

## SIMULTANEOUS SPILLS OF DIESEL AND ETHANOL — A CONTROLLED-RELEASE EXPERIMENT

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**ABSTRACT:** Natural attenuation was investigated in a controlled release experiment to simulate simultaneous spills of ethanol and diesel in Florianópolis, Santa Catarina, Brazil. Results of four field-monitoring campaigns indicate that the highest aqueous ethanol concentration was on the order of 10,000 mg/L, which suggests that cosolvency is not enhancing the solubilization of BTEX and PAHs in the aquifer. After 18 months since the beginning of the spill, the concentrations of BTEX and PAHs are still increasing near the source zone and most of the ethanol was biodegraded. However large concentrations of acetate in the area caused a decrease of one order magnitude in pH. The presence of large concentrations of acetate and methane in the experimental area indicate that BTEX and PAHs degradation is being hindered by the presence of ethanol and its biodegradation products.

### INTRODUCTION

Brazil has developed the most significant program of ethanol use as fuel in the world. Since ethanol is used in vehicles as sole fuel (hydrated) or is mixed with 20–26% in gasoline (anhydrous) all over the country, most gas stations (about 30,000 in the country) and terminals have storage tanks containing hydrated ethanol, gasohol and diesel oil. Currently, there is a big incentive worldwide to increase the use of oxygenates in fuels. In Brazil, due to the high gasoline prices, it is increasing again the number of cars running only on hydrated ethanol, and the government is testing the possibility to add 8% ethanol on diesel. In this case, it is possible that simultaneous spills of hydrated ethanol and diesel may reach the water table, where high aqueous concentrations of ethanol can enhance the solubility of BTEX and PAHs and hinder biodegradation of these hazardous chemicals in the aquifers (Corseuil et al. 1998; Powers et al., 2001).

With the increasing number of areas contaminated with petroleum hydrocarbons in the country, there is a need to find low cost solutions to clean up these areas taking in consideration the characteristics of our fuels. The presence of ethanol in groundwater makes the scenario more complicated since ethanol can increase the plume length of the most toxic contaminants (Corseuil et al. 2000). One of the technologies that are frequently used in soil and groundwater remediation is natural attenuation. However, little information is still available about the impact of ethanol on biodegradation of BTEX and PAHs in groundwater. The objective of this study is to present results of an on going natural attenuation controlled release field experiment that simulates a simultaneous release of diesel oil and hydrated ethanol in groundwater.

### METHODOLOGY

The experiment was set up at Ressacada, the Federal University of Santa Catarina experimental farm, in Florianópolis, SC, Brazil where the university and Petrobras, the

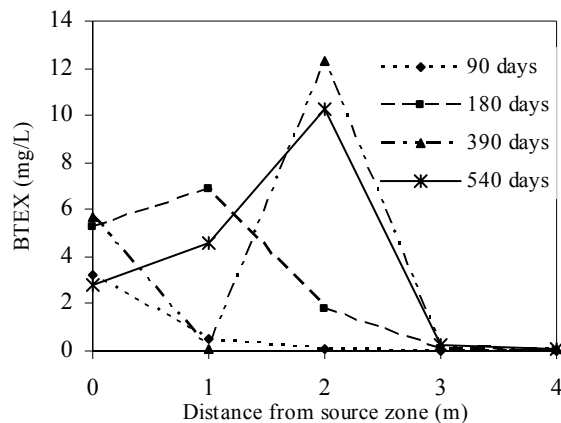
Brazilian Oil Company, have a field study area to evaluate impacts of different types of fuels and ethanol in the subsurface. The source zone was created in an area of 2m x 1m that was excavated 0.5 m below groundwater table where 20 L of diesel, 20 L of hydrated ethanol and 1 Kg of potassium bromide were spilled in January 2001. In the area, 23 multilevel piezometers were installed to delineate the distribution of BTEX and PAHs in the aquifer. Changes in groundwater characteristics due to biological processes were followed by OD, pe, alkalinity, acidity, nitrate, iron II, sulfate, acetate and methane analyses.

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 soil organic carbon content is 0.06%. Depth to the seasonal water table is approximately 1 m and the measured groundwater temperature in the aquifer is approximately 25°C. Groundwater velocity in the experimental area is 6.6 m/year. Four sampling campaigns were made since January, 2001.

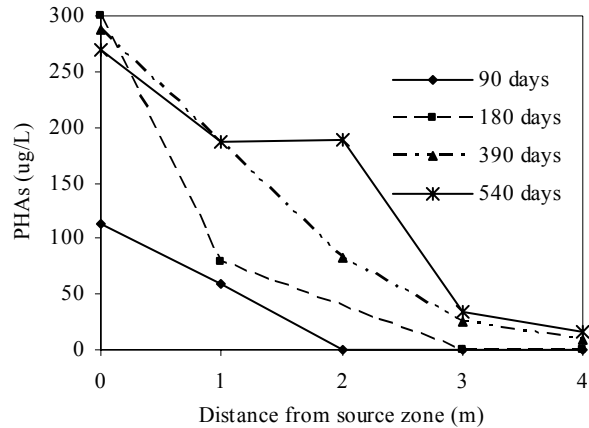
## RESULTS AND DISCUSSION

Results of aqueous BTEX and PAHs concentrations near the source zone in the preferential direction of groundwater flux are presented in Figures 1 and 2. Even though it is usually said that the monoaromatic hydrocarbons are present in minor concentrations in diesel, total BTEX concentrations of more than 12 mg/L were found after 390 days since the start of the experiment (Figure 1) and benzene was the aromatic hydrocarbon present at the highest concentration (5 mg/L). Trace levels of all BTEX were found 14 meters from the source zone after 540 days.

The maximum concentration of PAHs (300 µg/L) was obtained at the source zone (Figure 2) where concentrations are still increasing after 540 days. Among the PAHs, naphthalenes are present at the highest concentrations (170 µg/L) in groundwater and are spreading away from the source zone and also detected 14 meters downgradient.



**FIGURE 1. Total BTEX (mg/L) in groundwater - four sampling campaigns.**



**FIGURE 2. Total PAHs aqueous concentrations (µg/L) in four sampling campaigns.**

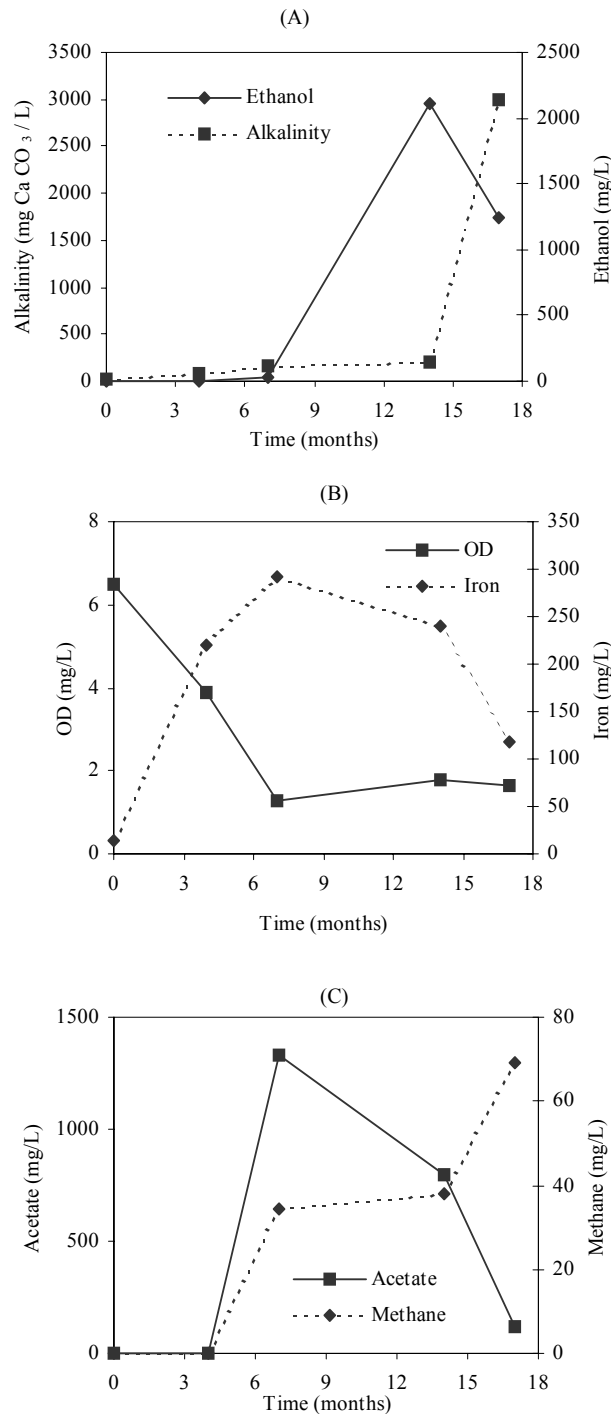
The highest ethanol concentration near the source zone was 9,600 mg/L. This concentration is about 50% lower than the maximum ethanol concentration that would be obtained if all the ethanol released were instantaneously transferred to groundwater and is not sufficient to cause the cosolvency effect problem (Corseuil et al, 1999). After 390 days, most of the ethanol had moved away from the source zone (Figure 3A). After 540 days, the highest concentration of ethanol in the experimental area was 1,740 mg/L. Traces of ethanol were detected 14 meters from the source. As was also observed in the controlled release experiment with gasohol (Corseuil et al, 2000), ethanol was still present in the aquifer 18 months after the contamination, which indicates that the low levels of nutrients present in the groundwater reduced ethanol biodegradation rate.

Ethanol in groundwater accelerated the consumption and depletion of dissolved electron acceptors. Figure 3B and C shows that near the source zone, a sharp decrease of dissolved oxygen, an increase of iron II and methane, indicating that that aerobic degradation, iron reduction and methanogenesis were the main biodegradation processes in the site. Methane and acetate concentrations of 140 mg/L and 1330 mg/L, respectively, were detected in the experimental area. The highest concentrations of acetate and methane occurred, respectively, 180 days and 540 days after contamination. Production of acetate also caused a pH decrease of one order of magnitude in groundwater and an increase in acidity and alkalinity increased in the area after the degradation of acetate.

## CONCLUSION

Analysis of a diesel and ethanol controlled release experiment indicates that natural attenuation is occurring in the area. However, the presence of ethanol in groundwater consumes electron acceptors and nutrients that could be available for bioattenuation of the mono and polycyclic aromatic hydrocarbons. Geochemical indicators show that aerobic degradation, iron reduction and methanogenesis are the biological processes responsible mainly for degradation of the ethanol. While ethanol was being degraded, the aqueous concentrations of BTEX and PAHs were increasing downgradient of the source zone. Preferential degradation of ethanol is indicated by the large increase of acetate and the pH decrease of one order of magnitude in the experimental area. The presence of large concentrations of methane after 540 days of the

contamination shows that BTEX and PAHs plumes may have a long lag phase before biodegradation becomes the dominant mechanism for these compounds attenuation. This lag phase in the contaminated area prior to biodegradation will be dependent not only on degradation rates of ethanol, but also of its byproducts acetate and methane.



**FIGURE 3. Biogeochemical indicators and ethanol at 1.4 meters from source zone.**

## ACKNOWLEDGMENTS

This research is sponsored by Cenpes-Petrobras Research Center, Financiadora de Estudos e Projetos -FINEP and Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq.

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