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Biodiesel presence in the source zone hinders aromatic hydrocarbons attenuation in a B20-contaminated groundwater

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ABSTRACT

The behavior of biodiesel blend spills have received limited attention in spite of the increasing and widespread introduction of biodiesel to the transportation fuel matrix. In this work, a controlled field release of biodiesel B20 (100 L of 20:80 v/v soybean biodiesel and diesel) was monitored over 6.2 years to assess the behavior and natural attenuation of constituents of major concern (e.g., BTEX (benzene, toluene, ethyl-benzene and xylenes) and PAHs (polycyclic aromatic hydrocarbons)) in a sandy aquifer material. Biodiesel was preferentially biodegraded compared to diesel aromatic compounds with a concomitant increase in acetate, methane (near saturation limit ($\approx$22 mg L^{-1})) and dissolved BTEX and PAH concentrations in the source zone during the first 1.5 to 2.0 years after the release. Benzene and benzo(*a*)pyrene concentrations remained above regulatory limits in the source zone until the end of the experiment (6.2 years after the release). Compared to a previous adjacent 100-L release of ethanol-amended gasoline, biodiesel/diesel blend release resulted in a shorter BTEX plume, but with higher residual dissolved hydrocarbon concentrations near the source zone. This was attributed to greater persistence of viscous (and less mobile) biodiesel than the highly-soluble and mobile ethanol in the source zone. This persistence of biodiesel/diesel NAPL at the source zone slowed BTEX and PAH biodegradation (by the establishment of an anaerobic zone) but reduced the plume length by reducing mobility. This is the first field study to assess biodiesel/diesel blend (B20) behavior in groundwater and its effects on the biodegradation and plume length of priority groundwater pollutants.

1. Introduction

Renewable fuels, such as biodiesel and ethanol, are increasingly being added to the worldwide energy matrix and used as transportation fuels due to the environmental benefits they generally provide (e.g., reduction of atmospheric emissions and oil dependence). Biodiesel and ethanol are commonly blended with fossil fuels that contain priority contaminants (e.g., benzene and benzo(*a*)pyrene) and require remedial actions if released to the environment through accidental or incidental spills. In Brazil, the current mandatory blending percentage of ethanol to gasoline is in the range of 18–27.5%, while diesel formulations must be blended with 8% of biodiesel and are planned to increase to 15% by 2020 (National Council of Energy Policy – Brazil, 2016). Furthermore, the voluntary use of biodiesel blends (with biodiesel content above the mandatory limit) was recently authorized (National Council of Energy Policy – Brazil, 2015). While the influence of ethanol on BTEX (benzene, toluene, ethyl-benzene and xylenes) migration and biodegradation in groundwater has been extensively studied (Corseuil et al., 1998; Powers et al., 2001; Lovanh and Alvarez, 2004; Da Silva et al., 2005; Mackay et al., 2006; Feris et al., 2008; Corseuil et al., 2011a; Ma et al., 2013; Corseuil et al., 2015; Ziegler et al., 2015), limited attention has been given towards the behavior of biodiesel blends and their effect on aromatic hydrocarbons in subsurface environments. This is an important knowledge gap because of the sharp increase in use of biodiesel over the past 10 years.

Microcosm studies have shown that biodiesel is readily biodegradable (Pasqualino et al., 2006; Mariano et al., 2008; Bücker et al., 2011; Cyplick et al., 2011; Sϕrensen et al., 2011; Yassine et al., 2012; Yassine et al., 2013b; Passman, 2013; Meyer et al., 2014; Ng et al., 2015). However, under the strongly anaerobic conditions encountered in aquifers contaminated by biodiesel blends (Corseuil et al., 2011b; Ramos et al., 2013; Smith et al., 2016), biodegradation of associated priority pollutants, such as benzene, becomes much slower, leading to their higher persistence. Potential inhibitory processes exerted by biodiesel over

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BTEX and PAHs (polycyclic aromatic hydrocarbons) biodegradation are likely similar to those attributed to ethanol: (1) preferential biodegradation (as a result of the simpler molecular structure relative to aromatic compounds), (2) faster consumption and depletion of favorable terminal electron acceptors, (3) hindered thermodynamic feasibility due to accumulation of byproducts such as acetate or hydrogen, (4) catabolite repression, and (5) metabolic flux dilution (Da Silva and Alvarez, 2002; Corseuil et al., 2011a; Lovanh and Alvarez, 2004; Corseuil et al., 2015).

Different biofuels can exhibit distinct dynamics in subsurface environments due to their different chemical structure and partitioning behavior. Ethanol is highly soluble and migrates relatively rapidly away from the source zone, and thus, contributes to BTEX plume elongation and exerts minimal long-term effects over source-zone dynamics. Conversely, biodiesel is not readily miscible and dissolves slowly into the groundwater, which is conducive to a more pronounced effect over source-zone natural attenuation. Accordingly, the behavior of biodiesel blend spills might be more complex than previously recognized. The kinetics of source-zone biodiesel dissolution and biodegradation in a groundwater aquifer might have long-term effects that are difficult to assess in microcosm studies.

In this work, a controlled field release of biodiesel B20 (20:80 v/v soybean biodiesel and diesel) was monitored over 6.2 years to characterize the behavior of BTEX and PAHs under natural attenuation. To the best of our knowledge, this is the first field study to assess the dynamics of diesel/biodiesel blend spills in groundwater.

2. Materials and methods

2.1. Field experiment

The experiment was conducted at Ressacada Experimental Farm, in Florianopolis, SC, Brazil (Latitude 27°30′ S, Longitude: 48°30′ W). Regional geology was characterized by unconsolidated deposits of aeolian, alluvial, lacustrine and marine sands (IPUF, 2004). The subsurface layer was composed by 89.7% of sand, 2.83% of silt and 7.45% of clay. Organic carbon ranges between 0.23% and 1.4%. Groundwater flow velocity was 6 m year^{-1} and effective porosity of 0.19. The climate was mesothermic humid with a mean annual precipitation of 1360 mm. Average groundwater temperature monitored over 6.2 years was 22.6 °C, with a maximum temperature of 27 °C and a minimum of 19 °C.

The controlled release experiment source zone was established by releasing 100 L of B20 (20:80 v/v soybean biodiesel and diesel) into an excavated area of 1 m^2 and 1.5 m depth (at the top of the water table). The groundwater experiment covered a 330 m^2 area with 47 monitoring wells (Fig. 1). Each well contained a bundle of 3/16″ ID polyethylene tubing for groundwater sampling at different depths (2, 3, 4, 5 and 6 m below ground surface (bgs)). A previous adjacent (240 m from the B20 experiment) 100-L release of ethanol-amended gasoline (24:76 v/v ethanol and gasoline (E24)) was used to compare the behavior of different biofuel blends in impacted aquifers. The site configuration, hydrogeological characterization and chemical analysis are detailed described in Corseuil et al. (2011a).

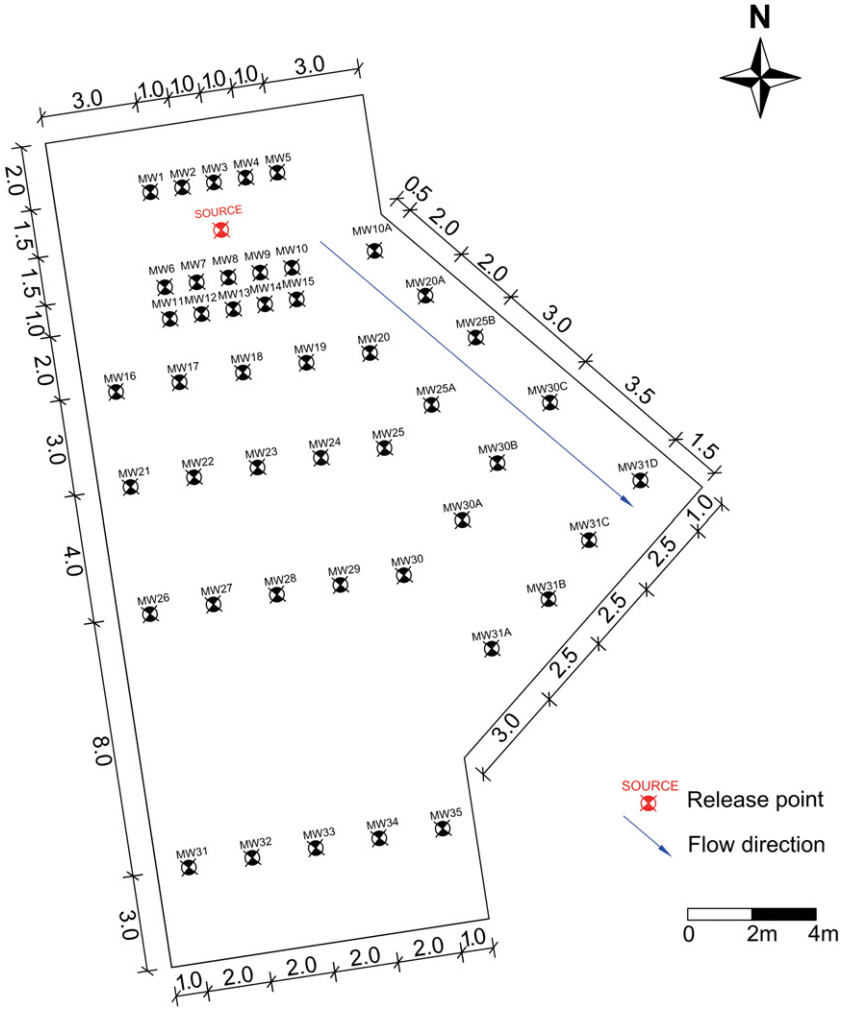

Fig. 1. Schematic view of B20 field experiment.