record fluctuations of water table and total BTEX concentration are in phase. This pattern breaks down from 2004 until the end of the period when total BTEX concentrations decline

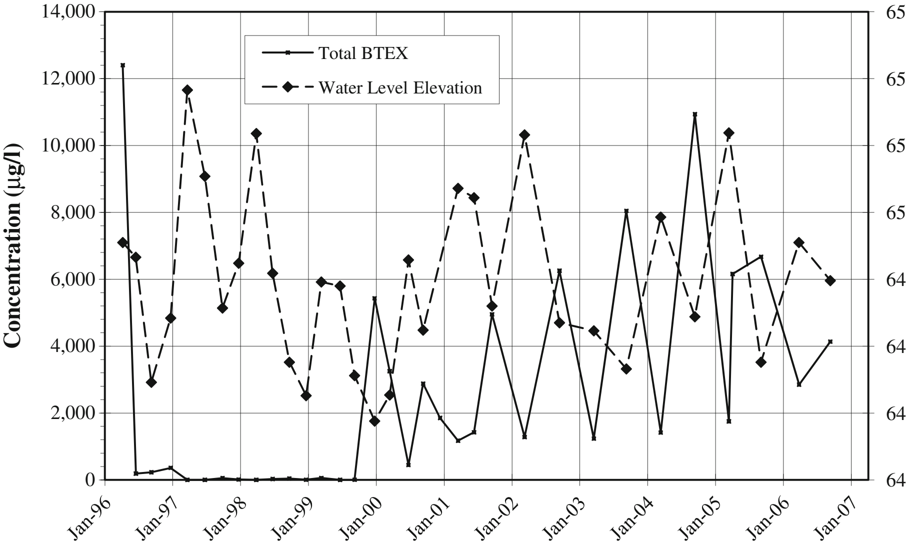


Fig. 6 Plot of Total BTEX concentrations and water-level elevation versus time for an 11-year period in a downgradient monitor well (MW-9sR). Concentrations were controlled by a purge well until late 1999. Fluctuations form a mirror-image pattern after that

For example, when water tables rise in the spring, concentrations fall, and rise in the summer and fall when the water table is dropping (Fig. 6). This pattern of seasonal fluctuations occurs most commonly in monitor wells that are located within the contaminant plume downgradient of the source area.

Type I trends: in-phase fluctuations

Monitor wells that display fluctuations of water table and concentration that are in phase with each other typically occur in or near the source area. Total BTEX concentrations in Fig. 5 illustrate this relationship. The positive correlation between concentration and water level is better when considering longer trends in the water table, for example, rises or falls that occur over several years. For the monitor well displayed in Fig. 5, total BTEX concentrations and water levels are generally high between 1991 and mid-1993, decline between mid-1993 and late 1996, rise again until mid 1999 and then decline again. Seasonal fluctuations in concentration are superimposed on these longer term trends and a general decline in total BTEX is occurring during the overall period of monitoring. The in-phase relationship breaks down in the last few years of record as BTEX compounds are nearly gone from the aquifer at this point. A possible explanation for this type of behavior is that residual phase product remains in the vadose zone within the vertical interval known as the smear zone. As demonstrated by Zemo (2006), when the monitor well screen intersects the smear zone, a component of the concentration measured in groundwater samples originates from free or residual phase product in the smear zone. For monitor wells that exhibit this type of in-phase relationship, a section of the well screen may intersect the smear zone when the water table is high, but may not intersect this zone when the water table declines as a result of declines in precipitation and recharge. Alternatively, when the water table is high, it may intersect a larger vertical proportion of the smear zone than when the water table is lower. This relationship is illustrated in Supplementary Fig. 7.

Type II trends: inverse seasonal fluctuations

Concentrations of total BTEX and water-table elevations from the monitor well plotted in Fig. 6 will be used as an example of this type of pattern. This monitor well (MW-9sR) is discussed in more detail later in the paper. Between 1995 and 2000, the operation of an upgradient purge well kept BTEX concentrations very low in this well. After purging was terminated in 2000, however, BTEX concentrations rebounded to levels ranging between 1,000 and 11,000 µg/l. The inverse relationship between concentration and water-table elevations is quite apparent for most sampling events, although it is more pronounced in some events than in others. For several years after the termination of purging, the overall trend of total BTEX concentrations was upward, as shown in Fig. 8. The R^2 value of this plot is very low because of large seasonal fluctuations. Concentration trends of individual parameters, however, vary. Benzene concentrations during this period show an overall decline with a low R^2 (Fig. 9a). Because of the seasonal fluctuations, however, a different result can be obtained by plotting only fall or spring data. In Fig. 9b, the consistently high fall concentrations show a weak, increasing trend. The spring concentrations, however, show a relatively strong decreasing trend. These differences illustrate the necessity of quarterly, or at least semiannual sampling for accurate recognition of trends in monitor wells of this type. The exclusion of either spring or fall data could lead to a very different interpretation of the concentration trends at this well.

An important question is, why do the concentration and water-table fluctuations exhibit this particular inverse relationship? A possible explanation to this question lies in the position of the monitor well with respect to the source area. Monitor well MW-9sR is located approximately 150 feet (46 m) downgradient of the source area. As mentioned earlier, concentrations rise in monitor wells located in the source area, perhaps as the water table rises to the level of a smear zone in the unsaturated zone. Downgradient of the source area, however, a smear zone does not exist. The rise in water table occurs in response to recharge moving downward through the clean vadose zone to the water table. The most likely result of the recharging water is to dilute the upper part of the hydrocarbon plume that is sampled by the monitor well. In addition, the recharging water may contain electron acceptors, such as oxygen, nitrate, and sulfate (McGuire et al. 2000; Scholl et al. 2006). However, because monitor wells in chlorinated solvent plumes, in which biodegradation is considered to be much slower than in BTEX plumes, display the same mirror-image pattern, the decline in hydrocarbons primarily occurs by dilution. Addition of electron acceptors and enhanced biodegradation may also play a role, but over the course of months rather than days or weeks. In the summer and fall, the lack of recharge creates the opposite conditions, in which the plume moving away from the source area experiences minimal dilution and hydrocarbon concentrations peak. The mechanism proposed for this type of concentration trend is illustrated in Supplementary Fig. 10.

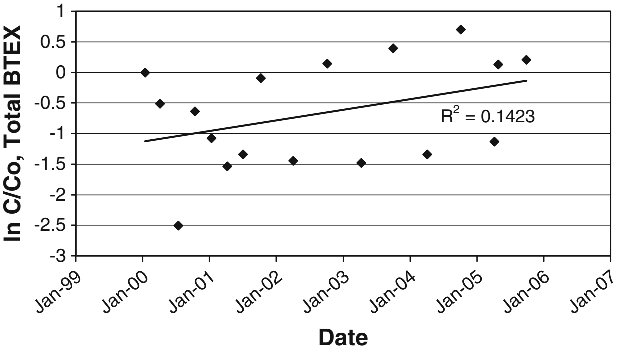


Fig. 8 Concentrations of total BTEX in monitor well illustrated in Fig. 6 following termination of pumping from upgradient purge well. High seasonal fluctuations produce low R^2

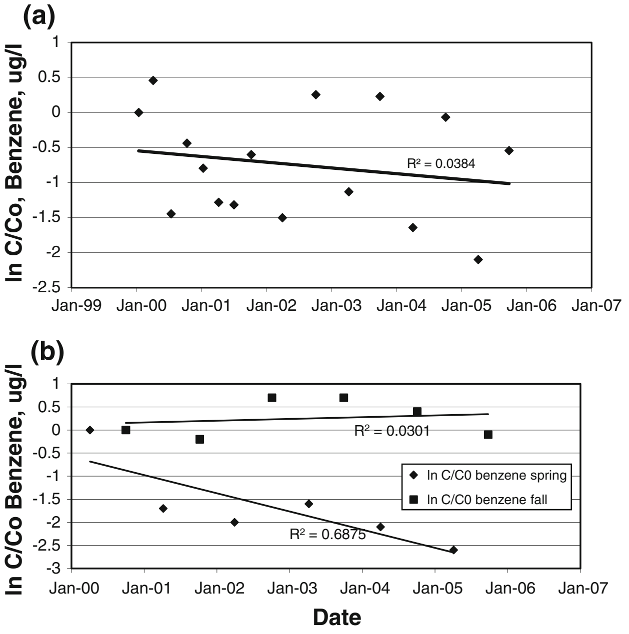


Fig. 9 **a** Benzene concentrations in monitor well shown in Fig. 8 showing a weak decline. **b** Benzene concentrations for same well plotted separately for spring and fall values. Fall concentrations are uniformly higher and show a weak, increasing trend. Spring concentrations are lower and exhibit a fairly significant declining trend

Short-term concentration trends

In order to test the hypothesis that dilution of the upper part of the plume by seasonal recharge causes the inverse relationship between concentrations and water-table elevation, a downgradient monitor well (MW-9sR) was sampled at weekly to monthly intervals over a period of a year.

Site description and methods

The site (Fig. 11 in ESM) is underlain by an unconfined aquifer composed mainly of sand. Contaminated soil was detected in an excavation during the removal of seven USTs at the study site in 1990. Soil contamination was observed to extend to the water table, which occurred at approximately 12 feet (3.7 m) below land surface As part of initial abatement activities, approximately 450 yard^3 (342 m^3) of soil were excavated and removed. The release appeared to be the result of overflow from the fill ports of the USTs. A groundwater investigation included the installation of 24 monitor wells and 2 test/purge wells at the site. Purging from the downgradient purge well was utilized as part of an interim recovery and treatment system that was in operation between 1995 and 2000. The plume from the UST site extended approximately 450 feet (137 m) downgradient from the tank excavation. The downgradient part of the plume, however, may have been co-mingled with a plume from a separate downgradient source. Monitor well MW-9sR was selected for sampling in this study. Concentration trends for total BTEX in MW-9sR are shown in Fig. 6. This well was installed as a replacement for a monitor well at that same site in 1991. Monitor well MW-9sR is located about 150 feet (46 m) downgradient from the tank excavation near the centerline of the plume in a vacant lot across a main road from the UST site. The well is 18 feet (5.5 m) deep with a 2-in. (5.08 cm), 7-slot stainless steel screen between 11 and 18 feet (3.4–5.5 m) below ground level. The water table is approximately 12–13 feet (3.7–4.0 m) below land surface. A 7-foot (2.1 m) screen was used so that water-table fluctuations occur within the screened zone. Although this type of monitor well precludes detailed analysis of biodegradation processes, it does allow more general interpretation of hydrogeochemical conditions at the tops of contaminant plumes.

The BTEX concentration trends for monitor well MW-9sR are shown in Fig. 6. These trends display a mirror-image pattern with respect to water-level elevations in the well, beginning after 2000, when the purge well was shut down. At the time of shutdown, approximately 51 million gallons (193,000 m^3) of water had been purged and treated.

The experimental design for the short-term sampling phase of this project consisted of sampling at an initial frequency of approximately weekly during the spring of 2007, which was later scaled back to a monthly interval until the late winter of 2008. The parameters analyzed included the required GIPs: benzene, toluene, ethylbenzene, o-, m-, and p-xylene (reported as total xylenes), MTBE, naphthalene, 2-methylnaphthalene, 1-2-4, TMB, 1,3,5-TMB, 1,2-dibromomethane, and 1,2-dichloromethane (Table 1). In addition, a suite of additional chemical parameters was obtained, including major cations and anions as well as parameters that reflect the inorganic chemistry of the plume, redox conditions, and microbial metabolism of organic compounds. These parameters included calcium, magnesium, sodium, potassium, iron, manganese, ammonia, chloride, nitrate, alkalinity, sulfate, and dissolved organic carbon (Table 2). Dissolved sulfide was measured twice during the study.

Table 1 Concentrations of petroleum compounds (μg/l), monitor well 9sR (Fig. 11 in ESM)

Date	Water-level elevation (feet)	Benzene	Toluene	Ethylbenzene	Total xylenes	Total BTEX	1,2,4-TMB	1,3,5-TMB	Naphthalene
3/15/2007	651.56	31	5.7	1,300	5,900	7,236.7	1,500	NA	NA
3/25/2007	652	62	0	1,800	9,160	11,022	2,300	NA	NA
4/1/2007	652.01	29	2.5	160	408	599.5	110	NA	NA
4/10/2007	651.85	50	5.7	910	3,620	4,585.7	1,400	Na	NA
4/16/2007	651.98	31	3.4	980	3,686	4,700.4	1,400	NA	NA
4/22/2007	651.99	26	3.6	260	1,051	1,340.6	350	NA	NA
5/30/2007	651.45	87	4.3	660	2,577	3,328.3	940	NA	NA
7/1/2007	650.42	91	7.8	1,400	5,062	6,560.8	1,900	NA	NA
8/9/2007	649.77	37	7.1	440	1,559	2,043.1	580	NA	NA
9/16/2007	650.35	34	9.2	690	2,710	3,443.2	1,100	270	280
10/28/2007	649.55	62	18	1,400	4,820	6,300	2,000	480	590
12/2/2007	649.15	37	13	1,300	5,290	6,640	2,200	500	590
1/27/2008	650.99	13	7.6	1,000	4,084	5,104.6	1,500	350	370
2/24/2008	651.8	15	13	1,000	4,079	5,107	1,800	390	450

NA not analyzed

Table 2 Water quality parameters (mg/l unless otherwise indicated), monitor well 9sR

Date	Water-level elevation (feet)	DOC	Calcium	Magnesium	Sodium	Potassium	Iron	Ammonia	Chloride	Bicarbonate	Sulfate	Nitrate	Sulfide	ORP (mv)
3/15/2007	651.56	7.2	110	18	130	7.8	8.4	0.55	180	439.2	5.8	1.2	NA	−48.9
3/25/2007	652	5.8	110	18	160	7.7	9	0.76	250	488	4.8	1.1	NA	−94.1
4/1/2007	652.01	8.2	130	23	160	11	9.6	0.88	380	475.8	6.6	1.0	NA	−96.4
4/10/2007	651.85	3.8	230	43	270	13	17	1	950	427	7.2	0.29	NA	−100
4/16/2007	651.98	4	350	68	330	15	23	0.99	1,400	353.8	12	<0.50	NA	−88.3
4/22/2007	651.99	3.8	260	54	420	15	11	0.76	1,400	402.6	20	0.62	NA	−89.4
5/30/2007	651.45	8.3	160	33	290	10	5.7	0.32	580	549	16	1.1	NA	−78.1
7/1/2007	650.42	8.5	150	28	250	12	7.7	0.51	500	597.8	18	<2.0	NA	−104.3
8/9/2007	649.77	9.5	130	25	280	9	6.6	0.34	440	549	9.5	0.24	NA	−106.4
9/16/2007	650.35	9.6	110	19	220	9.1	7.3	0.6	340	622.2	7.2	0.39	NA	−159.6
10/28/2007	649.55	10	110	16	230	9.7	8.7	0.84	310	610	4.1	0.13	NA	−134.9
12/2/2007	649.15	9	120	19	210	10	12	1	290	524.6	3.8	<0.1	0.03	−52.3
1/27/2008	650.99	8.8	39	10	140	7.6	10	0.79	230	427	5	0.49	<1.0	−140
2/24/2008	651.8	4.6	140	25	200	9.6	9.4	0.91	530	402.6	6.9	0.23	NA	−134.7

NA not analyzed

Sampling was performed by low-flow techniques using a peristaltic pump, pumping at a rate which created negligible drawdown in the well (~300 ml/min). Dissolved oxygen, specific conductance, pH, temperature, and ORP were measured during sampling in a flow-through cell with a YSI 556 MPS Multi Probe System calibrated according to instrument specifications. Turbidity was measured with a Hach Model 2100P portable turbidimeter. Samples were not collected until stabilization of the field parameters, which usually took an hour or more. Samples for metals analysis were field filtered using 0.45 μ filters. GIP samples were collected in 40-ml glass vials capped with Teflon®-lined septa. After collection, samples were kept refrigerated until transported to a commercial laboratory for analysis, usually within 24 h. Samples for BTEX were analyzed using US EPA Method 8260.

GIP concentrations

Short-term sampling enabled a much more accurate analysis of water level and concentration changes than biannual samples. One of the more interesting observations was the degree of short-term variability in concentrations. For example, total BTEX decreased from more than 11,000 µg/l on 25 March 2007 to 600 µg/l on 1 April 2007, more than a factor of 20. This degree of variation in a 1-week period introduces some uncertainty into the validity of trends based on annual, semi-annual, or even quarterly sampling data.

The inverse relationship of concentration and water-level elevation determined from the semi-annual sampling frequency generally held up with the weekly to monthly frequency. This relationship is manifested in a major depression of concentrations of organic compounds (Figs. 12, 13) at the peak of the water table rise during the winter/spring recharge event followed by reversal in which organic concentrations rise as the water-level elevation falls. The only exception to this trend occurred between 1 July 2007 and 16 September 2007, in which the concentrations fluctuated largely in phase with each other. The reason for this deviation from the expected trend is not known, but if the 9 August 2007 sample was experiencing an anomalously low concentration in a very short-term fluctuation as described above, it could explain this result. Overall, however, total BTEX and water-level elevation fluctuated inversely with each other. Benzene displays a similar inverse relationship, with the exception of the same sampling period as total BTEX. Dissolved organic carbon (Fig. 13) displays a more consistent inverse relationship.

Several processes could possibly explain the inverse relationship between BTEX compounds and water levels. One possible explanation is that the lower concentrations at

Fig. 12 Concentrations of total BTEX and water-level elevation

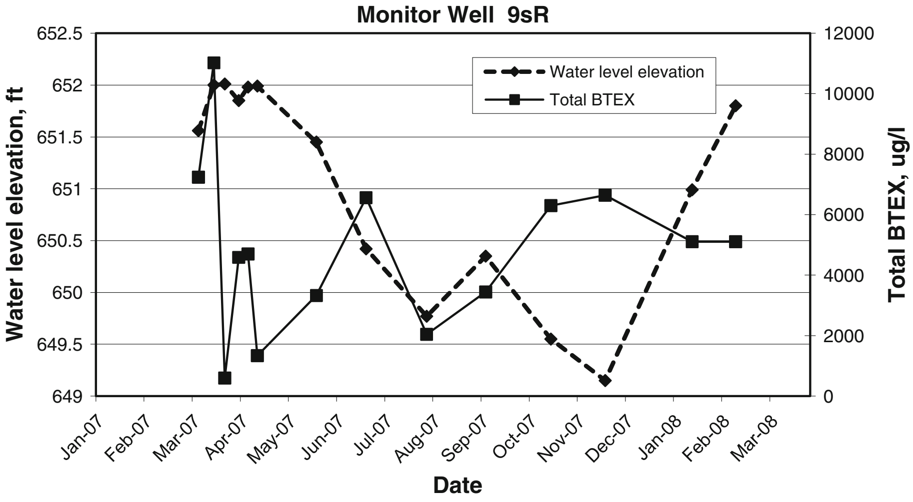
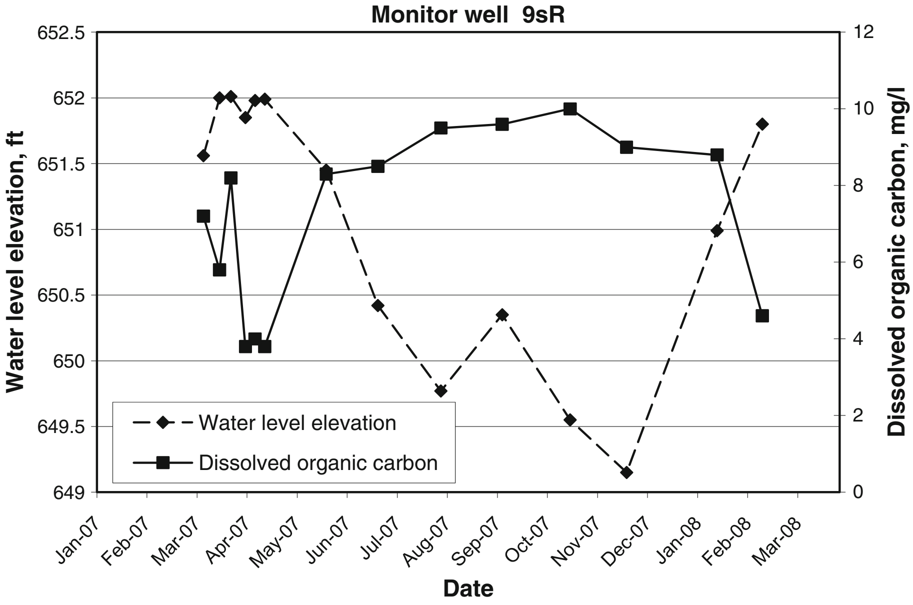


Fig. 13 Concentrations of dissolved organic carbon and water-level elevation



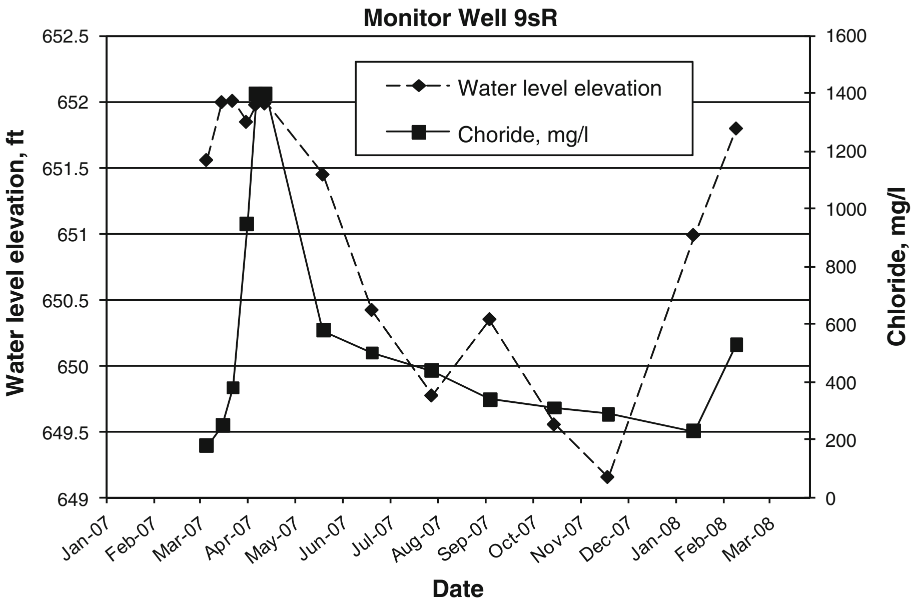
times of high water-table elevation result from enhanced biodegradation caused by recharge-containing electron acceptors arriving through the vadose zone. Lower concentrations from the source area during recharge events are ruled out because concentrations there are commonly higher, perhaps due to the higher water table intersecting more of the smear zone. If the water table in the source area contacts a larger area of the smear zone, more residual phase contaminants could dissolve into the groundwater flow system. A second hypothesis is that recharge through the vadose zone mainly acts to dilute contaminants moving at the top of the saturated zone (Fig. 10 in ESM). The volume of recharge might also impart a downward component to the hydraulic gradient and the samples obtained from the monitor wells might therefore represent a cleaner interval at the top of the aquifer.

The winter/spring recharge event

Precipitation in southern Michigan is distributed throughout the year with substantial amounts occurring as snowfall in the winter and as rainfall in the other seasons. The major factor controlling recharge is evapotranspiration (ET), which restricts recharge during the time when plants are active, from the late spring to late fall. The main recharge event in this area, referred to as the winter/spring recharge event, begins when ET terminates in the fall and ends when ET increases in the spring.

The winter/spring recharge event produces a rapid rise in water-table elevation in monitor well MW-9sR, as well as dramatic changes in concentrations. The peak of the winter/spring recharge event is captured by the 2007 data. At the time of the first sample, 15 March 2007, the water

Fig. 14 Concentration of chloride and water-level elevation in monitor well 9sR



level had already reached an elevation about 0.5 feet (0.15 m) less than its maximum, which was achieved on 1 April (652.01 feet; 198.73 m). Lagging shortly behind the rise in the water table, a large slug of inorganic solutes was flushed from the vadose zone to the water table. The best illustration of the timing of the water table rise and ion flush is the chloride concentration trend, shown in Fig. 14. The water table reached its peak on 25 March, at a time when the chloride concentration was still quite low (250 mg/l), but was just starting to increase. Chloride then began a rapid and extraordinary rise to 1,400 mg/l on 16 April. This slug of chloride is most likely the result of winter road salt applications to the highway just upgradient of the monitor well (Fig. 11 in ESM). The chloride concentration dropped almost as fast as it had risen and by 30 May, it had reached 580 mg/l, after which it slowly declined throughout the remainder of the year. The water table reached its minimum elevation on or near the 2 December 2007 sampling event and then began its seasonal rise. By 27 January 2008, it had risen nearly 2 feet. The chloride concentration on 27 January 2008, however, remained low. It is likely that this early rise in water-table elevation is the result of recharge from fall rains occurring after the time at which plants become dormant and evapotranspiration is at a minimum. Since road salt applications are minimal during this period (late October through December), the chloride concentrations are low. The 24 February 2008 sampling event detected another 1 foot rise in the water table, coupled with an increase in the chloride concentration from 230 to 530 mg/l. The interval between the 27 January 2008 and 24 February 2008 samples reflects the arrival of the first recharge impacted by road salt, which peaks in concentrations measured in March and April.

Concentration trends of other major ions are shown in Fig. 15. Cations, including calcium, magnesium, sodium, and potassium (not shown) peak at the same time as chloride. A significant proportion of these ions can also be attributed to highway deicing because sodium chloride is mixed with calcium chloride brine during application. Of the other major anions, bicarbonate and sulfate also show a characteristic response to the winter/spring recharge event. Sulfate increased along with chloride and the major cations, but bicarbonate concentration showed a temporary decrease at the same time as the spring peak of the other anions. This suggests that bicarbonate is diluted by the recharge event. As the road salt ions decreased after spring recharge, bicarbonate followed an increasing pattern, showing that its concentration is controlled by a different process, as discussed below. The increase in sulfate is also attributed to the road salt, which contains 1.26–2.62% calcium sulfate (personal communication, Sifto Canada Corp.) The ions plotted in Fig. 15 also began to rise in the 24 February 2008 sample, corresponding to the beginning of the chloride rise.

Discussion

As the plume moves downgradient, concentrations of petroleum compounds are reduced by natural attenuation. Aside from physical processes such as sorption and dispersion, the most important process responsible for natural attenuation is biodegradation, because biodegradation actually breaks down the contaminant compounds to less toxic forms. The processes involved in biodegradation can be assessed by an analysis of the geochemical environment of the plume, as reflected by the concentrations of electron

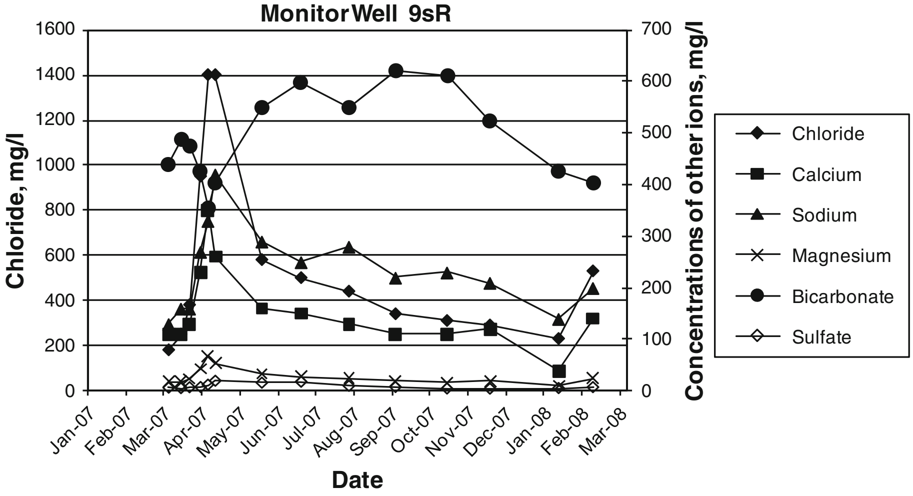


Fig. 15 Concentrations of major ions in monitor well 9sR showing effects of spring recharge event

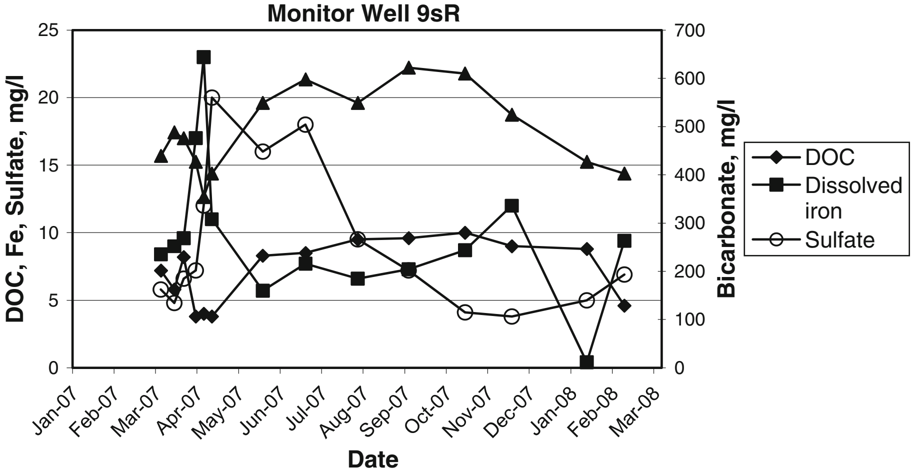


Fig. 16 Concentrations of selected constituents at monitor well 9sR. DOC and bicarbonate both decline during the spring recharge event and then increase during the summer and fall. Iron peaks sharply during recharge and then declines for the remainder of the period. Sulfate peaks during spring recharge, then declines gradually during summer and fall

donors, electron acceptors, and metabolic byproducts. Organic compounds, including GIPs and other compounds that are not analyzed derived from the petroleum release, serve as the dominant electron donors. In the aquifer, these compounds are metabolized by heterotrophic bacteria that derive carbon and energy from transferring electrons from electron donors to electron acceptors (respiration). In this process, organic carbon is oxidized to carbon dioxide, which reacts with water to form carbonic acid. Carbonic acid dissociates to form bicarbonate ion at mid-range pH levels, and hydrogen ions.

Oxygen, the preferred electron acceptor, has not been detected in Monitor Well 9sR at levels above realistic instrumental detection limits (approximately 1 mg/l). Most DO is likely to be consumed through aerobic respiration as it reaches the top of the plume. In the absence of oxygen, biodegradation proceeds anaerobically, utilizing nitrate, ferric iron, sulfate, and carbon dioxide as electron acceptors. Nitrate does not reach significant levels in any sample, suggesting that it is not present in recharge water, or is rapidly consumed at the water table. The presence of detectable ammonia nitrogen in the plume indicates that redox levels are below the range of stability for nitrate. After any available nitrate has been removed as an electron acceptor, ferric iron becomes the next available electron acceptor. Ferric iron is derived from aquifer solids where it is present either in primary minerals or as oxide grain coatings that develop during weathering (Lovley 1997). As it accepts electrons during biodegradation, ferric iron is reduced to soluble ferrous iron, which is assumed to make up a very high percentage of measured dissolved iron. Figure 16 shows the concentration trends of several parameters involved in biodegradation reactions. Dissolved iron spiked to 23 mg/l during the winter/spring recharge event and then dropped back to a range 4.6–12 mg/l for the remainder of the monitoring period. The low concentration measured on 27 January 2008 is anomalous and probably represents sampling or lab error. These concentrations indicate low redox potential in the plume, but the reason for the spring spike is not known. It is possible that iron is present in the road salt solution.

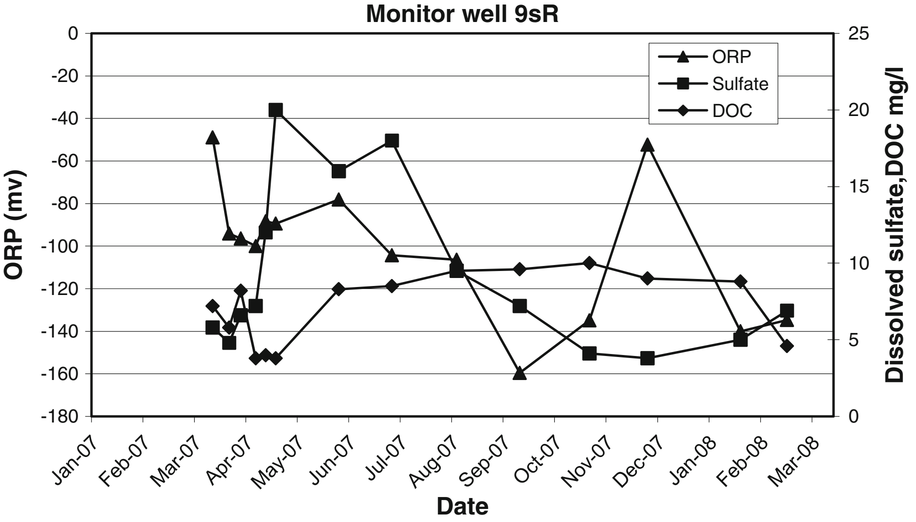


Fig. 17 Indicators of biodegradation in monitor well 9sR. ORP and sulfate are both high in the spring and decrease during the rest of the year. DOC is lowest in the spring and increases afterward. Sulfate reaching the water table during spring recharge is gradually consumed during sulfate reduction. ORP declines simultaneously although it rebounds in December

Sulfate spiked to 20 mg/l during the winter/spring recharge event, and then began a gradual decline to 3.8 mg/l during the summer and fall (Fig. 16). The sulfate that recharged to the water table may serve as an important electron acceptor for biodegradation reactions, one that is slowly consumed over the course of the summer and fall as the plume becomes more anaerobic (Scholl et al. 2006). Dissolved sulfide, which was measured once above detection limits in the monitor well, is consistent with the process of sulfate reduction during biodegradation. Support for this hypothesis includes the increase in bicarbonate concentrations after winter/spring recharge. Bicarbonate increased after winter/spring recharge rather than decreasing as did most other major ions. The source of the sulfate is most likely road salt, as the salt product used contains a small percentage of calcium sulfate. In the sequence of biodegradation reactions (Chapelle et al. 1995), sulfate reduction is followed by reduction of CO_2 to methane. Because sulfate remains above detection limits in the plume at times when the plume achieves its lowest redox potential, it likely that methanogenesis is minimal, although dissolved methane was not measured in the plume.

The low levels of dissolved organic carbon (Fig. 13) and various GIP parameters (Fig. 12) during the winter/spring recharge event raises two possibilities. Biodegradation could be enhanced during this time due to the arrival of recharge water enriched in electron acceptors. Alternatively, the decrease in these parameters could be the result of dilution. Support for the later hypothesis is provided by the bicarbonate concentration, which was depressed during recharge and then steadily increased afterward. If biodegradation were to be enhanced during recharge, bicarbonate levels might be expected to increase. Instead, they decreased, followed by a steady increase and peaked during the summer and fall months. This pattern suggests that electron acceptors supplied during winter/spring recharge are gradually consumed over the summer and fall during biodegradation, leading to increases in bicarbonate.

As a final indicator of biodegradation, the field ORP values are presented in Fig. 17. As DOC peaks in the summer and fall, in response to the lack of diluting recharge, the redox potential, as indicated by ORP, gradually falls to a minimum in late September and then rebounds to some extent. The decline in ORP tracks the decline in sulfate, as sulfate reduction is the dominant biodegradation process and redox potential declines as the dissolved sulfate is used up as an electron acceptor. It is likely that the anomalously high ORP value on 12 December 2007 was the result of sampling or instrumental problems.

Conclusions

Concentration trends yield important information pertaining to natural attenuation of BTEX plumes in an aquifer. The position of the monitor well with respect to the source determines the relationship between the water table and the concentration. Monitor wells located in or near the source area often exhibit in-phase fluctuations between concentrations of GIPs and water-level elevation. This may be due to intersection of the smear zone by the water table during the spring water table rise or to contact with a greater vertical thickness of the smear zone. Droplets of residual phase product in this zone may directly dissolve into groundwater, thus increasing concentrations.

Monitor wells located downgradient typically display inverse behavior, in which concentrations are low during seasonal rises in the water table. This relationship is probably the result of dilution by less impacted water from the vadose zone. The cessation of recharge in the summer and fall terminates dilution and concentrations rise. With an adequate period of monitoring data, declining trends often can be modeled as a first-order process and trendlines fitted to the data can be extrapolated to levels of regulatory standards to predict times to achieve regulatory compliance. The actual time at which standards are reached will probably fall within several years of the predicted time due to a period of fluctuations above and below the standard. Sampling should be biannual with samples collected in the in the spring and fall at a minimum in order to assess the effects of seasonal fluctuations in concentration. In some cases, trends obtained from spring and fall samples may indicate opposite slopes. To use this procedure to predict site closure, each regulated compound may be plotted separately because of different rates of natural attenuation and different levels of regulatory standards.

Weekly to monthly sampling of a monitor well in a hydrocarbon plume for a range of organic and inorganic parameters yields concentration trends that can be used to interpret the timing and mechanisms of natural attenuation. Monitor well MW-9sR, the subject of this research, displays an inverse seasonal concentration pattern with water-level elevation. Depression of GIP parameters in the spring coincides with a rapid increase in major ions, including sodium, potassium, calcium, magnesium, chloride, and sulfate. Bicarbonate decreases during this spring peak. The hypothesized cause for these spring concentration changes is rapid arrival of recharge to the water table containing ions derived from road salt application during the preceding winter. This slug of water temporarily dilutes the GIP compounds in the contaminant plume and also contributes electron acceptors presumably including oxygen and sulfate. Oxygen must be consumed in biodegradation reactions very rapidly, as it is never detected in the well above 1 mg/l. Sulfate, on the other hand declines slowly throughout the summer and fall as bicarbonate, and total organic carbon and GIP concentrations increase. ORP decreases during most of this period. These patterns are explained by a decrease in the arrival of diluting recharge after the winter/spring recharge event and the gradual decline in redox potential in the plume. Sulfate probably serves as the dominant electron acceptor in the slow, anaerobic biodegradation of the plume organics. Concentrations of these compounds reach a peak in late fall and early winter, when the water-table elevation is at a minimum.

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References

Baedecker MJ, Cozzarelli IM, Eganhouse RP, Siegel DI, Bennett PC (1993) Crude oil in a shallow sand and gravel aquifer—III. Biogeochemical reactions and mass balance modeling in anoxic groundwater. Appl Geochem 8:569–586

Barker JF, Patrick GC, Major D (1987) Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. Groundw Monitor Rev 7:64–71

Borden RC, Gomez CA, Becker MT (1995) Geochemical indicators of intrinsic bioremediation. Ground Water 33:180-188

Borden RC, Daniel RA, LeBrun LE IV, Davis CW (1997a) Intrinsic biodegradation of MTBE and BTEX in a gasoline contaminated aquifer. Water Resour Res 33:1105–1115

Borden RC, Hunt MJ, Shafer MB, Barlaz MA (1997b) Anaerobic biodegradation of BTEX in natural aquifer material. USEPA environmental research brief. EPA/600/S-97/003

Chakraborty R, Coates JD (2004) Anaerobic degradation of monoaromatic hydrocarbons. Appl Microbiol Biotechnol 64:437–446

Chapelle FH, McMahon PB, Dubrovsky NM, Fujii RF, Oaksford ET, Vroblesky DA (1995) Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. Water Resour Res 31:359–371

Chapelle FH, Widdowson MA, Brauner JS, Mendez E III, Casey CC (2003) Methodology for estimating times of remediation associated with monitored natural attenuation. U.S. geological survey, water resources investigations report 03-4057

Davis EL (1997) How heat can enhance in situ soil and aquifer remediation: important EPA groundwater issue EPA/540/S-97/50218

Davis JW, Klier NJ, Carpenter CL (1994) Natural biological attenuation of benzene in groundwater beneath a manufacturing facility. Groundwater 32:215–226

Dou J, Liu X, Hu Z, Deng D (2008) Anaerobic BTEX biodegradation linked to nitrate and sulfate reduction. J Hazard Mater 151:720–729

Flyvberg J, Arvin E, Jensen BK, Olsen SK (1993) Microbial degradation of phenols and aromatic hydrocarbons in creosote-contaminated groundwater under nitrate-reducing conditions. J Contam Hydrol 12:133–150

Haag FM, Reinhard M, McCarty PL (1991) Degradation of toluene and *p*-xylene in an anaerobic microcosm: evidence for sulfate as a terminal electron acceptor. Environ Toxicol Chem 10:1379–1389

Hu Z, Dou J, Liu X, Deng D (2007) Anaerobic biodegradation of benzene series compounds by mixed cultures based on optimal electronic acceptors. J Environ Sci 19:1049–1054

Johnson SJ, Woolhouse KJ, Prommer H, Barry DA, Christofi N (2003) Contribution of anaerobic microbial activity to natural attenuation of benzene in groundwater. Eng Geol 70:343–349

Kehew AE (2001) Applied chemical hydrogeology. Prentice-Hall, Inc, Upper Saddle River

Lovley DR (1997) Microbial Fe(III) reduction in subsurface environments. FEMS Microbiol Rev 20:305–313

Lovley DR, Lonergran DJ (1990) Anaerobic oxidation of toluene, phenol, and *p*-cresol by the dissimilatory iron-reducing organism GS-15. Appl Environ Microbiol 56:1858–1864

Lovley DR, Phillips EJP (1988) Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. Appl Environ Microbiol 54:1472–1480

Lovley DR, Baedecker MJ, Lonergran DJ, Cozzarelli IM, Phillips EJP, Siegel DI (1989) Oxidation of aromatic contaminants coupled to microbial iron reduction. Nature 339:297–299

Major DW, Mayfield CI, Barker JF (1988) Biotransformation of benzene by denitrification in aquifer sand. Groundwater 26:8–14

McGuire JT, Smith EW, Long DT, Hyndman DW, Haack SK, Klug MJ, Velbel MA (2000) Temporal variations in parameters reflecting terminal electron-accepting processes in an aquifer contaminated with waste fuel and chlorinated solvents. Chem Geol 169:471–485

Scholl MA, Cozzarelli IM, Christenson SC (2006) Recharge processes drive sulfate reduction in an alluvial aquifer contaminated with landfill leachate. J Contam Hydrol 86:239–261

Schreiber ME, Carey GR, Feinstein DT, Bahr JM (2004) Mechanisms of electron acceptor utilization: implications for simulating anaerobic biodegradation. J Contam Hydrol 73:99–127

Scow KM, Hicks KA (2005) Natural attenuation and enhanced bioremediation of organic contaminants in groundwater. Curr Opin Biotechnol 16:246–253

USEPA (1997a) http://www.epa.gov/OUST/rbdm/index.htm

USEPA (1997b) Use of monitored natural attenuation at Superfund, RCRA corrective action, and underground storage tanks. Office of solid waste and emergency response, Directive 9200.4-17, p 42

USEPA (1999) Final OSWER monitored natural attenuation policy. Office of solid waste and emergency response, Oswer directive 9200.4-17P

USEPA (2008) http://www.epa.gov/OUST/index.htm

Zemo DA (2006) Sampling in the smear zone: evaluation of nondissolved bias and associated BTEX, MTBE, and TPH concentrations in groundwater samples. Groundw Monit Remed 26:53–59