

BTEX Plume Dynamics Following an Ethanol Blend Release: Geochemical Footprint and Thermodynamic Constraints on Natural Attenuation

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S Supporting Information

ABSTRACT: In this 10 year study, Brazilian gasoline (100 L, containing 24% ethanol by volume) was released to a sandy aquifer to evaluate the natural attenuation of benzene, toluene, ethylbenzene, and total xylenes (BTEX) in the presence of ethanol. Groundwater concentrations of BTEX, ethanol, and degradation products (e.g., acetate and methane) were measured over the entire plume using an array of monitoring well clusters, to quantify changes in plume mass and region of influence. Ethanol biodegradation coincided with the development of methanogenic conditions while acetate (a common anaerobic metabolite) accumulated. The benzene plume expanded beyond the 30 m long monitored area and began to recede after 2.7 years, when ethanol had disappeared. Theoretical calculations suggest that the transient accumulation of acetate (up to 166 mg L⁻¹) may have hindered the thermodynamic feasibility of benzene degradation under methanogenic conditions. Yet, benzene removal proceeded relatively fast compared to literature values (and faster than the alkylbenzenes present at this site) after acetate concentrations had decreased below inhibitory levels. Thus, site investigations of ethanol blend releases should consider monitoring acetate concentrations. Overall, this study shows that inhibitory effects of ethanol and acetate are relatively short-lived, and demonstrates that monitored natural attenuation can be a viable option to deal with ethanol blend releases.



INTRODUCTION

Efforts to alleviate dependence on imported oil and concern about increases in greenhouse gas emissions due to fossil fuel combustion have fostered new policies to incorporate renewable biofuels, such as ethanol, into the world's energy grid. The United States, for example, has mandated the use of 7.5 billion gallons of corn ethanol per year by 2012.¹ Brazil has been using ethanol at a large scale for more than 30 years, demonstrating its potential for widespread application in other countries.² Ethanol is added to Brazilian gasoline in proportions between 20 and 25% according to its availability in the national market. The demand for ethanol is increasing in Brazil because of the flex-fuel fleet,³ which represented 90% of the cars sold in the country in 2009. Despite potential reductions in harmful automotive air emissions, laboratory studies suggest that the presence of ethanol could hinder the natural attenuation of monoaromatic hydrocarbons in groundwater impacted by fuel releases, thus increasing the associated risk of exposure.^{4,5}

Ethanol can affect the fate and transport of BTEX through various mechanisms. When releases of ethanol-blended gasoline reach the groundwater, a light nonaqueous phase liquid (LNAPL)

typically forms at the water table interphase. The LNAPL can serve as a source for sustained groundwater contamination by BTEX, which slowly leaches into the aqueous phase. In contrast, ethanol readily partitions into the groundwater and aqueous ethanol concentrations above 10% may exert a cosolvent effect that enhances BTEX dissolution resulting in higher BTEX concentrations.^{5,6} However, ethanol is rapidly biodegraded and/or migrates away from the source zone, eventually becoming unavailable to accelerate LNAPL dissolution. Preferential ethanol biodegradation may consume electron acceptors and nutrients that would otherwise be available for hydrocarbon biodegradation, thereby hindering their intrinsic bioremediation and promoting longer BTEX plumes.^{4,7-13} Assessing the net effect of ethanol on BTEX natural attenuation is also confounded by compound-specific differences in transport, retardation, dilution, and fate following changes in electron-accepting conditions. Furthermore,

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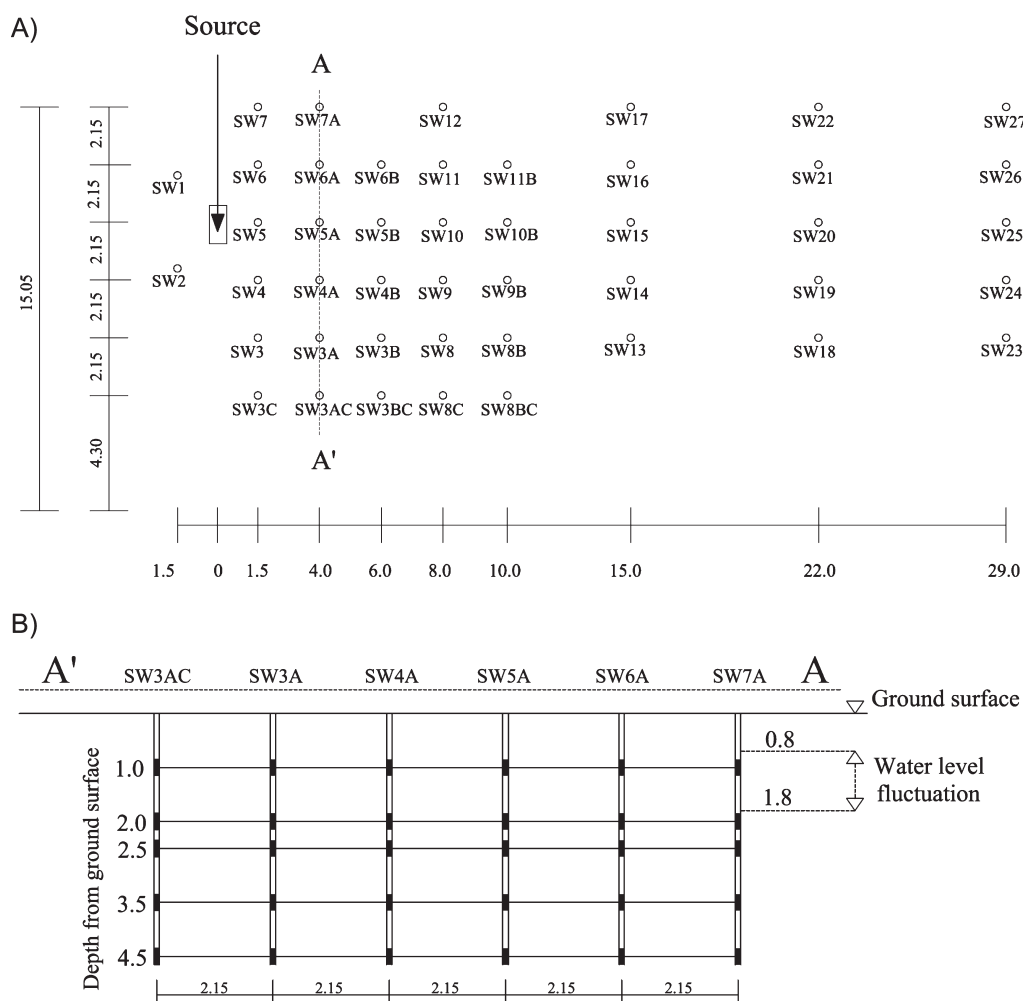


Figure 1. Ressacada Experimental Area sampling locations (A) plan view and (B) cross section from A' to A. All distances are given in meters. Well cluster screens are shown as black shaded areas in the cross section.

the rate and extent of hydrocarbon biodegradation in aquifers is compound specific and varies with redox transitions.^{14–18} Thus, it is very difficult to characterize the dynamics of natural attenuation of ethanol-blend releases in the laboratory, which underscores the need for long-term natural attenuation studies at the field scale.

This article summarizes a 10 year field study of the natural attenuation of a release of Brazilian gasoline, which contained 24% ethanol (v/v). To our knowledge, this is the first controlled field study to describe BTEX and geochemical footprint dynamics, and to quantify mass removal rates under fermentative methanogenic conditions. The long-term nature of this study also permitted the observation of important transient processes that occur over various time scales, and enabled the identification of acetate as a potential transient thermodynamic inhibitor of BTEX fermentation.

EXPERIMENTAL SECTION

Site Description. The experimental area is located in the Ressacada Farm, Florianópolis, SC, Brazil (Latitude: 27°30'S, Longitude: 48°30'W). The climate in the region is mesothermic humid with an annual average precipitation of 1600 mm and average groundwater temperature of 22 °C. Regional geology is characterized by unconsolidated deposits of eolian, alluvial,

lacustrine, and marine sands with less than 5% of silt and clay, and an average organic carbon content of 0.06%.¹⁹ Depth to the water table is approximately 0.8 to 1.8 m. Groundwater flow direction varies locally up to 40°, with a seepage (pore) velocity of 3.1 m year⁻¹. Brazilian gasoline (100 L, containing 24% ethanol, for composition, please refer to ref 6) and a tracer solution (1 kg of potassium bromide) were released in one pulse in an excavated area of 2 × 1 m that exposed the phreatic surface. Background groundwater characteristics were: pH 5.0–5.3; redox potential 32–69 mV, dissolved oxygen 4–7 mg L⁻¹; nitrate 0.05–0.137 mg L⁻¹; sulfate 0.3–4.3 mg L⁻¹; iron(II) 0–1.6 mg L⁻¹; phosphate 0.1–0.5 mg L⁻¹; methane 0–0.01 mg L⁻¹; and alkalinity 4–30 mg L⁻¹ as CaCO₃. Aquifer material samples were collected at 1.5 to 2.5 m below ground surface (bgs) and were analyzed by atomic absorption spectrophotometry (CIDASC, Brazil) for calcium (0.06–0.18 mg kg⁻¹), magnesium (0.06–0.12 mg kg⁻¹), manganese (0.5–0.8 mg kg⁻¹), aluminum (30–80 mg kg⁻¹), potassium (3–6 mg kg⁻¹), sodium (0–1 mg kg⁻¹), iron (50–100 mg kg⁻¹), copper (0.005 mg kg⁻¹), sulfur (60–100 mg kg⁻¹), zinc (0.24–1.5 mg kg⁻¹), and phosphorus (2–7 mg kg⁻¹).

Sample Collection. The site was monitored with 45 miniature multilevel sampling wells (SWs) (Figure 1). The vertical sampling array consisted of a bundle of 3/16" ID polyethylene tubing

with each tube cut to a length that corresponded to the depth of interest. The end of each tube was thermally bonded to a narrow diameter, 20 cm long, 200 mesh stainless steel wire-cloth screen. The array was attached to the outside of a small diameter PVC tube that extended to the bottom of the hole and was installed with conventional drilling. The annular space between the samplers and the aquifer was filled with fine sand to prevent channeling. Low-flow sampling was conducted using a peristaltic pump connected individually to each of the SWs. Each sampler had 5 sampling points with depths varying from 1.0 to 4.5 m bgs.

Analytical Procedures. BTEX (detection limit $1 \mu\text{g L}^{-1}$ each), ethanol (detection limit 1 mg L^{-1}), and methane (detection limit $10 \mu\text{g L}^{-1}$, soil gas was not monitored) were analyzed by gas chromatography using a GC HP model 6890 II equipped with a HP 7694 headspace auto sampler. Bromide, nitrite, nitrate, sulfate, phosphate, and acetate were analyzed using a Dionex ICS-1000 by ion chromatograph. Their detection limits were equal, at 0.1 mg L^{-1} . Ferrous iron was analyzed using a HACH DR/2500 spectrophotometer with a detection limit of 0.01 mg L^{-1} . Temperature, pH, dissolved oxygen, redox potential, and conductivity were measured with a QED Micropurge Flow Cell, model MP20. Additional details of the analytical methods are given in the Supporting Information.

Plume Contours. Plume boundaries for acetate and methane were defined as 3 and 20 mg L^{-1} contours, respectively. These relatively high concentrations imply their presence primarily as ethanol metabolites, rather than byproducts of degradation of BTEX or background organic matter.^{20,21} The ethanol plume boundary was defined by the 1 mg L^{-1} contour and BTEX was contoured at $5 \mu\text{g L}^{-1}$, which is the maximum contaminant level (MCL) established by the U.S. EPA for benzene in drinking water. The anaerobic zone was defined as the area with dissolved oxygen (DO) concentrations lower than 0.5 mg L^{-1} .²² Typically, groundwater is considered anoxic or hypoxic when DO concentrations are lower than 0.5 mg L^{-1} ,²³ which was also the detection limit for DO.

Estimation of Contaminant Mass. Fluctuations in electron donor and/or acceptor concentrations along groundwater flow-paths are subject to various processes that are difficult to separately quantify. This includes separating concentration decreases due to biodegradation from abiotic processes such as hydrodynamic dispersion and sorption.²⁴ Total mass estimates are used in this study to show changes in the contaminant mass between successive monitoring periods, which is a more effective indicator of natural attenuation than concentration-based methods.²⁵ Minimum curvature interpolation^{26–28} was used to calculate the dissolved mass of petroleum hydrocarbons, ethanol, DO, bromide, ferrous iron, acetate and methane (Supporting Information).

Microbial Analysis. Real-time quantitative PCR (RTQ-PCR) was used to quantify 16S rDNA gene copy number for various microbial groups in groundwater samples collected from SW1, SW2, and SW4 (Figure 1) 9.5 years after the release. Prerelease microbial concentrations were not assessed since many of the targeted biomarkers had not been discerned at that time (December 1998). Universal primers BACT1369F, PROK1492R, and probe TM1389F²⁹ were used to quantify total bacteria. Sulfate reducing bacteria were quantified using the EUB1 probe with 361F and 685R primers.³⁰ Nitrate reducing bacteria were quantified using the primers nirK1F and nirK5R as well as nirS1F and nirS6R.³¹ *Geobacteraceae* primers 361F, and 685R with the GBC1 probe,³⁰ were used to target dissimilatory iron reducing

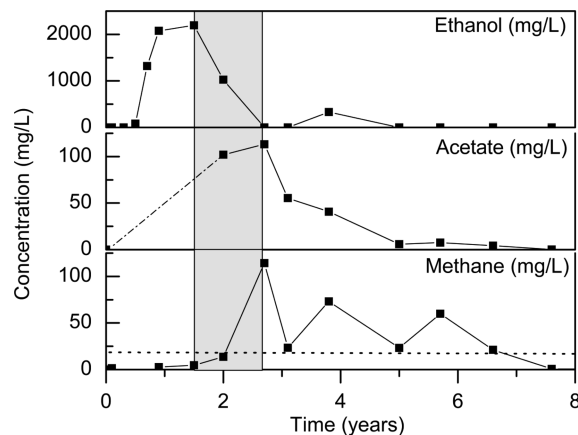


Figure 2. Ethanol, acetate and methane concentrations at SW4 (Figure 1) near the source zone -2.5 m bgs. The highest ethanol, BTEX, and byproduct concentrations were generally found at 2.0 to 2.5 m bgs. Acetate was not analyzed during the first year. The dashed line represents the methane saturation level in water, and the shadowed box represents the period of decreasing ethanol concentrations.

bacteria, recognizing that 685R can also amplify other closely related *δ-proteobacteria*, including sulfate reducers of the same *Desulfuromonadales* order.^{30,32} Archaea (including methanogens) were analyzed using the forward primer ARCHMIX1369F (ARCH1–1369F and ARCH2–1369F), the reverse primer PROK1541R, and the TM1389F probe.³³ Gene copy numbers were estimated as previously described.⁷ DNA extraction and RTQ-PCR methods are described in the Supporting Information.

RESULTS AND DISCUSSION

Plume Life Cycle Dynamics. The lifecycle of a plume, including expansion and recession dynamics, is an important consideration for site investigation and remedial action decisions. Yet, little is known about the overall region of influence and longevity of BTEX plumes in the presence of ethanol or its degradation products such as acetate.⁵

Ethanol partitioned rapidly from the released blend into the groundwater, reaching concentrations as high as 2500 mg L^{-1} near the source zone (Table S2 of the Supporting Information). This concentration is 1 order of magnitude lower than that reported to exert antimicrobial activity.^{34,35} The high biochemical oxygen demand exerted by ethanol exceeded the natural recharge of DO, resulting in the development of strongly anaerobic (methanogenic) conditions. A decrease in the ethanol concentration near the source (e.g., at SW4, 2.5 m bgs) coincided with increases in both acetate and methane concentrations (Figure 2). Previous studies of accidental ethanol-blended releases also reported the accumulation of acetate, butyrate, and methane during ethanol degradation.³⁶

Similar to previous laboratory studies,^{4,11,13,37,38} ethanol was preferentially degraded over BTEX and disappeared earlier. The ethanol plume (1 mg L^{-1} contour) reached a maximum extension of 11 m and began to recede after 1.5 years, disappearing by year 3 (Figure 3). Acetate, which is a known byproduct of anaerobic ethanol degradation⁵ and a potential BTEX metabolite,³⁹ also accumulated transiently, reaching concentrations as high as 166 mg L^{-1} near the source zone (Table S2 of the

Supporting Information) and expanding to 11 m (3 mg L^{-1} contour) within 2.7 years of the release (Figure 3).

As a result of the release, an anaerobic zone ($\text{DO} \leq 0.5 \text{ mg L}^{-1}$ contour) developed and expanded beyond the 30 m long monitored area. The test area remained predominantly anaerobic during most of the experiment, which was corroborated by the widespread presence of methane (Figure 3). Methane was detected above

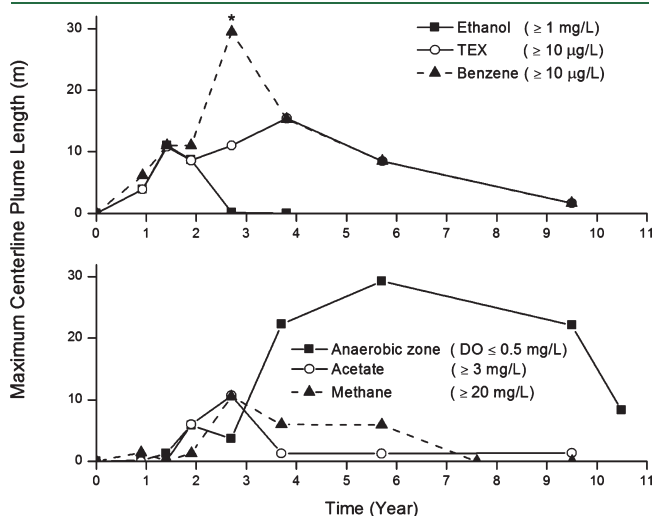


Figure 3. Ethanol, benzene, TEX, oxygen, acetate, and methane centerline plume length as a function of time since the release. * The benzene plume temporarily migrated off the 30 m long monitored area, so its maximum reach is unknown.

saturation (24 mg L^{-1} at 1 atm and $20 \text{ }^\circ\text{C}$) in the vicinity of the source. The high-methane-concentration plume ($\geq 20 \text{ mg L}^{-1}$ contour) also reached an extension of about 11 m at year 2.7 after the release, and receded thereafter.

Benzene, which is the most soluble of the BTEX compounds, had a longer reach than alkylbenzenes, temporarily migrating beyond the 30 m long monitored area compared to a maximum reach of 15.4 m for TEX (Figure 3). BTEX plumes receded after the removal of ethanol (Figure 3), following the onset of the decrease in acetate concentrations (Figure 5). This recession demonstrates that significant BTEX natural attenuation occurred.

BTEX and Ethanol Plume Mass Attenuation Kinetics. The total plume mass of dissolved plus sorbed BTEX initially increased as these compounds dissolved from the LNAPL, and up to 15% of the total BTEX mass released (6.9 kg) was accounted for after 2.7 years, followed by a decrease in near-source BTEX concentrations (Figure 4). A much higher recovery (56%) of the bromide tracer mass was obtained (part a of Figure 4), corroborating that the BTEX plume recession was due to natural attenuation (mainly biodegradation and possibly volatilization). The tracer recovery obtained in this study is within the reported range for similar field experiments,^{40,41} where poorly understood site heterogeneities often preclude closing mass balances. The bromide mass decreased after four years mainly due to offsite migration, whereas the TEX and ethanol plumes stayed within the monitored area.

The mass of ethanol released was 18.9 kg. Before its complete removal in the monitored area, the BTEX mass in the plume increased as the rate of BTEX dissolution from the source zone

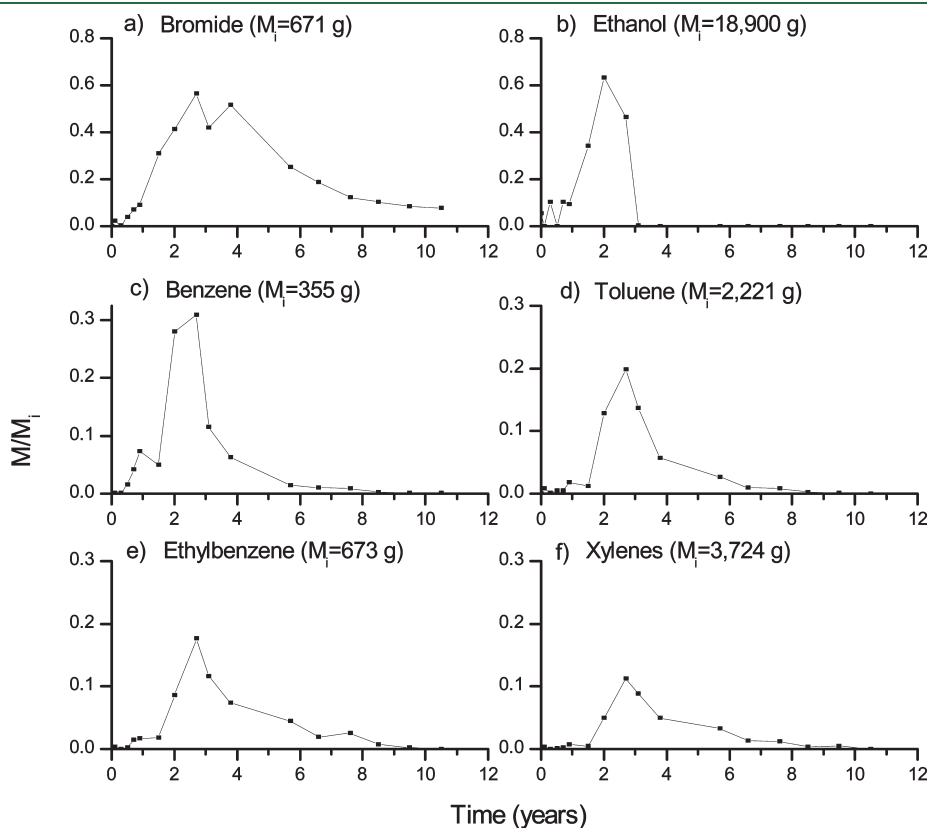


Figure 4. Fractions of total plume mass (M_t , sorbed plus dissolved) relative to released mass (M_i) for bromide, ethanol and BTEX compounds. M_i values are given in the panels. The decrease in bromide mass after 2.7 years is primarily due to off-site migration, which was not a factor for TEX.

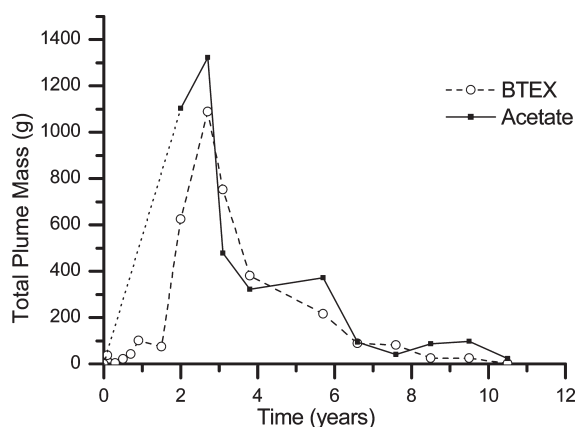


Figure 5. Total BTEX plume mass (sorbed plus dissolved) and acetate mass in the experimental area.

exceeded the attenuation rate (parts b–e of Figure 4). After 2.7 years, when ethanol had disappeared, BTEX plume masses started to decrease exponentially with pseudo-first-order decay coefficients of $0.81 \pm 0.34 \text{ year}^{-1}$ for benzene, $0.73 \pm 0.11 \text{ year}^{-1}$ for toluene, $0.55 \pm 0.15 \text{ year}^{-1}$ for ethylbenzene, and $0.48 \pm 0.11 \text{ year}^{-1}$ for total xylenes (Figure 4). These rate coefficients are likely representative of methanogenic conditions since methane was consistently detected throughout the plume during the first 7 years (Figure 3). The importance of methanogenesis to the biodegradation of this ethanol-blend release is suggested by stoichiometric considerations; the peak total mass of methane in the area (3.20 kg, Table S4 of the Supporting Information) could account for the mineralization of up to 6.15 kg of ethanol (based on a methane to ethanol mass ratio of 0.52:1). However, the contribution from other electron accepting processes (e.g., aerobic BTEX biodegradation in the fringes of the plume) cannot be ruled out.

Soluble anaerobic electron acceptors (e.g., nitrate and sulfate) were present at relatively low concentrations (up to 0.14 and 4.3 mg L^{-1} , respectively) and represent a relatively small fraction of the oxidation capacity at this site. Solid electron acceptors such as Barite (which can be a source of sulfate⁴²) and iron oxides were not quantified, so their contribution cannot be accurately determined. Soluble Fe(II) accumulated within the impacted area (up to 206 mg L^{-1} , 2.6 kg total mass) but not in upgradient groundwater samples (<2 mg L^{-1}), indicating that iron reducers contributed to bioremediation. However, their contribution cannot be quantified based on stoichiometric relationships with soluble Fe(II) alone because a majority of reduced iron generally exists in the solid phase,²⁰ which was not measured.

Benzene, which is generally the most recalcitrant BTEX compound under anaerobic conditions,^{43,44} was removed faster than the alkylbenzenes, and 80% of the total mass of benzene in the plume was removed within one year following the onset of its degradation (part c of Figure 4, also page S19 of the Supporting Information). The observed rates are relatively fast compared to 359 petroleum (predominantly gasoline) contaminated sites,⁴⁵ where the average BTEX first-order decay coefficients were at least one-half of those found here. Much lower benzene degradation rates have also been observed under methanogenic conditions in other field studies.^{46,47}

The higher removal rates at Ressacada could be explained not only by the temperature at this site (22 °C average), which is

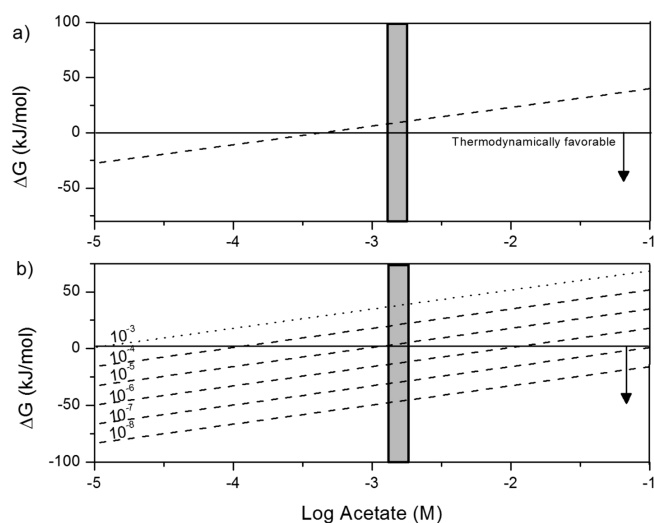


Figure 6. Thermodynamic feasibility (dashed lines) of benzene oxidation (10 mg L^{-1}) to (A) acetate alone (eq 1, linked only to acetoclastic methanogenesis); or (B) acetate and H_2 (eq 4, linked to hydrogenotrophic and acetoclastic methanogenesis) for a range of H_2 concentrations (10^{-8} to 10^{-3} M). The dotted line (near 10^{-3} M) represents solubility for H_2 . Shaded regions are the range of highest acetate concentrations measured near the source (Table S2 of the Supporting Information). Calculations details can be found in the Supporting Information.

higher than in most North American and European sites considered in the literature, but also by an ethanol-stimulated increase in biomass. Total bacteria concentrations in groundwater near the source ($1.2 \pm 0.2 \times 10^6 \text{ gene copies mL}^{-1}$) were 3 orders of magnitude higher than in control upgradient samples ($1 \times 10^3 \text{ gene copies mL}^{-1}$). Sulfate reducers (many of which are capable of fermentative growth in the absence of sulfate (48)) and *Geobacteraceae* (which can reduce Fe(III) and commonly coexist with sulfate reducers^{49–51}) were also relatively abundant near the source zone (both on the order of 10^5 to $10^6 \text{ gene copies mL}^{-1}$). *Archaea* (including methanogens) were below the detection limit ($10^2 \text{ gene copies mL}^{-1}$), consistent with the lack of methane detection at the time of sampling (9.5 years after the release). Previous aquifer column studies simulating natural attenuation of ethanol blends under methanogenic conditions showed that ethanol stimulates biomass growth, including sulfate-reducing bacteria associated with anaerobic BTEX biodegradation⁵² and fermentative/methanogenic microorganisms.⁸

There is little published information on ethanol degradation kinetics in aquifers. Laboratory and pilot-scale studies suggest that ethanol degradation rates should be relatively fast, except for very high ethanol concentrations ($>100\,000 \text{ mg/L}$ ³⁵) near the source, where potential alcohol toxicity and nutrients depletion may inhibit ethanol degradation. A linear decrease in ethanol concentrations with time was observed near the source, indicative of zero-order (saturated enzymes) kinetics that are common when substrate concentrations are much greater than Monod's half-saturation coefficient (K_s). The zero-order degradation rate for ethanol was $6.6 \pm 2.4 \text{ kg year}^{-1}$, corresponding to a half-life of about 1.5 years (Figure S6 of the Supporting Information). A similar half-life for ethanol degradation in aquifers (2.1 years) was previously reported.⁵³

Thermodynamic Implications of Acetate Accumulation. Acetate and other low molecular weight (LMW) organic acids

Table 1. Stoichiometry and Thermodynamics of Alternative (Syntrophic) Benzene Degradation Pathways under Methanogenic Conditions. eqs 1–3 Reflect a Pathway Dominated by Acetoclastic Methanogens, and eqs 4–7 Reflect the Participation of Hydrogenotrophic Methanogens^a

eq no.	stoichiometry	ΔG° (kJ/mol)
1	$C_6H_6 + 3H_2O + 1.5HCO_3^- \rightarrow 3.75CH_3COO^- + 2.25H^+$ (1)	81.91
2	$3.75CH_3COO^- + 2.25H^+ + 1.5H_2O \rightarrow 2.25CO_2 + 3.75CH_4 + 1.5HCO_3^-$ (2)	-216.86
3 (sum 1–2)	$C_6H_6 + 4.5H_2O \rightarrow 2.25CO_2 + 3.75CH_4$ (3)	-134.95
4	$C_6H_6 + 6H_2O \rightarrow 3CH_3COO^- + 3H^+ + 3H_2$ (4)	190.19
5	$3CH_3COO^- + 3H^+ \rightarrow 3CO_2 + 3CH_4$ (5)	-227.09
6	$3H_2 + 0.75CO_2 \rightarrow 0.75CH_4 + 1.5H_2O$ (6)	-98.05
7 (sum 4–6)	$C_6H_6 + 4.5H_2O \rightarrow 2.25CO_2 + 3.75CH_4$ (7)	-134.95

^a Gibbs free energy values were calculated using values from Thauer et al.⁶³ and were adjusted for site-specific temperature and pH as detailed in the Supporting Information section. Values for eqs 1 and 4 were used to calculate thermodynamic thresholds shown in parts A and B of Figure 6, respectively (Table S2 of the Supporting Information).

are common metabolites produced by the anaerobic degradation of ethanol, BTEX, and other organic compounds. LMW organic acids (specifically acetic acid) generally accumulate to a greater extent in methanogenic systems than in systems where other electron-accepting processes dominate.^{54,55} Similarly, in this study acetate concentrations increased concomitantly as ethanol degraded and methane concentrations increased (Figure 2). Significant BTEX mass removal started after 2.7 years (Figure 4), when ethanol had been removed from the system (Figure 2), also following the onset of acetate consumption (Figure 5). The transient accumulation of acetate (and possibly H₂) apparently inhibited BTEX fermentation (Figure 6). Specifically, under methanogenic conditions, some hydrocarbons such as benzene can be fermented through different pathways to acetate and H₂ (Table 1), which can be respectively converted to CH₄ by acetoclastic (eq 2) and hydrogenotrophic (eq 6) methanogens. Acetoclastic methanogenesis has been proposed to be a rate limiting step for anaerobic (fermentative) hydrocarbon degradation.⁵⁴ However, the initial syntrophic biotransformations (eq 1 and eq 4) are exergonic under standard conditions, and require the commensal consumption of acetate and/or H₂ to proceed.⁵⁶

Theoretical thermodynamic calculations (Supporting Information section) suggest that, at the concentrations measured near the source (e.g., up to 166 mg L⁻¹ acetate with alkalinity at 54 mg L⁻¹ as CaCO₃, Table S2 of the Supporting Information), the system was temporarily endergonic regarding benzene fermentation via the strictly acetogenic pathway (eq 1, part A of Figure 6). To be thermodynamically feasible ($\Delta G < 0$), the acetate concentration would need to decrease below 64 mg L⁻¹. Acetate accumulation is known to be thermodynamically inhibitory to other anaerobic biotransformations, such as butyrate fermentation.⁵⁷

Through the hydrogenogenic pathway (eq 4), H₂ concentrations could influence the threshold at which acetate becomes thermodynamically inhibitory to benzene fermentation. H₂ concentrations in methanogenic aquifers can vary widely, from 5 nM to 255 μ M.^{58–61} Theoretically, at 100 μ M H₂, an accumulation of 26.5 mg L⁻¹ acetate or more would make the reaction endergonic (part B of Figure 6), making it plausible for the observed transient accumulation of acetate (Figure 2) to have hindered the thermodynamic feasibility of this benzene fermentation pathway.

Nevertheless, caution should be exercised against generalizations about inhibitory thresholds for acetate, which are system-specific and potentially affected by other terminal electron accepting processes.⁵⁸

Previous microcosm,^{4,13} column,⁵² and field experiments¹² showed that ethanol hinders BTEX degradation, especially under methanogenic conditions. This study extends this axiom and suggests that the inhibitory effect exerted by ethanol (mainly due to accelerated depletion of dissolved oxygen, catabolite repression and metabolic flux dilution¹¹) may exist beyond the relatively short life-span of the ethanol plume, due to the transient (longer-lasting) accumulation of acetate. Because acetate accumulation may decrease the thermodynamic feasibility of BTEX fermentation, monitoring acetate concentrations may be important during site investigation and natural attenuation assessment of ethanol-blended fuel releases. Overall, this inhibitory effect was relatively short-lived, and natural attenuation of BTEX eventually proceeded at relatively fast rates comparable to sites impacted with regular (unblended) gasoline.⁶² Thus, this study demonstrates that MNA (in conjunction with source control measures, when appropriate) can be a viable option to deal with ethanol blend releases.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed site description, experimental methods, data analysis (including plume mass calculations), kinetic analyses, and thermodynamic calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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