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 (≈ 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.

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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; Sørensen 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 m² and 1.5 m depth (at the top of the water table). The groundwater experiment covered a 330 m² 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).
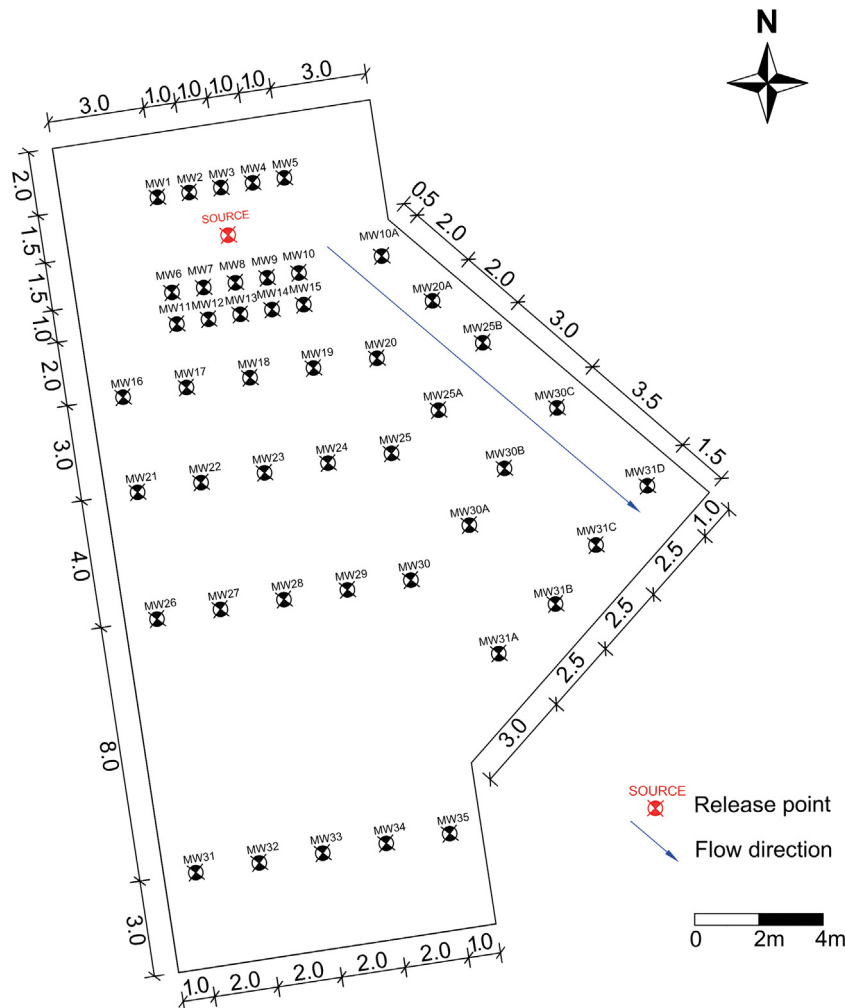

Fig. 1. Schematic view of B20 field experiment.

2.2. Chemical analysis

Groundwater was monitored by collecting samples from monitoring wells at depth 2, 3, 4, 5 and 6 m bgs with the aid of a peristaltic pump. Samples were collected into capped sterile glass vials without headspace to prevent volatilization losses. Groundwater samples for BTEX and methane were preserved in a 40-mL flask containing 1 mL of HCl (1:1). BTEX, PAHs and methane were analyzed by gas chromatography using a GC HP model 6890 II equipped with a flame ionization detector (FID) and a HP 7694 headspace auto-sampler. A HP 1 capillary column was used for BTEX and methane analysis and HP 5 capillary column for PAHs. PAHs groundwater extraction method and detection limits of each individual compound are described elsewhere (Ramos et al., 2014). Redox potential (ORP), pH, dissolved oxygen (DO) and temperature were measured on site using a Micropurge Flow Cell (MP20). Samples for acetate were collected in a 200 mL-amber flask and analyses were performed by ion chromatography using a Dionex ICS-1000 equipped with a conductivity detector and an AS14A column. Detection limits were: $1\,\mu g\,L^{-1}$ for BTEX, $10\,\mu g\,L^{-1}$, for methane, $0.1\,mg\,L^{-1}$ for acetate, $0.2\,mg\,L^{-1}$ for dissolved oxygen. Vials were packed in coolers containing ice (Termogel Ice-X mini) and kept at 4 °C during transport to the laboratory (~1 h) and analyzed shortly after arrival. Extensive information related to field experiments can be found in Corseuil et al. (2011a).

2.3. Plume contours

Benzene plume boundary was defined by the maximum contaminant level (MCL) for drinking water, established by regulatory guidelines ($5\,\mu g\,L^{-1}$) (Macler, 2007). Plume contours were based on benzene MCL since it is the most soluble BTEX compound and can migrate away from the source zone more rapidly than the other compounds. The carcinogenicity and higher aqueous solubility of benzene makes it a priority contaminant presenting greater environmental risks than the other BTEX compounds. The anaerobic zone was defined by measured DO concentrations lower than $0.5\,mg\,L^{-1}$ (according to Wiedemeier (1999) and Schreiber and Bahr (2002)).

3. Results and discussion

Under anaerobic (methanogenic) conditions, the energetic yield needed to sustain microbial growth on hydrocarbons is close to the minimum required for ATP formation (Schink, 1997), and BTEX and PAH biodegradation reactions are much slower than under aerobic conditions. The release of 100 L of B20 resulted in the development of anaerobic conditions, indicated by low measured DO concentrations (below $0.5\,mg\,L^{-1}$), a decrease in redox potential values and methane production (Fig. 2A and E), which is consistent with high biodiesel biochemical oxygen demand (BOD) previously reported (Corseuil et al., 2011b). Hence, emphasis was placed on assessing the effects of biodiesel on the anaerobic biodegradation of BTEX and PAHs.

Converging lines of evidence indicate that biodiesel was preferentially biodegraded over BTEX and PAHs, including (1) increasing dissolved concentrations of BTEX and PAHs up to 2.5 and 1.5 years after the release, respectively (Fig. 2C), (2) acetate (common metabolite of biodiesel long-chain fatty acids (LCFAs) anaerobic biodegradation (Sousa et al., 2009)) and (3) methane concentrations that exceeded nearly one order of magnitude the theoretical yield from anaerobic transformation of benzene (Lovley, 2000; Rakoczy et al., 2011) and naphthalene (Dolfing et al., 2009), thus suggesting that source of these metabolites was primarily biodiesel (Fig. 2E). Over 6.2 years, BTEX and total PAH concentrations decreased from 17,400 to $1510\,\mu g\,L^{-1}$ and from 294 to $213\,\mu g\,L^{-1}$, respectively (Fig. 2C). However, 6.2 years after the release, the concentrations of priority contaminants, such as carcinogenic benzene ($98\,\mu g\,L^{-1}$) and benzo(a)pyrene ($4.8\,\mu g\,L^{-1}$) were still substantially higher than regulatory guidelines

(5.0 and $0.2\,\mu g\,L^{-1}$ for benzene and benzo(a)pyrene, respectively) (Macler, 2007). The persistence of these aromatic compounds could be attributed to the influence of biodiesel as discussed below, although control experiments with diesel alone would be necessary to quantitatively discern the effect of biodiesel.

Biodiesel has a relatively low aqueous solubility (Krop et al., 1997) and slowly dissolves into the groundwater, and thus, behaves as a fixed and long-lived source zone (Corseuil et al., 2011b) similar to LNAPLs (light non-aqueous phase liquids) (Smith et al., 2016). In contrast, highly-soluble ethanol migrates away from the source-zone exerting a shorter-term influence on source dynamics (Corseuil et al., 2011b). These differences could affect BTEX dissolution patterns and subsequent off-source migration and biodegradation in groundwater. Biofuels high BOD generally leads to the development of anaerobic zones by exceeding natural aquifer DO recharge which in turn; can influence the extension of contaminants plume in groundwater since biodegradation rates are slower under anaerobic conditions. In the present work, the benzene plume centerline reached a maximum length of 6 m 1.6 years after the release (Fig. 3A). Comparatively, in a past adjacent 100-L release of ethanol-amended gasoline (24:76 v/v ethanol and gasoline (E24)) (Corseuil et al., 2011a), benzene temporarily migrated beyond 30 m from the source-zone and receded only after significant ethanol removal (Fig. 3A). Thus, the maximum aromatic hydrocarbon plume length was much shorter for the fuel mixed with biodiesel rather than with ethanol. Moreover, the extension of anaerobic zones is linked to biofuels dynamics and migration in groundwater, as reflected by the longer anaerobic zone plume length in E24 (up to 30 m) relative to B20 experiment anaerobic zone plume length (6 m) (Fig. 3B). Apparently, biofuels behavior in groundwater significantly influence the region of influence of hydrocarbon plumes; when diesel that is blended with biodiesel impacts groundwater, BTEX and PAHs would exhibit a shorter plume length but tend to persist with biodiesel near the source-zone.

The observed persistence of aromatic compounds in groundwater when blended with biodiesel can be explained in part by the partitioning behavior between diesel and biodiesel in water. Diesel aromatic compounds have been reported to hinder fatty acid methyl ester (FAME) partitioning and dissolution in water (Wu et al., 2015). Therefore, some biodiesel FAMEs (of relatively low water solubility) are likely to remain in the NAPL due to their relatively high viscosity, low density and hydrophobicity (Smith et al., 2016; Energy Institute, 2008). The decreased biodiesel FAMEs dissolution would result in a slower biodegradation due to reduced bioavailability (as the microbial degradation is usually facilitated in the dissolved phase) (Yassine et al., 2013a; Wu et al., 2015). Since biodiesel FAMEs would be released slowly over a relatively long period and are likely biodegraded preferentially to diesel-borne aromatic compounds, the BTEX and PAH biodegradation in the source zone will be negatively affected. Hence, the biodiesel dissolution rate from the NAPL could significantly influence the persistence of aromatic hydrocarbons in groundwater. FAMEs long-lived effects on the source and preferential biodegradation may delay the complete removal of diesel aromatic hydrocarbons as compared to spills with diesel alone. Therefore, future diesel/biodiesel blend remediation efforts should prioritize biodiesel removal (e.g. by enhancing FAMEs dissolution from the NAPL pool and providing bioavailable substrates for microbial uptake) as aromatic hydrocarbon dynamics in subsurface environments is likely controlled by biofuels dissolution and partitioning into groundwater.

While caution should be exercised against direct comparisons between E24 and B20 experiments due to the higher fraction of aromatic hydrocarbons in gasoline relative to diesel, the different length of the experiments and the opposite trends followed by biodiesel and ethanol mobility in groundwater, these experiments provide insight into the different scenarios undergone by the different biofuel blends. The rapid partitioning of the soluble ethanol to the groundwater was demonstrated by the high dissolved ethanol concentrations and its
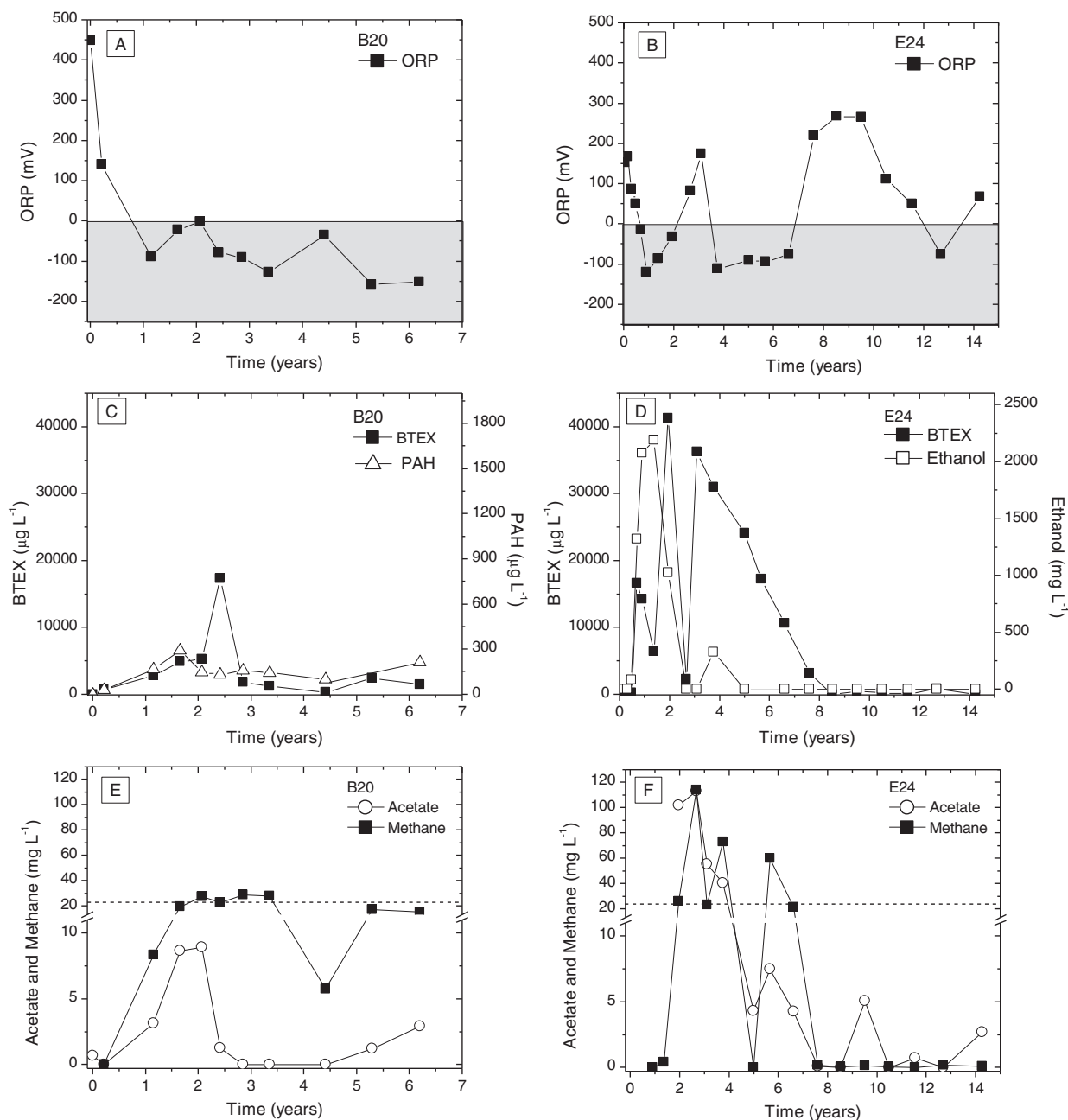
Fig. 2. Time series of geochemical footprint in the source zone groundwater of E24 and B20 releases (at depth 2 m bgs). Shaded boxes indicate negative ORP values. Dotted black lines (2E and 2F) represent the approximate methane saturation limit in groundwater (22 mg L^{-1}).

anaerobic metabolites (acetate and methane) detected after the ethanol-gasoline release (Fig. 2D and F). The poorly water-soluble biodiesel partitions considerably slower than ethanol in groundwater (Chen et al., 2015; Smith et al., 2016), as reflected by the lower acetate and methane concentrations (Fig. 2E) relative to the E24 release. Furthermore, in the E24 site, the BTEX natural attenuation rate adequately fit zero-order kinetics (determined after the onset of BTEX biodegradation) (k = 7231 μg L^{-1} year^{-1}, r^2 = 0.99). BTEX concentrations were significantly higher than reported half-velocity constants (Alvarez et al., 1991; Chang et al., 1993) which support the possible pseudo-zero order kinetics. The BTEX natural attenuation rate in B20 experiment did not fit either zero (k = 83.13 μg L^{-1} year^{-1}, r^2 = 0.02) or first order kinetics (k = 0.049 μg L^{-1} year^{-1}, r^2 = 0.009), which suggests that biodegradation was not the rate-limiting driving force and other abiotic processes (such as dissolution) might have prevailed during the 6.2 years

monitored. In both experiments, BTEX concentrations were monitored until they were relatively stable. In the E24 experiment, stable BTEX concentrations were considerably lower (between 848 and 27 μg L^{-1}, from 8 years onwards) than in the B20 experiment (between 1841 and 379 μg L^{-1}, from 2.5 years onwards) (Fig. 2C and D). The higher residual BTEX (and PAH) concentrations detected in the B20 experiment could be explained by the long-term effects of biodiesel in the source-zone. This effect was reflected by the continuous methane production near saturation limit and the negative ORP values up to 6.2 years. In contrast, in the E24 experiment, methane was depleted and ORP values were mostly positive after BTEX concentrations were stable (Fig. 2A–F). This is consistent with the shorter-term influence of ethanol on the source zone as opposed to the B20 experiment. Therefore, the longer-lasting effects of biodiesel in the source-zone may delay the complete removal of aromatic hydrocarbons leading to higher residual
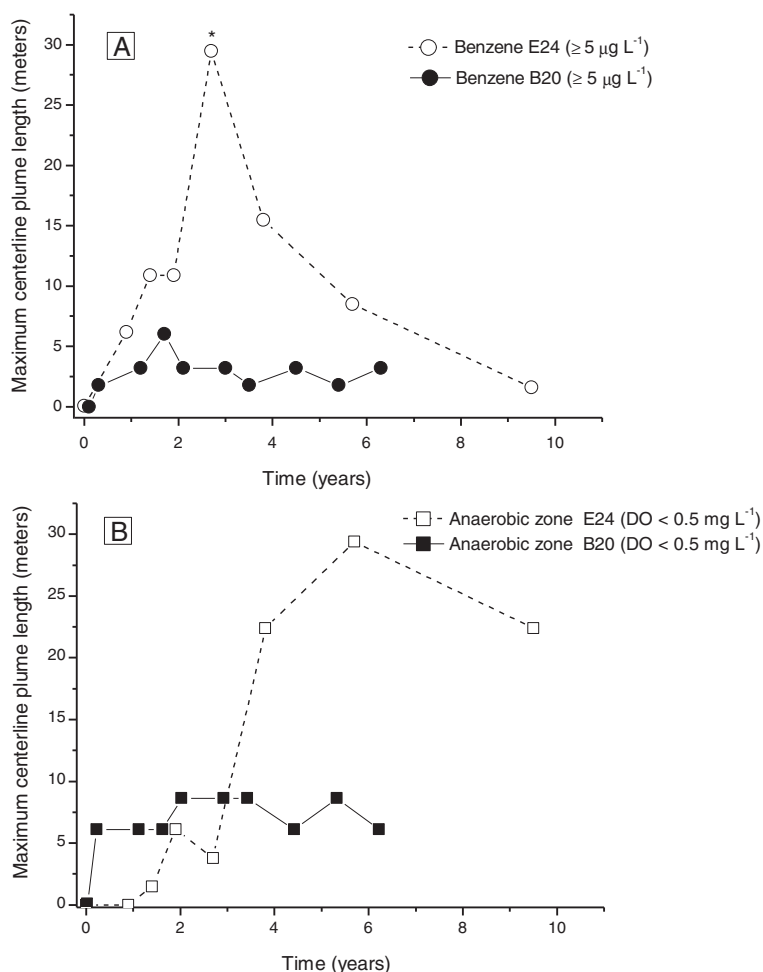
Fig. 3. The centerline plume lengths over time for E24 (24% ethanol in gasoline) and B20 (20% biodiesel in diesel) field release experiments. (A) Benzene (≥5 μg L^{-1}) and (B) anaerobic zone (measured DO ≤0.5 mg L^{-1}). *Benzene plume in E24 temporarily migrated out of the 30 m long monitored area (Corseuil et al., 2011a).

concentrations in biodiesel/diesel blends relative to ethanol/gasoline. These findings underscore the complexity of biodiesel blend behavior in groundwater even though biodiesel itself is not harmful and is a biodegradable renewable fuel.

4. Conclusions

Biofuel-amended releases could exhibit very different behavior in groundwater depending on their partitioning characteristics and mobility. Compared to ethanol, biodiesel would have lower mobility and undergo slower degradation at the source zone due to its slower dissolution. The persistence of biodiesel at the source zone and its preferential (albeit slow) degradation exerts a long-term negative effect on BTEX and PAH biodegradation and contributes to their persistence in the source zone. On the other hand, biodiesel's limited aqueous solubility would reduce plume lengths of aromatic hydrocarbons in the persistent NAPL zone as compared to ethanol-blended hydrocarbon plumes by limiting the anaerobic zone. Thus, when diesel is blended with biodiesel, BTEX compounds may form shorter plumes but with higher residual BTEX dissolved concentrations near the source zone when compared to ethanol-blended releases. This is the first field study to assess biodiesel blend behavior in groundwater and underscore its potential effects on the biodegradation and plume length of priority groundwater pollutants.

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