NATURAL ATTENUATION RATES OF ETHANOL AND BTEX COMPOUNDS IN GROUNDWATER CONTAMINATED WITH GASOHOL

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ABSTRACT

Natural attenuation biodegradation rate is a key parameter to perform a risk assessment of hydrocarbon plumes. This study determines first-order kinetics for a gasohol controlled release experiment site in Brazil using data of BTEX and ethanol concentrations of eight sampling campaigns. The rates of individual BTEX compounds and ethanol were estimated using the methods of trimethylbenzene correction, Buscheck and Alcantar (1995), mass flux, and Bioscreen fate and transformation model. Results showed that the fate and transport model is the method that best fits transient state flow conditions of BTEX and ethanol plumes. Biodegradation first-order coefficients calculation with the model showed the following half-lives: ethanol = 0.60 year, toluene = 0.70 year, benzene = 1.00 year, ethylbenzene and total xylenes = 1.20 year. However, due to the interference of ethanol on BTEX degradation, neither Bioscreen nor any other model that do not incorporate multiple substrate interference are adequate to correctly predict the behavior of gasohol plumes.

KEYWORDS

Natural attenuation; BTEX; ethanol; biodegradation rates; first-order decay kinetics.

INTRODUCTION

Ethanol-blended gasoline has been used in Brazil for 20 years and, probably, is going to be more widely used in North America due to the MTBE environmental effects on groundwater. Concerned with the possible impacts that this fuel 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 preferential substrate utilization by soil microorganisms (Corseuil et al., 1998). 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 (Powers et al., 2001). Moreover, length and persistence of hydrocarbon plumes is directly related to the mass of ethanol in the source and the rate of contaminants biodegradation. 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;). 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.

Natural attenuation is being considered as an important strategy to remediate soils and groundwaters contaminated with petroleum hydrocarbons. The application of this technology is directly dependent on transport models to predict how far the plumes will migrate. Since the biodegradation rate is very sensitive in these models, it is important to determine, under real conditions, what are the ethanol-blended gasoline degradation kinetics. This paper compares four methods that are usually used to calculate site-specific biodegradation rates using monitoring well data and hydrologic properties of the aquifer. The methods utilized were the Tracer-Corrected Method, the Buscheck and Alcantar Method (1995), the Mass Flux and the Bioscreen fate and transport model.

STUDY SITE DESCRIPTION

To evaluate the impact of ethanol in gasohol spills a controlled release experiment was set up at Ressacada, a Federal University of Santa Catarina experimental farm, in Florianópolis, SC, Brazil. 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 commercial gasoline containing 24% ethanol was spilled in December 98. 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. 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 ^{o}C and in the winter 17 ^{o}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. The average of soil organic carbon content is 0.06%. Depth to the seasonal water table is approximately 0.7 – 1.1 m and the measured groundwater temperature in the aquifer is approximately 25^{o}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 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 and 2). Potassium bromide was used as a tracer because it was not present in significant concentration in the groundwater.

METHODOLOGY

Since December 98, we made eight monitoring campains in the controlled release experiment at Ressacada Farm. BTEX, 1,2,4 and 1,3,5 trimethylbenzene and ethanol were analyzed with by gas chromatography and bromide (tracer) by ionic chromatography. Four methods were used to calculate the first order biodegradation constant for benzene, toluene, ethylbenzene, total xylenes and ethanol using data from monitoring wells and the hydrologic properties of the aquifer. The first method (Correct Tracer) uses a recalcitrant tracer in groundwater associated with the hydrocarbon plume to normalize changes in concentration of BTEX under aerobic/anaerobic conditions. Attenuation of the tracer is attributed do dilution, sorption, and/or volatilization. Attenuation of BTEX in excess of the attenuation of the tracer is attributed to biodegradation. In this case, 1,3,5-trimethylbenzene was utilized as tracer, because it migrates similarly to the BTEX compounds and is recalcitrant to biodegradation (Wiedemeier et al., 1996). This method estimates the degradation rate of a compound between two points on a groundwater flow path by calculating a corrected concentration of the compound at the downgradient point through the equation:

$$C_{B,corr} = C_B\left(\frac{TMB_A}{TMB_B}\right) \tag{1}$$

where $C_{B,corr}$ is the corrected concentration of the compound at downgradient point B, C_B is the observed concentration of the compound at point B, TMB_A is the observed concentration of trimethylbenzene at upgradient observation point A, and TMB_B is the observed concentration of trimethylbenzene at point B. If the corrected contaminant distribution approximates to first-order kinetics, we can calculate the biodegradation constant by:

$$C_{B,corr} = C_{A,corr}\, e^{-\lambda t} \tag{2}$$

where $C_{A,corr}$ is the measured compound concentration at upgradient point A, and t is the travel time between two points. The constant λ was calculated plotting log-linearly the tracer-corrected dissolved BTEX concentrations vs. downgradient travel time along the groundwater flow path at point A, B, C, D and E (Figure 1).

The second method was presented by Buscheck and Alcantar (1995). This method uses a one-dimensional analytical solution presented by Bear (1979) to interpret the steady-state configuration of the contaminant plume along flow path. The first-order biodegradation constant (λ) is determined by the following equation:

$$\lambda = \left(\frac{v_c}{4\alpha_x} \right) \left\{ \left[1 + 2\alpha_x \left(\frac{k}{v_x} \right) \right]^2 - 1 \right\} \quad (3)$$

where v_c is the retarded contaminant velocity in the groundwater flow path direction, α_x is the longitudinal dispersivity, and k/v_x is the slope of the a log-linear plot of contaminant concentration vs. distance downgradient along flow path ABCDE (Figure 1). The value k/v_x was determined from linear regression analysis.

The third method used to estimate BTEX and ethanol degradation was the mass flux approach (Borden et al., 1997; Kao and Wang, 1999). A simplified mass balance procedure was accomplished using the differences in total contaminant mass flux across two cross-sections of the contaminant plume (Figure 1). The advective mass flux (F_i) associated with an individual monitoring well on sample distance i was calculated as:

$$F_i = C_i \cdot A_i \cdot v_{xi} \quad (4)$$

where C_i is the contaminante concentration at across-section i, A_i is the effective concentration area at cross-section i, and v_x is the groundwater flow velocity. The mass flux equation was also applied to the first-order decay model:

$$F_x = F_0 \cdot \exp(-\lambda \cdot x) \quad (5)$$

where F_x is the total mass flux for a cross-section at distance x, F_0 is the total mass flux at source. The mass distribution over an area was given by Theissen Polygon technique (Borden et al., 1995). In this study, five cross-sections were selected along the plume (Figure 1). Figure 2 presents the discrete sampling points and the 36 influential areas for cross-section 1. The mass flux for each polygon was calculated and the total mass flux was given from the sum of the polygons.

The fourth method employed in this study, the Bioscreen model, is a public-domain spreadsheet-based screening tool for simulating the natural attenuation of dissolved hydrocarbons at petroleum fuel releases sites (Newell et all., 1997), that is represented mathematically by:

$$\frac{\partial C}{\partial t} = \frac{1}{R} \left[D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \lambda C \right] \quad (6)$$

were C is the concentration of dissolved contaminant, t is the time, D_x is the hydrodynamic dispersion , v_x is the groundwater velocity, x is the distance down gradient of source, λ is the biodegradation rate constant, and R is the retardation factor. In this study, the biodegradation rate was determined by adjusting the first-order decay coefficient until the predicted values match observed field data.

RESULTS

Results obtained for the first-order constant, λ, using the methods of trimethylbenzene correction, Buscheck and Alcantar, mass flow, and the Bioscreen model are presented in Table 1.

Table 1. First-order biodegradation (λ) constant and half-life of BTEX and ethanol obtained by four methods used to approximate site-specific biodegradation rates

Contaminant	1,3,5-TMB correction		Buscheck & Alcantar		Mass flux		Bioscreen model	
	λ (year^{-1})	$t_{1/2}$ (year)	λ (year^{-1})	$t_{1/2}$ (year)	λ (year^{-1})	$t_{1/2}$ (year)	λ (year^{-1})	$t_{1/2}$ (year)
Benzene	1.57	0.44	1.75	0.40	2.22	0.31	0.69	1.00
Toluene	2.37	0.29	2.63	0.26	2.95	0.23	0.99	0.70
Ethylbenzene	1.68	0.41	1.72	0.40	2.99	0.23	0.58	1.20
Xylene	1.72	0.40	1.75	0.40	2.48	0.28	0.58	1.20
Ethanol	*	*	2.37	0.29	3.29	0.21	1.15	0.60

* Tracer corrected method can not utilized with ethanol.

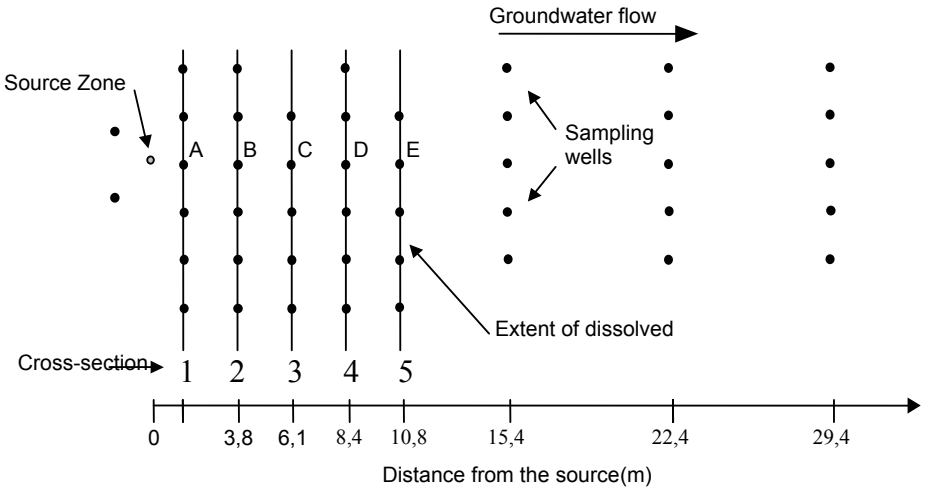

Figure 1. Site map showing sampling wells locations

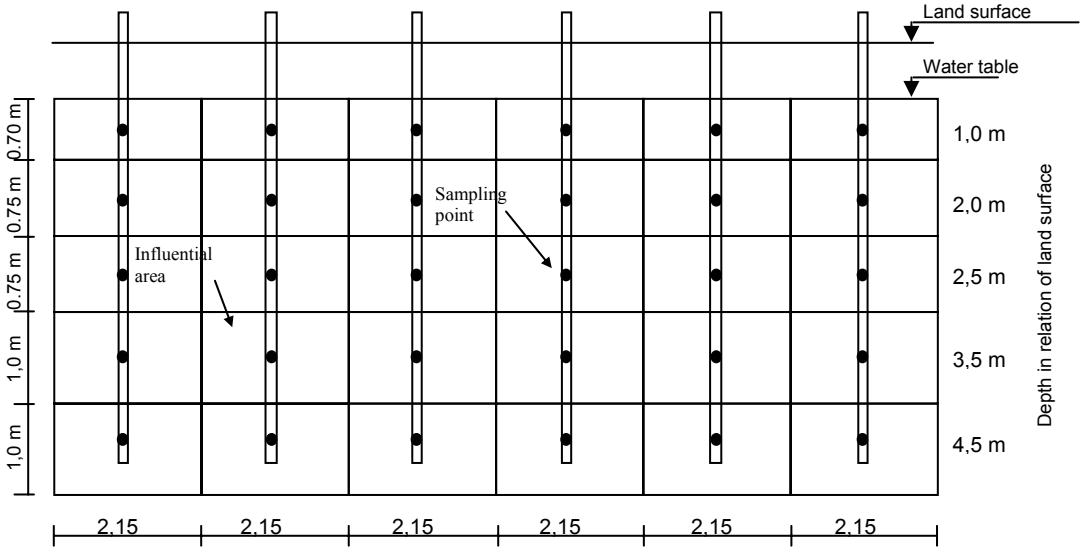

Figure 2. Cross-section 1 diagram with discrete sampling points and influential areas.

TMB normalization method is not adequate for this study because trimethylbenzene was biologically degraded at point A. Under this condition, BTEX/TMB ratio downgradient from the source increases which leads to an underestimation of λ. Buscheck and Alcantar method requires that the plume be at steady-state. In this study, steady-state conditions were not achieved limiting the applicability of this method as well.

The mass flux technique does not differentiate sinks (dispersion, volatilization, dilution and biodegradation). In this case, λ is an overall degradation rate and not a biodegradation rate. In addition, the mass flux method is more appropriated to pulse releases. The Bioscreen model overcomes the limitations associated with the previous methods. The model does not require a tracer and steady-state conditions and, therefore, is the method that best fits transient state flow conditions. Figure 3 presents the first-order decay curves for BTEX and ethanol fitted to field data. In these simulations, the retardation factor for the BTEX compounds was assumed equal to one, because of the low organic matter in the site and the presence of unknown ethanol effect on the hydrocarbons sorption. It can be seem that the model cannot fit the initial data points. This occurs because near the source zone, where ethanol is present in larger concentrations, the BTEX compounds are not degraded due to ethanol preferential biodegradation.

CONCLUSION

The use of different methods to estimate first-order degradation rates of ethanol and BTEX compounds in aquifers contaminated with ethanol-blended gasoline showed that the a fate and transport model more adequately fits transient flow conditions of BTEX and ethanol plumes. The calculation of biodegradation kinetics coefficients with the model showed the following half-lives: ethanol = 0.60 year; toluene = 0.70 year, benzene = 1.00 year; ethylbenzene and total xylenes = 1.20 year. These site-specific rates can be employed in analytical or numerical groundwater contaminant fate and transport as a first attempt to evaluate potential risks to downgradient receptors. Furthermore, these results indicate that ethanol degradation rate is slower than initially thought, which can cause an increase in the length of BTEX plumes in gasohol spills due to the longer persistence of ethanol in groundwater. However, it should be noted that Bioscreen and other models that do not incorporate multiple substrate interference are not adequate to correctly predict the behavior of gasohol plumes.

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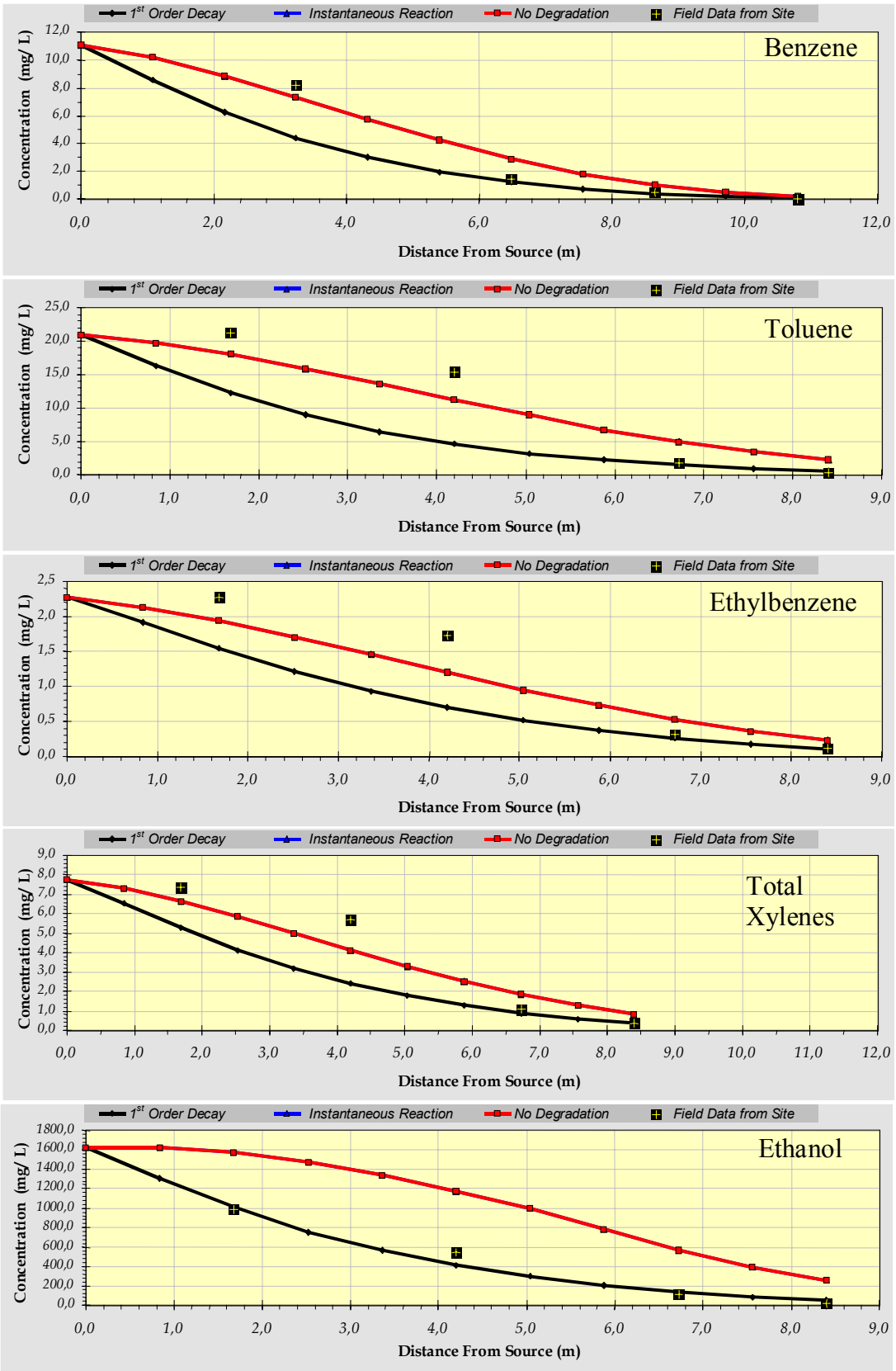

Figure 3. First-order decay curves for BTEX and ethanol fitted to field data in Bioscreen model.
first-order biodegradation no biodegradation

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