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Assessing Natural Attenuation of Diesel/Biodiesel Mixtures Spills in Groundwater

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Keywords: Monitored Natural Attenuation, Biodiesel, Groundwater.

INTRODUCTION

Implementing the use of biodiesel in the transport sector was one of the solutions found to decrease the amount of greenhouse gases generated by fossil fuels. Although biodiesel is considered a renewable and biodegradable fuel, it is well known that fuel storage and distribution systems are usually located underground and, in case of a spill, little is known about the real impacts from biodiesel and diesel/biodiesel mixtures interacting with soil and groundwater. The introduction of biodiesel in the Brazilian fuel market took place in 2005 and, since July 2009, it is added to commercial diesel oil at an obligatory minimum proportion of 4% in volume. Taking these facts into account, 100L of pure soy biodiesel (B100) and 100L the B20 mixture (20% in volume of methylic biodiesel derived from soy oil and 80% in volume of fossil diesel) were released in a controlled way to the subsurface of an experimental area in order to assess the natural attenuation of B100 and B20 in the subsurface environment and the influence of biodiesel compounds on the transport and fate of the main fossil diesel aromatic hydrocarbons (BTEX and PAH).

MATERIALS AND METHODS

This study is being conducted at the Experimental Farm of Ressacada, in Florianópolis, 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. Average groundwater temperature is 26°C in the summer and 22°C in the winter. The subsurface soil at the site is uniform gray fine sand with less than 5% of silt and clay. Depth to the seasonal water table is approximately 2.0 m and groundwater flow velocity is approximately 6 m/yr. For each experiment (B100 e B20), 36 multilevel wells were installed for monitoring groundwater (depths varying between 2-6 m) in an area of 10mx20m. In order to assess B100 and B20 natural attenuation, the main contaminants dissolved in groundwater (BTEX and PAHs), as well as the indicators of biodegradation (O_2 , NO_3^- , N_2 , Fe^{+2} , SO_4^{-2} , S^{-2} , CH_4) are being monitored over time. Acetic, propionic and butyric acids are also being monitored as metabolic byproducts of the soy oil esters (methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate).

RESULTS

Several studies have demonstrated the negative impact of ethanol-amended gasoline mixtures in gasoline in case of groundwater contamination. Ethanol can retard natural hydrocarbon degradation in groundwater due to the depletion of the electron acceptors pool. In case of mixtures of soy oil and diesel, soy oil will also be degraded prior to the aromatic hydrocarbons. However, ethanol and soy oil have completely different solubilities in water. Ethanol being completely miscible in water will partition to the aqueous phase and will be transported away from the source zone. Soy oil, on other hand, is immiscible in water and

will tend to stay at the source zone mixed with the petroleum hydrocarbons. Therefore, in case of subsurface spills with mixtures of biodiesel and diesel, the effect of soy oil on aromatic hydrocarbons degradation in groundwater may be completely different than the effects that are being observed for ethanol-amended gasoline spills.

The controlled release experiments started in June 2008. The degradation of soy oil in groundwater should change geochemical conditions towards more reduced conditions, which are usually more unfavorable for degradation of the aromatic hydrocarbons. Results indicated that after 430 days since the release, evidences of soy oil fermentation occurred only in the experiment with pure soy oil (B100), since redox conditions were negative (-100 mV) and acetic acid concentrations of up to 100 mg/L were found near the source zone. In the experiment with diesel/biodiesel mixture (B20) no significant concentrations of soy oil ester byproducts were observed in 430 days and increases in BTEX concentrations near the source zone indicate that dissolution rates are more significant than biodegradation for the monoaromatic hydrocarbons (Figure 1). Methane concentrations were lower than 3 mg/L in both experiments.

Since degradation of soy oil in the subsurface in 1.2 years is still shifting the experiment groundwater geochemical conditions towards methanogenesis, it is possible to envision that degradation of the aromatic hydrocarbons would be delayed, increasing the risk associated with potential exposure. A better understanding of the dynamics of soy oil esters biotransformation associated with the effects on BTEX and PAHs degradation will depend on the long term monitoring of the experiments. Careful attention should be given to spills of biodiesel/diesel mixtures in groundwater, since remediation costs could be more difficult and costly than conventional diesel.

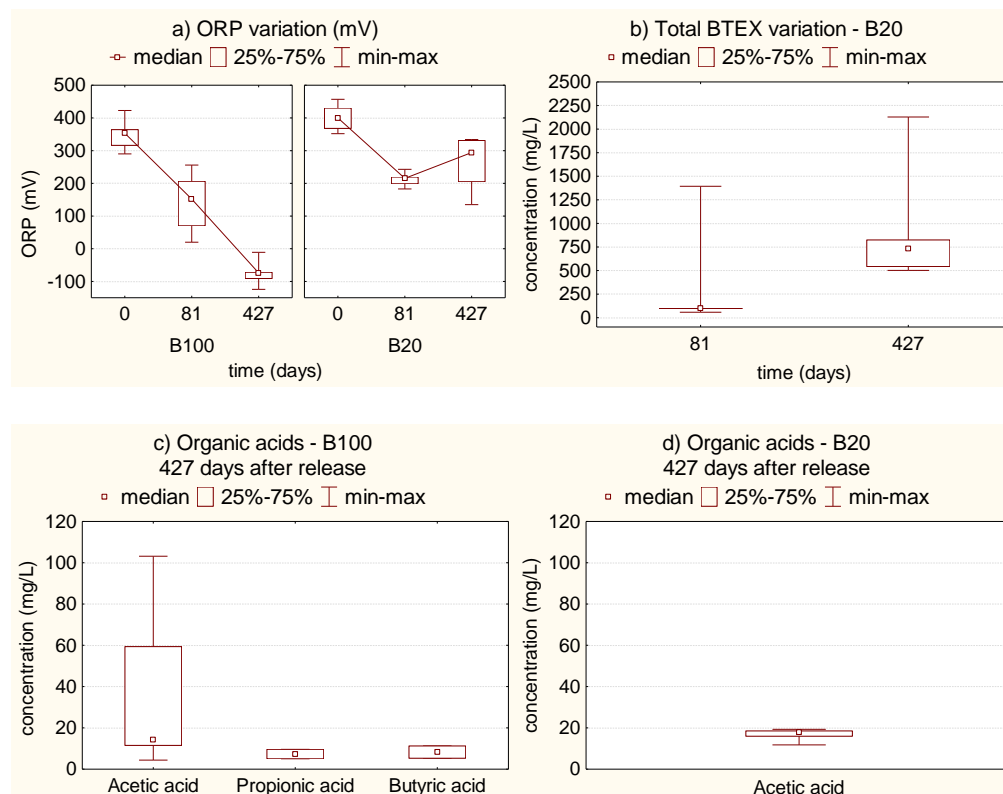


Figure 1- Hydrogeochemical concentrations (redox potential, total BTEX and organic acids in the experimental areas – (B100) pure soy oil – (B20) 20% soil oil and 80% diesel

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Abstract In case of accidents involving releases of pure biodiesel or blends of diesel/biodiesel on the environment, little is known about the real impacts from these mixtures interacting with soil and groundwater. In order to assess the natural attenuation of B100 and B20 in the subsurface environment and the influence of biodiesel compounds on the transport and fate of the main fossil diesel aromatic hydrocarbons, two independent experiments (started in June 2008) are being undertaken at Ressacada Farm, SC, Brazil. Preliminary results show evidence of soy biodiesel anaerobic degradation in the B100 experiment (negative redox conditions and acetic acid concentrations of up to 100 mg/L). In the B20 experiment, a lower acetate concentration was observed and the BTEX concentrations are still increasing after 1.6 years near the source zone. Although results are still preliminary, it is recommended that remediation technologies for these biofuels should prioritize the removal of the easily biodegradable esters and implement the monitoring of acetate and hydrogen, which can be considered the main thermodynamic constraints for biodegradation of aromatic hydrocarbons from diesel under fermentation/methanogenic conditions.

Keywords Biodiesel; Groundwater; Monitored Natural Attenuation.

INTRODUCTION

Implementing the use of biodiesel in the transport sector was one of the solutions found to decrease the amount of greenhouse gases generated by fossil fuels. The introduction of biodiesel in the Brazilian fuel market took place in 2005 and, since January 2010, it has been added to commercial diesel oil at an obligatory minimum proportion of 5% in volume (Brazil, 2009). Although biodiesel is considered a renewable and biodegradable fuel, it is well known that fuel storage and distribution systems are usually located underground and, in case of a spill, little is known about the real impacts from biodiesel and diesel/biodiesel mixtures interacting with soil and groundwater.

Several studies have demonstrated the negative impact of ethanol on monoaromatic hydrocarbon biodegradation in the case of ethanol-blended gasoline groundwater contamination (Corseuil and Alvarez, 1996; Corseuil et al., 1998; Corseuil et al., 2004; Corseuil et al., 2005). Ethanol can retard natural hydrocarbon degradation in groundwater due to the depletion of the electron acceptor pool. In case of mixtures of biodiesel and diesel, biodiesel will also be degraded prior to the aromatic hydrocarbons. However, ethanol and biodiesel have completely different solubilities in water. Ethanol being completely miscible in water will partition to the aqueous phase and will be transported away from the source zone. Biodiesel, on the other hand, is immiscible in water and will tend to stay at the source zone mixed with the petroleum hydrocarbons. Therefore, in case of subsurface spills with mixtures of biodiesel and diesel, the effect of biodiesel on aromatic hydrocarbon degradation in groundwater may be completely different than the effects that are being observed for ethanol-amended gasoline spills.

Laboratory-scale studies in marine environments showed that pure biodiesel (B100) aerobically degrades much faster than fossil diesel (B0). In a diesel/biodiesel mixture, the microorganisms use biodiesel as an energy source to promote degradation of fossil diesel and apparently metabolize esters of biodiesel and the aliphatic chains from fossil diesel at the same time and same rates (Zhang et al., 1998; DeMello et al., 2007; Prince et al., 2008). However, for the aromatic compounds that constitute diesel, increases in biodegradation rates only can be observed after complete biodegradation of biodiesel. Therefore, at first, biodiesel negatively influences the degradation of aromatic compounds from diesel (Gomes, 2008).

Experiments related to the ethanol influences on biodegradation of petroleum compounds, like gasoline, indicated that larger bioavailability of ethanol and its easy degradation makes this compound preferentially degraded compared to the gasoline hydrocarbons, which leads to an increase of biomass activity in groundwater. In field experiments, Nunes and Corseuil (2007) suggest that the rapid decay of BTEX concentrations near the source of contamination, after exhaustion of ethanol, could be attributed to the increasing of biomass stimulated during ethanol biodegradation. Likewise, the higher biodegradability of biodiesel could stimulate the activity of microorganisms, increasing the degradation of diesel compounds in diesel/biodiesel mixtures.

Other laboratory experiments have shown that the molecular structures of biodiesel esters are very similar to those of the surfactants compounds. Therefore, in mixtures with diesel where biodiesel is present at rates above 20% in volume, esters can reduce the oil-water interfacial tension. This effect could increase the rate of diesel hydrocarbons dissolution in the water, which can facilitate transport and intensify the impacts of contamination. On the other hand, increases in the rate of dissolution of hydrocarbons allows for greater bioavailable, which can promote its degradation (Taylor and Jones, 2001).

Taking these facts into account, 100 L of pure soy biodiesel (B100) and 100 L of the B20 mixture (20% in volume of methylic biodiesel derived from soy oil and 80% in volume of fossil diesel) were released to the subsurface in two controlled and independent experiments in order to assess the natural attenuation of B100 and B20 in the subsurface environment and the influence of biodiesel compounds on the transport and fate of the main fossil diesel aromatic hydrocarbons (BTEX and PAH).

METHODS

This study is being conducted at the Experimental Farm of Ressacada, in Florianopolis, Brazil. The regional geology is characterized by unconsolidated deposits of eolian, alluvial, lacustrine and marine sands. The regional climate in Florianopolis is humid mesotermic with a mean annual precipitation of 1530 mm. Average groundwater temperature is 26°C in the summer and 22°C in the winter. The subsurface soil at the site is uniform gray fine sand with less than 5% of silt and clay. Depth to the seasonal water table is approximately 2.0 m and groundwater flow velocity is approximately 6 m/yr. For each experiment (B100 e B20), 36 multilevel wells were installed for monitoring groundwater (depths varying between 2-6 m) in an area of 10 m x 26 m (Figure 1). In order to assess B100 and B20 natural attenuation, the main contaminants dissolved in groundwater (BTEX and PAHs), as well as the indicators of biodegradation (O_2 , NO_3^- , N_2 , Fe^{+2} , SO_4^{-2} , S^{-2} , CH_4) are being monitored over time. Acetic, propionic and butyric acids are also being monitored as metabolic byproducts of the soy biodiesel esters (methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate).

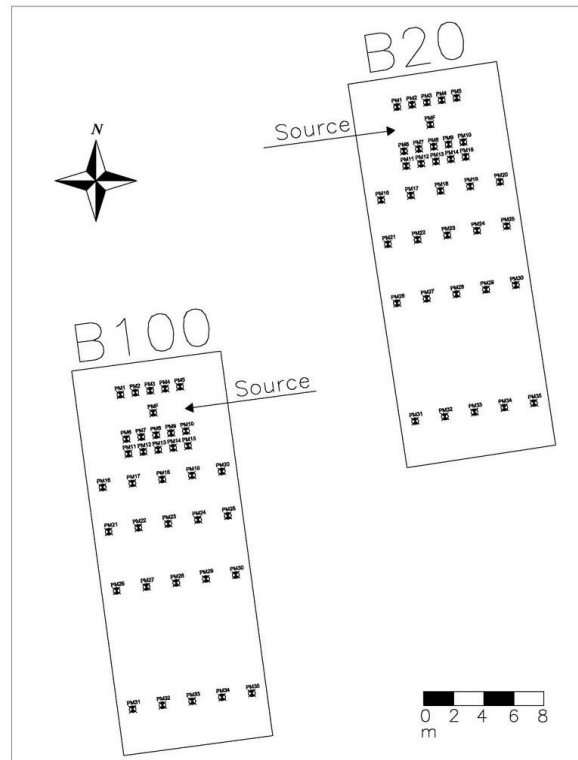


Figure 1- Experimental areas where the studies with B100 and B20 have been conducted.

RESULTS AND DISCUSSION

The controlled release experiments started in June 2008. After 430 days, results indicated evidence of soy biodiesel anaerobic degradation occurring only in the experiment with pure soy biodiesel (B100), since redox conditions were negative (Figure 2) and acetic acid concentrations, of up to 100 mg/L, were found near the source zone (Figure 4A). In the experiment with diesel/biodiesel mixture (B20) the redox conditions became negative only after 600 days and lower concentrations of soy biodiesel degradation byproducts were observed during this period (Figures 2 and 4B, respectively). Furthermore, in the experiment with B20, increases in BTEX concentrations near the source zone indicate that dissolution rates are more significant than biodegradation for the monoaromatic hydrocarbons (Figure 3), which is indicative of continuing plume migration. Methane concentrations were lower than 3 mg/L in both experiments after 430 days and continued to increase reaching levels higher than 5 mg/L after 600 days.

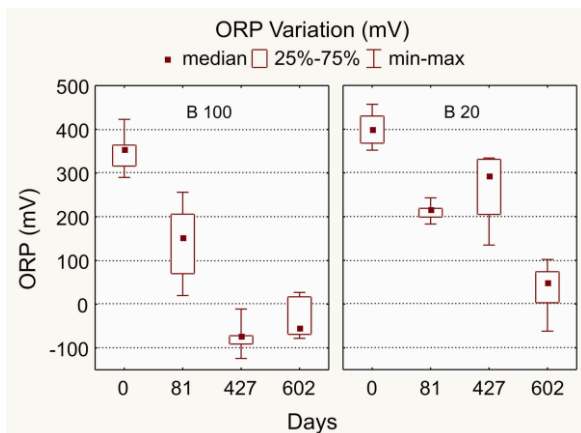


Figure 2 – redox potential results for B100 and B20 experiments.

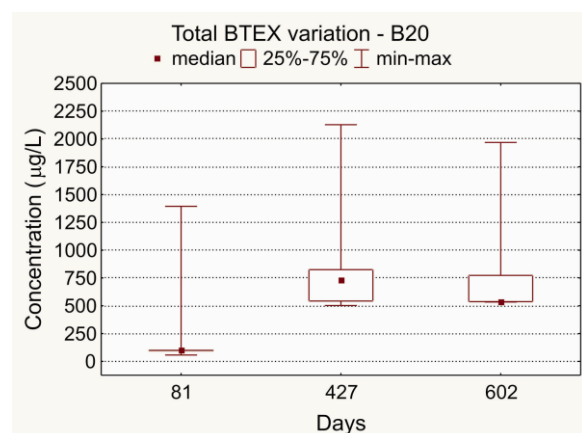


Figure 3 – Total BTEX concentration in the B20 experiment.

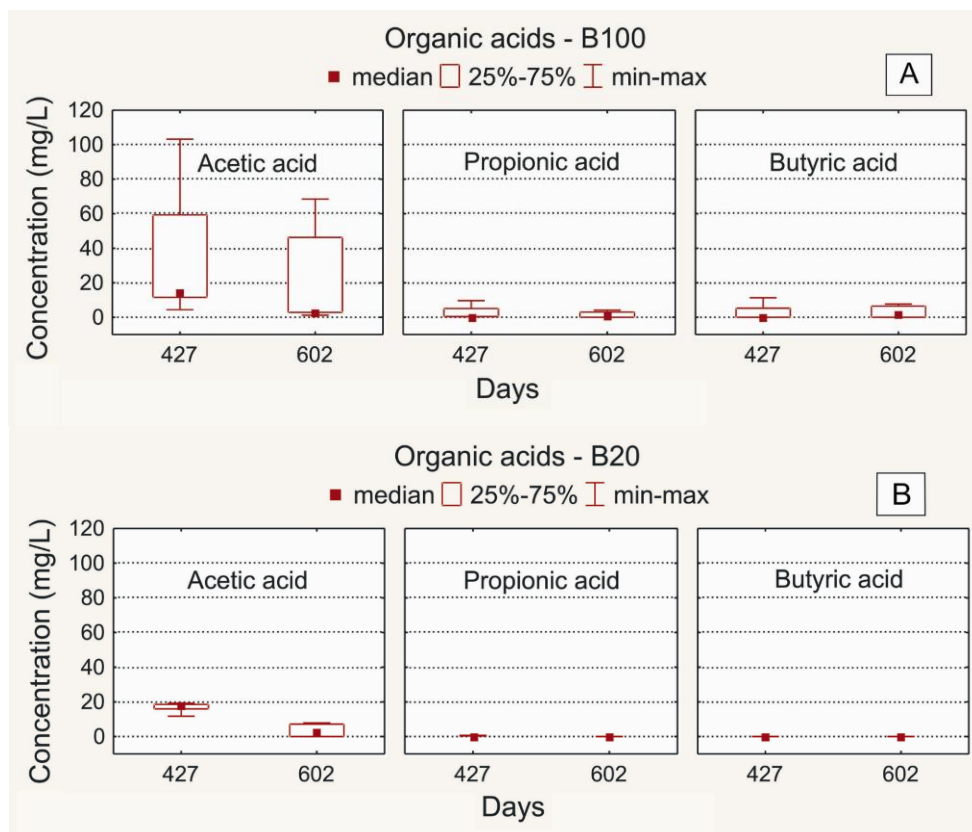


Figure 4 – Organic acids concentrations A) in the experiment with pure soil oil (B100) and B) in the experiment with B20 mixture.

The degradation of soy biodiesel in groundwater should change geochemical conditions towards more reduced conditions, as observed for gasohol spills. Ethanol exerts a biochemical oxygen demand much higher than the amount of oxygen available in groundwater, making the environment anoxic, which is usually more unfavorable for degradation of the aromatic hydrocarbons. Based on this context, Gomes (2008) has calculated the oxygen consumption in case of a biodiesel contamination in groundwater using McCarty's biodegradation energy model (McCarty, 1969). For a spill of one litre of biodiesel and one litre of ethanol, the theoretical oxygen demand to degrade biodiesel will be two times greater than that necessary to degrade ethanol. Therefore, anaerobic degradation will prevail in subsurface spills with blends of biodiesel and diesel. In an anaerobic environment, biodiesel components are first hydrolyzed to free LCFAs and then converted to acetate (or to a lesser extent propionate and butyrate) and hydrogen through the β -oxidation pathway (syntrophic acetogenesis) and ultimately to methane (Weng and Jeris, 1976). In the field experiments at Ressacada acetate concentrations are much higher than those of propionate and butyrate (Figure 4A and 4B). Acetate concentrations in the aqueous phase, near the source zone, are even higher (up to 100 mg/L) when the volume of biodiesel is greater (100 L) (Figure 4A).

Whereas the reactions of acetate production are endergonic, the metabolic processes of biodiesel will only be thermodynamically favorable in environmental conditions ($\Delta G' < 0$) if the reaction products (hydrogen and acetate) remain at low concentrations. For this, the syntrophic degradation of acetate will depend on the removal of hydrogen from the liquid medium by the hydrogenotrophic methanogenic bacteria. Thus, the accumulation of acetate and/or hydrogen in the dissolved phase can lead to thermodynamic inhibition of the fermentation process of aromatic compounds from diesel.

CONCLUSIONS

Although the results are preliminary and the field experiments are ongoing, there is evidence of anaerobic biodegradation occurring with pure soy biodiesel, mainly due to the negative redox conditions and high acetate concentrations found near the source zone. Regarding the B20 experiment, even after 1.6 years, biodegradation of soy biodiesel, in the subsurface, is still shifting the groundwater geochemical conditions towards methanogenesis. Therefore it is possible to envision that degradation of the aromatic hydrocarbons would be delayed, increasing the risk associated with potential exposure of groundwater to contamination.

Since the biochemical oxygen demand exerted by the esters will be higher than that exerted by soluble compounds of diesel, reducing processes should be more efficient for the remediation of diesel/biodiesel contaminated areas. In this sense, remediation technologies should target the rapid removal of the easily degradable esters through a process that will speed up the conversion of biodiesel esters to acetate. Monitoring acetate and hydrogen concentrations would be of utmost importance as they are the main thermodynamic constraints of the syntrophic process. Detection of high acetate and hydrogen concentrations may indicate that biodegradation of aromatic compounds is not occurring. A better understanding of the dynamics between soy biodiesel ester biotransformation and BTEX and PAHs degradation will depend on the long term monitoring of these experiments. Careful attention should be given to spills of biodiesel/diesel mixtures in groundwater, since remediation efforts could be more difficult and costly than for conventional diesel.

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