



PROCEEDINGS

of the

2000 Petroleum Hydrocarbons and Organic Chemicals in Ground Water:®

Prevention, Detection, and Remediation

Special Focus: Natural Attenuation and Gasoline Oxygenates

Conference and Exposition

November 15-17, 2000 • Anaheim, California



American
Petroleum
Institute



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**Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in
Ground Water
Prevention, Detection, and Remediation Conference
Special Focus: Natural Attenuation and Gasoline Oxygenates
November 14-17, 2000 ♦ Anaheim, California**

The 2000 Petroleum Hydrocarbons Conference and Exposition was sponsored by the National Ground Water Association and the American Petroleum Institute, and co-sponsored by the National Petroleum Technology Office of the U.S. Department of Energy, U.S. EPA Region 9 Office of Underground Storage Tanks, Equilon Enterprises, and the National Water Research Institute. The Conference and Exposition was comprised of three days of technical presentations which covered the following topic areas:

**Gasoline Oxygenates: Ethanol
Gasoline Oxygenates: MTBE
GIS Applications for Remediation and Wellhead Protection
The Soft Path to Remediation
Pushing the Envelope with Direct Push
Unsolved Mysteries: LNAPL
Vapors in the Vadose Zone
Is Natural Attenuation Appropriate for Remediating MTBE?**

In addition, more than 70 leading companies in the ground water and petroleum industries participated in the Conference and Exposition in which a variety of equipment and services for preventing, detecting, and remediating ground water contaminated by petroleum hydrocarbons and other organic chemicals were showcased.

This bound volume is a compilation of papers that were presented at the Conference. Materials appearing in the publication are indexed to Ground Water On-Line, the data base of the National Ground Water Information Center.

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Results of a Natural Attenuation Field Experiment for an Ethanol-Blended Gasoline Spill

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Abstract

Ethanol-blended gasoline has been used in Brazil for 20 year and, probably, is going to be more widely used in North America due to the MTBE environmental effects on groundwater. The main concerns in dealing with aquifer contamination by ethanol-amended gasoline is focused on the complex physical, chemical and biological interactions between gasoline constituents and ethanol, which may limit the selection of proper environmental restoration technologies. This paper shows results of a controlled release experiment performed in a sandy aquifer in Florianópolis, SC, Brazil where a source of 100 L of the Brazilian gasoline containing 24% ethanol was released 0.5 m below water table. The experiment has been monitored since December/98 in 45 miniature multilevel sampling wells covering an area of 10 m x 30 m. Each sampler has 5 vertical sampling points. Results indicate that after 480 days since the beginning of the contamination, the plume is approximately 10 meters away from the source zone and still expanding. Based on the site groundwater geochemical data, the biological processes responsible for bioattenuation are aerobic respiration, iron reduction and methanogenesis. The high levels of Fe^{2+} produced in the middle of the plume (58 mg/L), along with the low levels of dissolved oxygen (0 – 2 mg/L), suggest that iron reduction is the dominant biological process in the site. A mass flux approach was used to calculate first-order biological decay coefficients (λ) for ethanol and the BTEX compounds. Results indicated that λ is higher for toluene (0.41 year^{-1}) than for benzene (0.17 year^{-1}) and xylenes ($0.07\text{-}0.15 \text{ year}^{-1}$). The biological decay coefficient obtained for ethanol (0.42 year^{-1}) is similar to toluene. These results indicate that ethanol can persist in the aquifer for periods much longer than initially expected and interfere in the biodegradation of the more toxic BTEX compounds.

Introduction

Ethanol and ethanol-blended gasoline have been used as fuels in Brazil since the late 70's. Today, approximately 75% of all automobiles run on gasoline containing 24% ethanol. Concerned with the possible impacts that these type of fuels could cause on groundwater in Brazil, Petrobrás, the Brazilian oil company, in collaboration with the Federal University of Santa Catarina, have been studying the interactions of gasoline and ethanol in groundwater since 1995.

The main concern in dealing with aquifer contamination by ethanol-amended gasoline is related to the complex physical, chemical and biological interactions between gasoline constituents and ethanol, which may limit the selection of proper environmental restoration technologies. Ethanol can increase the mass of hydrocarbons in groundwater due to cosolvency (Corseuil and Fernandes, 1999), and can also cause a preferential substrate utilization by soil microorganisms (Corseuil et al., 1998; Hunt et. al., 1997). In an ethanol-blended gasoline spill, ethanol, being completely miscible in water, will migrate to groundwater. In this case, a high aqueous ethanol concentration could enhance concentration of the most common contaminants, benzene, toluene, ethylbenzene and xylenes (BTEX) in groundwater. Moreover, length and persistence of hydrocarbon plumes is directly related to the rate of contaminants biodegradation.

With respect to biodegradation inhibition, previous studies performed in our laboratories have shown that ethanol is preferentially degraded under all common electron acceptor conditions found in subsurface systems (Corseuil et al., 1998). Therefore, ethanol can impede, or at least retard, natural hydrocarbon degradation in groundwater due to the depletion of the electron acceptors pool. The presence of a large mass of petroleum hydrocarbons and ethanol in groundwater can make remediation of aquifers contaminated by ethanol-blended gasoline more difficult and costly than conventional gasoline.

It is expected that BTEX plumes could be larger in gasohol spills, because of the ethanol presence in the aqueous phase. It is said that ethanol is degraded at a faster rate than other gasoline constituents (Chapelle, 1993; Malcom Pirnie, 1998). Currently, there is no information in the literature about degradation rates of gasoline-ethanol plumes under real conditions. The net effect of the ethanol on the length and duration of a BTEX plume will depend on how fast ethanol is degraded in the aquifer.

Here we present results of an ongoing controlled release experiment being performed in a sandy aquifer in Florianópolis, SC, Brazil with a gasoline containing 24% ethanol. Our objectives are: 1) to determine if natural attenuation with adequate site characterization and monitoring is a practical and low cost alternative to remediate aquifers contaminated with gasohol; 2) to assess the occurrence and mechanisms of natural bioremediation in the presence of ethanol in the site; and 3) to determine the biodegradation rates of ethanol and BTEX plumes in the field experiment

Description of Experiment

Studies are being done at Ressacada, the Federal University of Santa Catarina experimental farm, in Florianópolis, SC, Brazil. The regional geology is characterized by unconsolidated deposits of eolian, alluvial, lacustrine and marine sands. The regional climate in Florianópolis is humid mesotermic with a mean annual precipitation of 1530 mm. Monthly mean temperature in the summer is 24 °C and in the winter 17 °C.

The surface soil at the site is gray-brown loamy sand and the subsurface layer is a uniform gray fine sand with less than 5% of silt and clay. Depth to the seasonal water table is approximately 0.7 – 1.1 m and the measured groundwater temperature in the aquifer is approximately 25°C. The horizontal gradient at the site is approximately 1.8‰ and hydraulic conductivity 10^{-4} cm/s. Using the effective porosity of 0.20 (measured in the laboratory) and the average hydraulic gradient, the groundwater flow velocity was calculated at 2.8 m/yr.

The experimental area covered with monitoring wells is 12m x 30m. The source zone was created in an area of 2m x 1m that was excavated up to 0.5 m bellow groundwater table where 100 L of the Brazilian commercial gasoline containing 24% ethanol was spilled in December 98. The sampling arrays are essentially miniature multi-level sampling wells that allow investigators to collect groundwater from discrete elevations within the groundwater column. The vertical sampling array consists of a bundle of 3/16" ID polyethylene tubing with

each tube cut to a length that corresponds to the zone of interest. The terminal end of each tube is thermally bonded to a narrow diameter, 20 cm long, 200 mesh stainless steel wire-cloth screen. The array is attached to the outside of a small diameter PVC piezometer that extends to the bottom of the hole and is installed with conventional drilling and steel casing. The annular space between the samplers and the native formation is filled with fine sand to prevent channeling. Low-flow sampling is conducted using a peristaltic pump connected individually to each of the multi-level samplers. In the test area, a total of 45 multilevel samplers were installed to delineate the longitudinal distribution of the contaminants. Each sampler has 4 or 5 sampling points with depths varying from 1.0 m to 4.5 m (Figure 1). Potassium bromide was used as a tracer because it was not present in significant concentration in the groundwater.

Since December 98, we made 7 monitoring programs in the experimental area. BTEX, 1,2,4 and 1,3,5 trimethylbenzene, ethanol and methane were analyzed with GC/FID (HP 5890) and headspace auto sampler (HP 7694) and bromide, nitrate, and sulfate by IC (Dionex DX 120). Sulfide and iron (II) were analyzed with HACH test kits and alkalinity and aqueous CO_2 by standard wet chemical assays (APHA, 1992). Temperature, pH, DO, redox potential and conductivity were measured with a water analyzer Micropurge Flow Cell (QED FC 4000).

Results

Background dissolved oxygen concentrations in the field experiment ranged from 4 to 7 mg/L and pH from 5.0 to 5.3. Background nitrate, sulfate, phosphate, methane and ferrous iron concentrations in groundwater are very low, varying from 0.13 to 0.62 mg/L $\text{NO}_3\text{-N}$, 0.3 to 4.3 mg/L, 0.12 to 0.9 mg/L $\text{PO}_4\text{-P}$, < 0.01 mg/L, and 0.0 to 4.4 mg/L, respectively. Oxidation-reduction potential, total alkalinity and aqueous CO_2 concentration in the aquifer before contamination ranged from +32 to +169 mV, 4 to 30 mg/L CaCO_3 and 18 to 109 mg/L CaCO_3 , respectively.

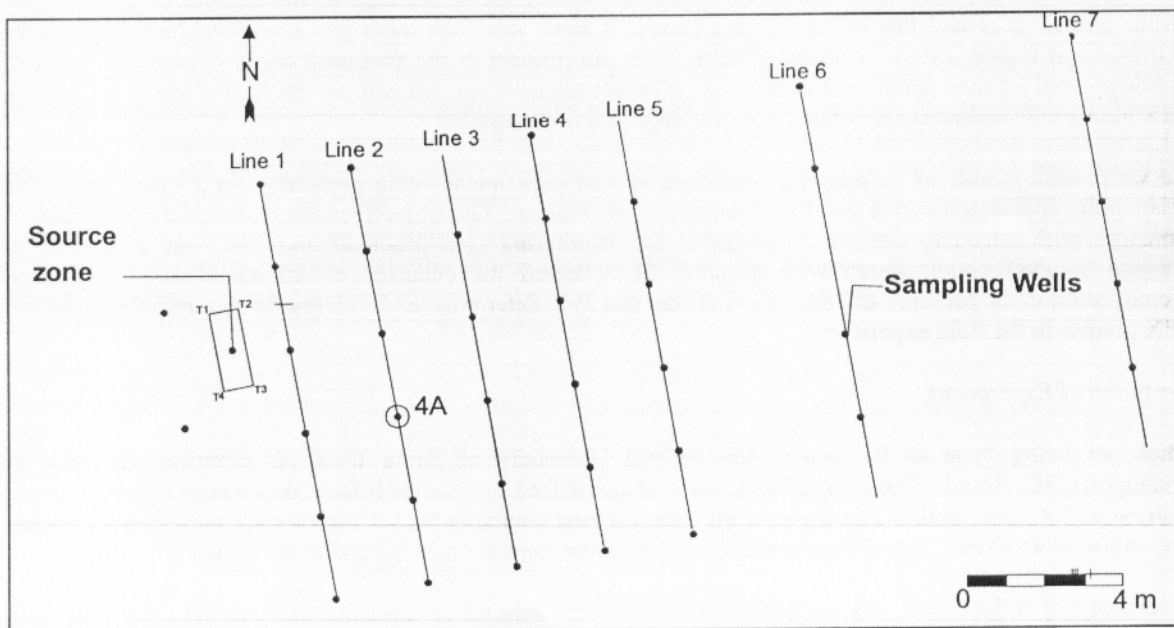


Figure 1 – Site map showing sampling wells locations.

Plan views of bromide, total BTEX, and ethanol plumes in April 2000 are shown in Figure 2. After 16 months since the gasohol release, bromide, plume moved 16 m from the source zone, and total BTEX and ethanol, 10.7 meters. The highest concentrations are still very near the source, between lines 1 and 2 in Figure 1. In line 1, 1.45 m from source zone, total BTEX, bromide and ethanol were detected even in sampling wells located 5 meters bgs. In all other sampling points, these compounds were not detected 3.5 m bgs.

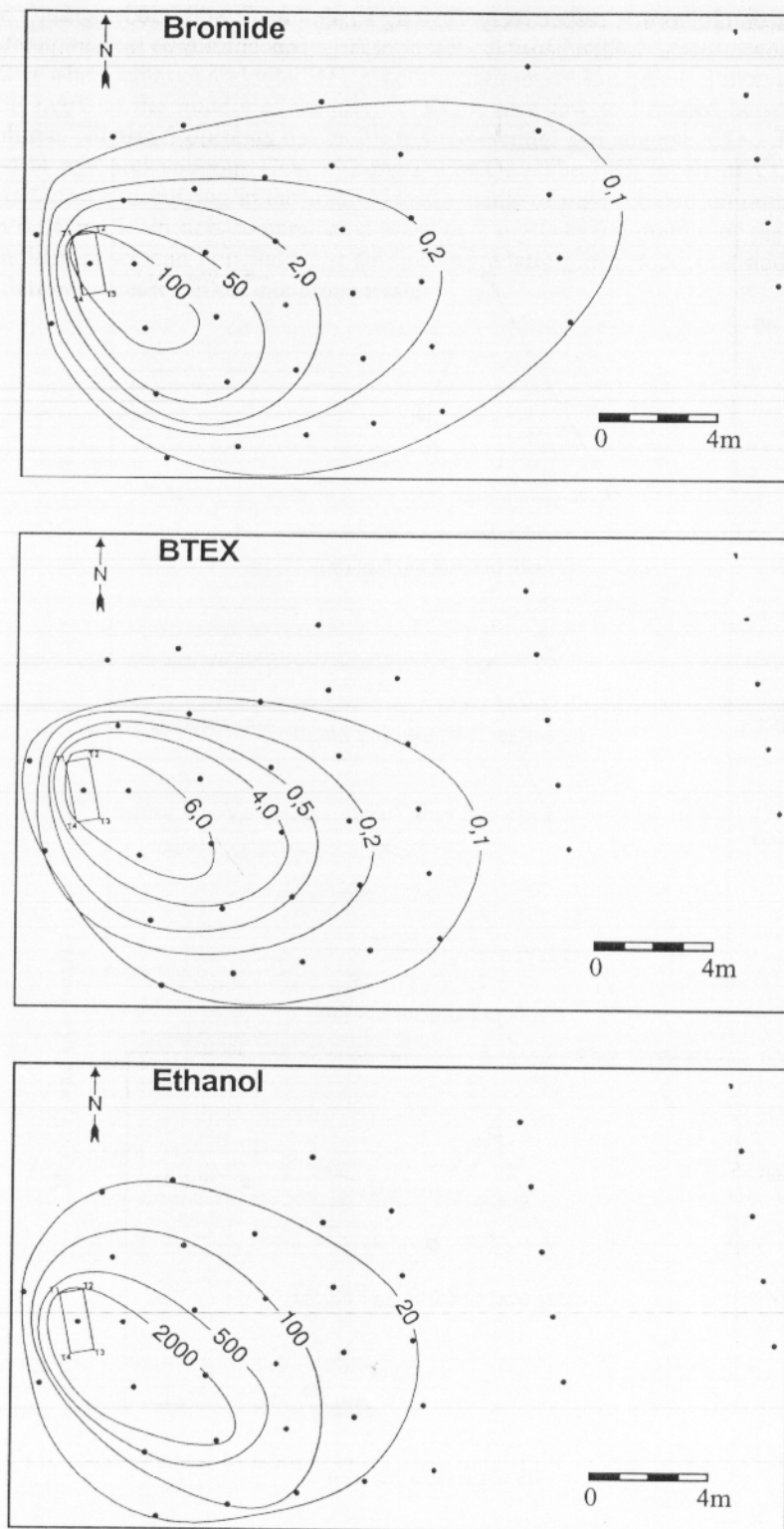


Figure 2 – Plan views and cross sections of the bromide, total BTEX and ethanol plumes (April 2000). Concentrations are in milligrams per liter.

Figure 3 shows vertical distribution of total BTEX, bromide, and ethanol in well 4A, located 3.8 m from source. Based on the site groundwater velocity of 2.8 m/year, well 4A represents the water traveling distance in 16 months. In this well, maximum vertical plume concentrations are located about 2 m bgs and total BTEX,

bromide and ethanol concentrations are, respectively 4730 $\mu\text{g/L}$, 49.7 mg/L and 2503 mg/L. It is interesting to note that even after 16 months of the spill, ethanol is present in large concentrations in the aqueous phase.

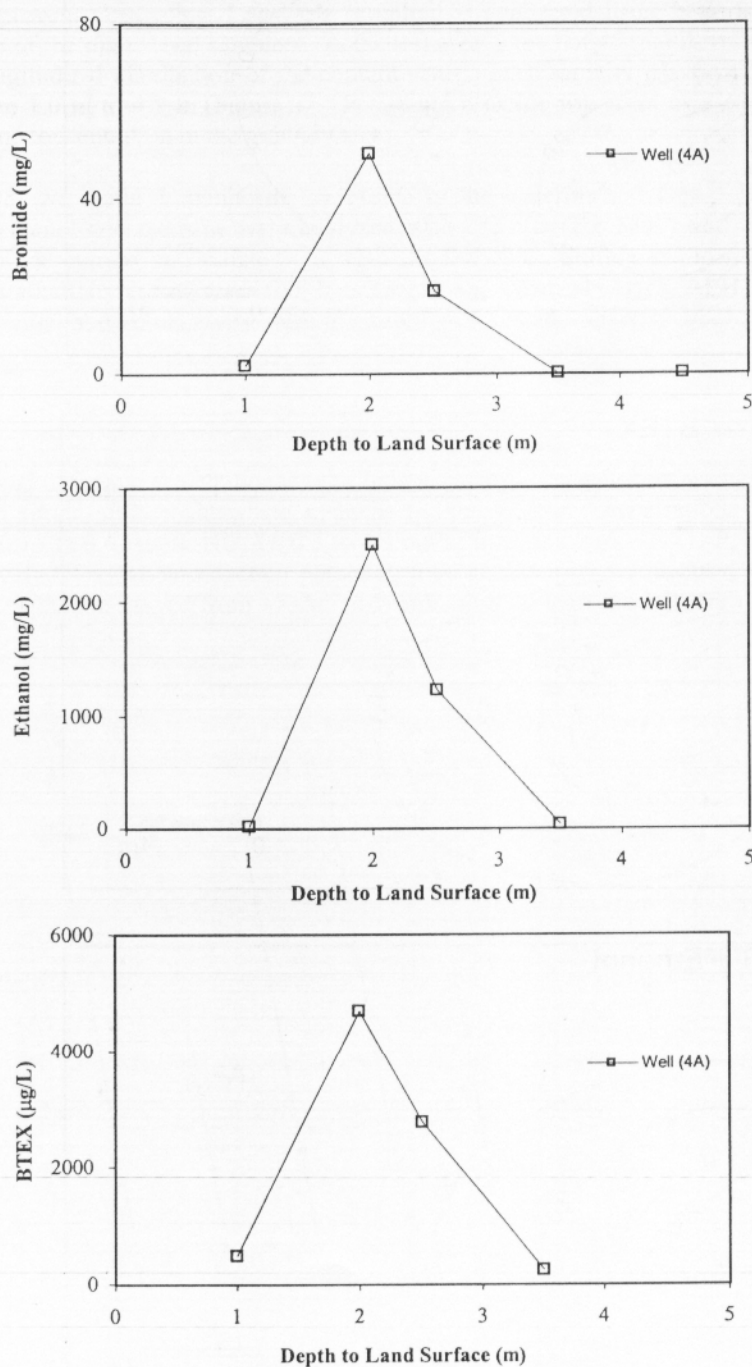


Figure 3 – Variations in bromide, ethanol and total BTEX concentrations in well 4A.

A zone in the plume where dissolved oxygen varied between 0 and 2 mg/L was developed immediately downgradient from the source zone. Figure 4 shows variations of dissolved oxygen and ferrous iron in well 4A. Results show that where ethanol and total BTEX concentrations are high, Fe (II) increased from 1 mg/L outside the plume to 58 mg/L in the middle of the plume. DO is also low and ranged between 1 and 2 mg/L in the center of the plume. Figure 5 presents results for redox-potential and aqueous CO₂. In the most contaminated area Eh was -134 mV and aqueous CO₂, 292 mg/L CaCO₃. The high levels of CO₂ observed indicate that natural biodegradation is occurring in the area. Measurements of methane concentrations in lines 1 and 2 show increases from 0.01 mg/L, in non-contaminated areas to 2 mg/L in the middle of the plume. Based on these geochemical indicators we can conclude that aerobic degradation, iron reduction and methanogenesis are the main biodegradation processes in the site groundwater.

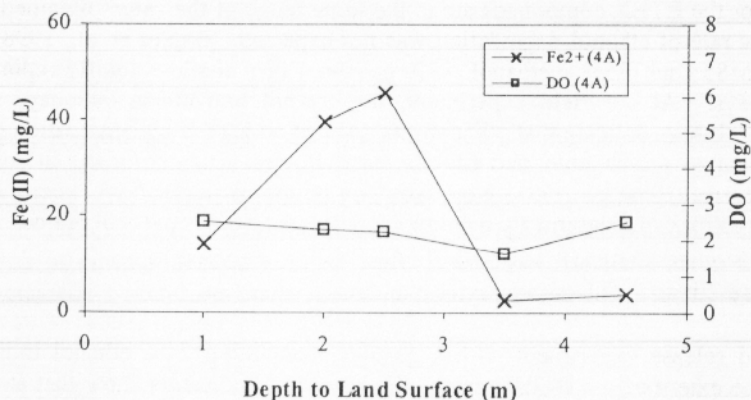


Figure 4 – Variations in Fe²⁺ and DO concentrations in well 4A.

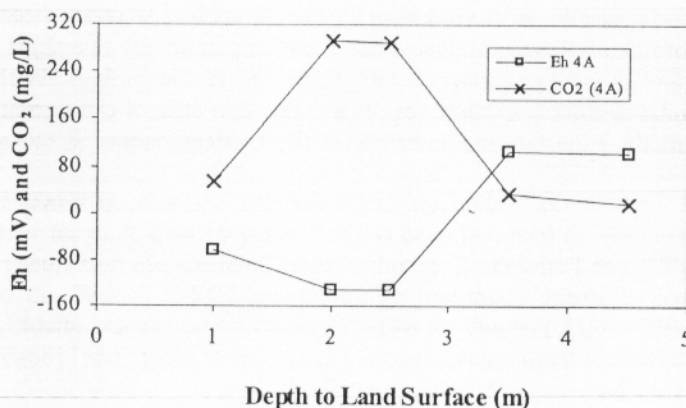


Figure 5 – Variations in redox-potential and Aqueous CO₂ concentrations in well 4A.

The mass flux approach described in Borden et. al., 1997 and in Kao and Wang, 2000, was used to determine the first order decay biodegradation rates for the BTEX and ethanol compounds. Mass fluxes for ethanol, benzene, toluene, ethylbenzene, *m,p*-xylene, *o*-xylene and bromide were calculated for lines 1 to 5 (Figure 1). Degradation rates were corrected for advection, dispersion and dilution from recharge using the bromide attenuation rate. Trimethylbenzene was not used as the conservative tracer (Weidemeier, et al., 1995) because it is being degraded in our plume. Besides, organic carbon content in the soil aquifer is low (0.2%) and contaminant sorption in groundwater in the presence of ethanol is not well understood. The corrected first-order decay rates obtained for ethanol, and the BTEX compounds are presented in Table 1.

TABLE 1. Effective first-order decay coefficients corrected with bromide

Compound	λ (year ⁻¹)
Ethanol	0.42
Benzene	0.17
Toluene	0.41
Ethylbenzene	0.30
<i>m,p</i> , xylene	0.07
<i>o</i> -xylene	0.15

Decay values obtained for the BTEX compounds are in the same range of the values obtained by Borden et. al., 1997. However, the low rate of ethanol degradation was not expected. Barker et. al., 1998, investigating the persistence and fate of M85 fuel (85% methanol, 15% gasoline) in a shallow aquifer reported a half-life for methanol of only 40 days. At our field experiment, the ethanol half-life is 600 days in a groundwater temperature of 25°C, which may indicate that ethanol interference on BTEX biodegradation can be significant, especially in colder climates. This high half-life for ethanol was also confirmed in microcosms studies performed in our laboratories (Benetti, 1999). New sampling programs in our field experiment are under way that should help to better explain the natural attenuation degradation rates for gasoline plumes.

Conclusion

Analysis of a controlled release experiment with a gasoline containing 24% ethanol indicates that natural attenuation is limiting the extent of the BTEX plume. Geochemical indicators show that aerobic degradation, iron reduction and methanogenesis are the biological processes responsible for degradation of the organic contaminants. The high levels of Fe²⁺ produced in the middle of the plume (58 mg/L), along with the low levels of dissolved oxygen (0 – 2 mg/L), suggest that iron reduction is the dominant biological process in the site.

A mass flux approach was used to estimate the first-order decay coefficients for ethanol and the BTEX compounds. The calculated rate constants were corrected for the effects of advection, dispersion and dilution from recharge with the tracer bromide. Results indicated that the biological decay rate (λ) is higher for toluene (0.41 year⁻¹) than for benzene (0.17 year⁻¹) and xylenes (0.07-0.15 year⁻¹). The biological decay value obtained for ethanol (0.42 year⁻¹) is similar to toluene. These results indicate that ethanol can persist in the aquifer for periods much longer than initially expected and interfere in the biodegradation of the more toxic BTEX compounds.

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