

WEATHERING OF ETHANOL-BLENDED GASOLINE IN AQUIFERS – A FIELD EXPERIMENT

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ABSTRACT: This paper presents results of a gasohol controlled release experiment to evaluate the effect of ethanol on BTEX weathering near the source zone. Results indicate that ethanol has a major influence on the BTEX mass flux reduction. In the following nine months after ethanol was weathered, BTEX mass flux was reduced by 60%. This indicates that BTEX plumes may expand while ethanol is present at the source zone, thus limiting the effect of natural attenuation of the monoaromatic hydrocarbons.

INTRODUCTION

Groundwater plays an important role as water supply for urban and rural areas in Brazil. According to the 2000 National Basic Sanitation Research, more than 60% of the municipalities in the country use groundwater for drinking purposes. However, groundwater quality has deteriorated due to sources such as buried deposits of hazardous wastes, leaking landfills, and spills from transport and storage of petroleum products. In Brazil there are more than 32 thousand gas stations. In 2003 more than 21.6 million cubic meters of gasoline were sold in the country (National Petroleum Agency, 2003); however, there are no precise statistics about the number of impacted areas due to underground storage tank spills.

Ethanol-blended gasoline has been used in Brazil for 25 years. Currently ethanol is used as the sole fuel or is mixed with gasoline (20–26%). Its use has increased in the country since last year, when the automobile industry started to sell flex-fuel cars that run on both fuels. In the United States, ethanol's presence in groundwater will probably be more frequent due to the incentives for expanding its use as an automotive oxygenated fuel (Powers et al., 2001). Although ethanol plays an important role in air pollution prevention, in the case of subsurface spills, it may increase the aqueous mass of hydrocarbons due to cosolvency (Corseuil et al., 2004) and may also inhibit BTEX biodegradation (Corseuil et al., 1998, Corseuil and Fernandes, 1999 and Powers et al., 2001).

Once released into the aquifer, the petroleum hydrocarbons are subject to natural processes such as dissolution, volatilization, and biodegradation. These processes together are known as weathering (Farhat, 2002, Douglas et al., 1996). The knowledge of source weathering rates is important to better predict plume lengths when risk assessment models are used. Little information is available with regard to weathering of BTEX in gasohol spills. In this context, this work evaluates the effect of ethanol's presence on the BTEX flux near the source zone on the basis of results from a controlled release experiment.

MATERIALS AND METHODS

Study Site. 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 12 m x 30 m. The source zone was created in an area of 2 m x 1 m that was excavated up to 0.5 m below the water table where 100 L of commercial gasoline containing 24% ethanol was spilled in December 1998. 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. 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 (depths varying from 1.0 m to 4.5 m) were installed to delineate the longitudinal distribution of the contaminants. Two wells (MW-04 and MW-05) that are the closest to the source were taken as representative for evaluating BTEX and ethanol decay at the source. Figure 1 presents the layout of the experimental area.

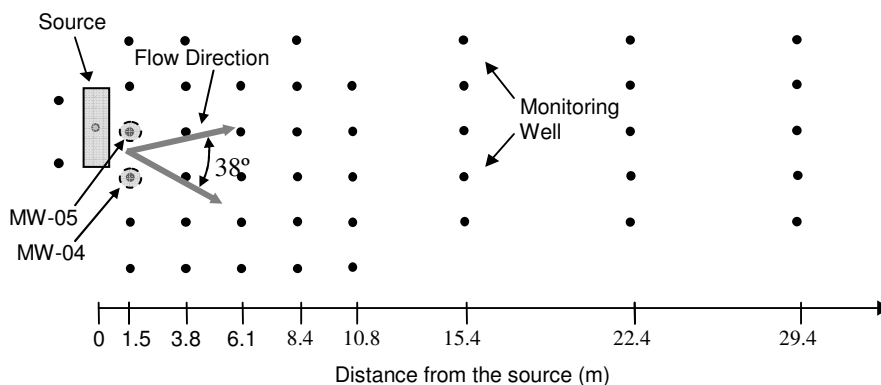


FIGURE 1. SITE MAP WITH THE LOCATIONS OF MONITORING WELLS

Source Weathering. The method used to estimate BTEX and ethanol source weathering was the mass flux approach (Borden et al., 1997; Kao and Wang, 1999). A simplified mass balance procedure was accomplished by using the differences in total contaminant mass flux across the two monitoring wells (MW-04 and MW-05) located in front of the source (Figure 1). The mass flux (F_i) associated with the monitoring wells was calculated as:

$$F_i = C_i \cdot A_i \cdot v_x \quad (1)$$

where C_i is the contaminant concentration at a designated polygon i , A_i is the area of the designated polygon (influence area), and v_x is the groundwater flow

velocity. A mass flux first-order decay model was used to estimate BTEX weathering rates:

$$F = F_0 \cdot \exp(-k \cdot t) \quad (2)$$

where F is the total mass flux through the MW-04 and MW-05 wells at a distance of 1.5 m from the source in time t , F_0 is the initial mass flux at the source, and k is the weathering rate constant. The mass distribution over the wells was given by Theissen's Polygon technique (Borden et al., 1995). Figure 2 presents the discrete sampling points and the influential areas for the cross-section at 1.5m from the source. The mass flux for each polygon was calculated and the total mass flux was given from the sum of polygons.

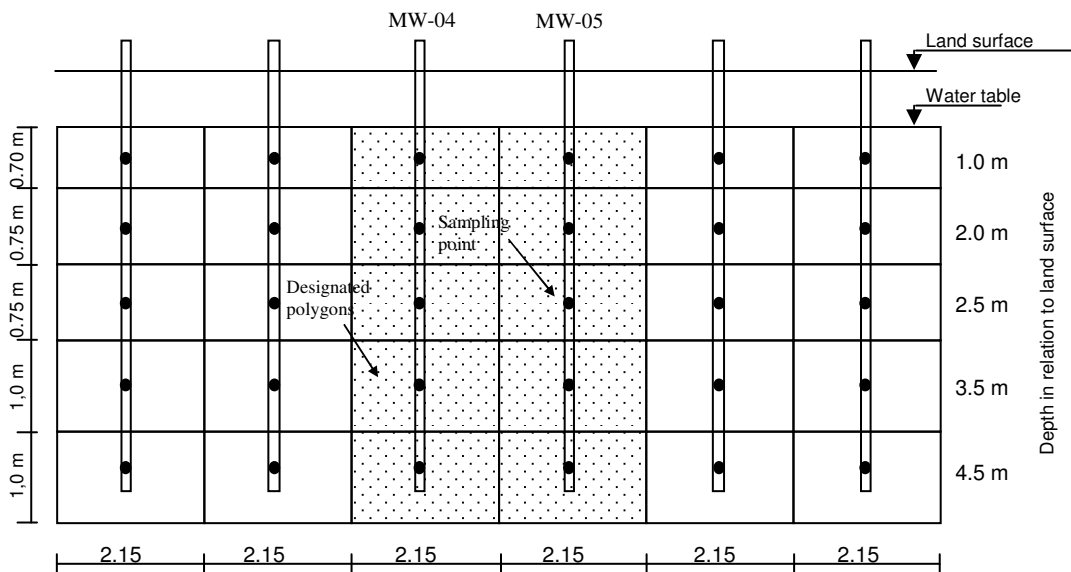


FIGURE 2. DIAGRAM SHOWING THE CROSS-SECTION WITH DISCRETE SAMPLING POINTS AND DESIGNATED POLYGONS (INFLUENCE AREAS).

RESULTS AND DISCUSSION

The results of BTEX and ethanol mass flux variation in the source during the 5.7 years since the start of the controlled release spill are presented in Figure 3. In the first three years ethanol was still present near the source zone and the BTEX flux was still increasing. BTEX flux reduction occurred only after the complete depletion of ethanol, due to its preferential biodegradation. Nine months after ethanol was weathered from the source zone, favorable geochemical conditions were reestablished, which increased the dissolved BTEX weathering kinetics, and reduced the total BTEX flux by almost 60%.

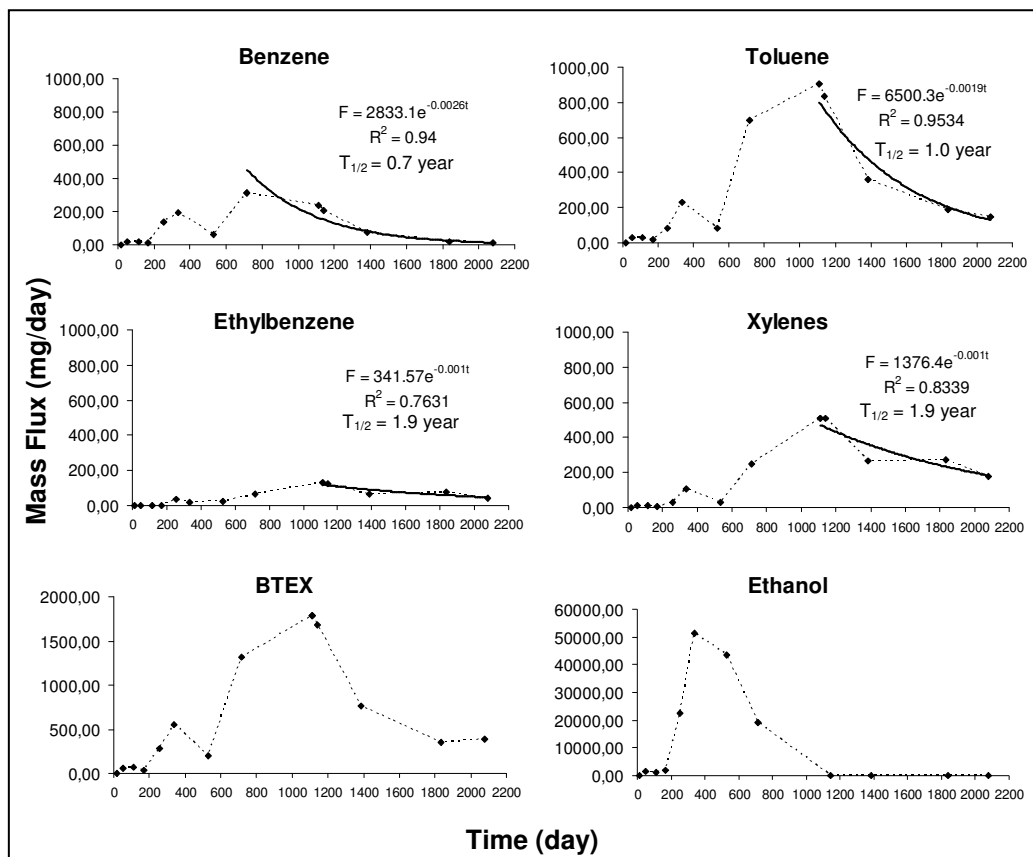


FIGURE 3. ETHANOL AND BTEX MASS FLUXES. FIRST-ORDER DECAY MODEL WAS FITTED TO MASS FLUX DATA AFTER ETHANOL WAS WEATHERED FROM SOURCE ZONE

After 5.7 years since the start of the experiment, the mass flux of benzene, toluene, ethylbenzene, total xylenes and total BTEX reduced, respectively, by 93, 84, 68, 65 and 78%. These mass flux reductions indicate that the 100 L of gasohol initially spilled in the area is been weathered, preventing the transport of the monoaromatic hydrocarbons away from the source zone and reducing the risk of exposure by yielding smaller dissolved plumes.

The estimated time for BTEX weathering in the source was obtained from fitting a first-order model to the mass flux after the period in which ethanol was depleted. The results indicated that the half-life of benzene, toluene, ethylbenzene and xylenes (mixed isomers) were 0.7, 1.0, 2.0 and 2.0 years, respectively. These rates, however, are only valid if ethanol is not present any more near the source zone.

CONCLUSIONS

Results of a controlled release experiment with gasohol, monitored for more than 5 years, indicate that the presence of ethanol prevents the weathering of BTEX flux near the source zone. This effect is more critical for benzene, which, among the BTEX compounds, has a higher dissolution rate and is also the most

difficult to be degraded in the presence of ethanol. Even though ethanol is considered an easily degraded compound, it was present near the source zone for three years. After its weathering from the source zone, BTEX mass flux was reduced by 60% in the following 9 months. Five and a half years since the experiment was initiated benzene mass flux was reduced by 93% from its peak and is now almost completely attenuated.

The significance of the ethanol effect on mass flux reduction is site specific and dependent on the size and duration of the release scenario, as in the case of a continuous gasohol spill, since the longer the presence of ethanol in the source zone, the longer may be the time for mass flux reduction to start to take place.

ACKNOWLEDGEMENTS

This research was sponsored by Petróleo Brasileiro S.A. and CNPq.

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