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Aerobic biodegradation of *iso*-butanol and ethanol and their relative effects on BTEX biodegradation in aquifer materials

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ABSTRACT

The aerobic biodegradability of *iso*-butanol, a new biofuel, and its impact on benzene, toluene, ethylbenzene and xylenes (BTEX) degradation was investigated in aerobic microcosms consisting of groundwater and sediment from a California site with a history of gasoline contamination. To the best of our knowledge this is the first study directly examining the effects of *iso*-butanol on BTEX degradation. Microcosms that received either low (68 μM) or high (3400 μM) concentrations of *iso*-butanol showed complete biodegradation of *iso*-butanol within 7 and 23 d, respectively, of incubation at 15 °C under aerobic conditions. A maximum utilization rate coefficient of $2.3 \pm 0.1 \times 10^{-7}$ μmol cell^{-1} h^{-1} and a half saturation constant of 610 ± 54 μM were regressed from the *iso*-butanol data. *Iso*-butanol biodegradation resulted in transient formation of the degradation intermediate products *iso*-butylaldehyde and *iso*-butyric acid, and both compounds were subsequently degraded within the timeframe of the experiments. Ethanol was biodegraded more slowly than *iso*-butanol. Ethanol also exhibited greater adverse impacts on BTEX biodegradation than *iso*-butanol. Results of the study suggest that *iso*-butanol added to fuels will be readily biodegraded in the environment under aerobic conditions without the accumulation of major intermediate products (*iso*-butylaldehyde and *iso*-butyric acid), and that it will pose less impacts on BTEX biodegradation than ethanol.

1. Introduction

The rising cost and finite supply of crude oil has led fuel providers to seek alternative fuels to reduce the consumption of petroleum. In addition, the Energy Independence and Security Act of 2007 (Congressional Record, 2007) mandated the use of renewable fuels to reduce foreign oil dependence and greenhouse gas emissions. The law requires production and use of 136×10^6 m^3 of fuel from renewable sources by 2022. To date, the vast majority of research and development on alternative fuels has focused on ethanol, but other biofuels suitable for use in gasoline are under development. Biologically produced butanol currently is being considered as a potential alternative (Mariano et al., 2009). Notably, *iso*-butanol, for example, is particularly attractive as a biofuel molecule because it can be produced from renewable feedstocks and has many properties that potentially make it a better fuel additive than ethanol; it has a greater energy density, lower water absorption, better blending ability, and it can be used in conventional combustion engines without modification (Durre, 2007). The contemplated addition of any chemical to the fuel supply, however, requires careful consideration of its environmental fate and its effect on the fate of other gasoline components.

Much work has been done to evaluate the effect of ethanol on the environmental fate of gasoline components. Early research in this area demonstrated that in aerobic systems fuel ethanol is preferentially biodegraded before the benzene, toluene, ethylbenzene and xylenes (BTEX) components of gasoline, and that ethanol degradation in aquifers rapidly consumed dissolved oxygen and other nutrients (Corseuil et al., 1998; Da Silva and Alvarez, 2002; Capiro et al., 2007). The presence of ethanol in gasoline therefore could result in a lag in BTEX degradation and ultimately might elongate BTEX plumes (Powers et al., 2001). Model simulations by Deeb et al. (2002) predicted a 16–34% increase in benzene plume lengths in the presence of ethanol. In contrast, other studies have suggested that the lifespan of benzene plumes actually decreases with greater ethanol concentration in gasoline due to a decreased mass of benzene in ethanol blended gasoline, and due to increased microbial biomass (and subsequent benzene biodegradation) produced by growth on ethanol (Gomez and Alvarez, 2009). Thus, the impact of ethanol on benzene plumes likely will need to be evaluated on a site-specific basis.

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Few studies have evaluated the effects of alternative biofuels on the fate of gasoline in the environment, or compared the relative effects of ethanol and alternative fuel additives. A recent study by Mariano and colleagues (2009) used indirect measurements (CO_2 evolution and dye reduction) to evaluate the affect of *n*-butanol on gasoline biodegradation in aerobic microcosms containing uncontaminated soil, river water, or a combination of uncontaminated soil and river water. Results of the study suggested that *n*-butanol may enhance gasoline degradation in soil, and that the enhancement factor may be greater than that achieved with ethanol. Results obtained by Garcia-Rivero et al. (2007) also suggested that addition of *n*-butanol to hydrocarbon mixtures may enhance the rate of hydrocarbon aerobic biodegradation. Studies performed in the 1970s used biological oxygen demand-based measurements to evaluate *iso*-butanol biodegradation (Dias and Alexander, 1971; Price et al., 1974), and several studies (Vainberg et al., 2002; Pruden and Suidan, 2004; Somsamak et al., 2005) have evaluated the biodegradation of *tert*-butyl alcohol which is the primary biodegradation product of the gasoline oxygenate methyl *tert*-butyl ether (Steffan et al., 1997; Hatzinger et al., 2001). To the best of our knowledge, however, no previous studies have evaluated the effect of *iso*-butanol on BTEX biodegradation in environmental samples. In this paper we describe aerobic microcosm studies performed to assess the potential fate of *iso*-butanol in the environment and to evaluate how the addition of *iso*-butanol to gasoline could impact biodegradation of BTEX compounds when presented together as co-contaminants.

2. Materials and methods

2.1. Soil and groundwater

Soil and groundwater for the laboratory microcosm testing were collected from within Site 60 at Vandenberg Air Force Base, CA. The site has a history of gasoline contamination, but has undergone an extensive cleanup program. Collected groundwater was containerized in sterile stainless steel soda kegs (18.5 L) under nitrogen headspace. Soil located approximately 2.4–3.7 m below ground surface was collected using a Geoprobe 6620DT with acetate core sleeves. Soil cores (6.1 cm diameter) were collected using a Geoprobe 8.3 cm outside diameter dual tube sampling system. The core samples in acetate sleeves were capped and sealed in the field to minimize exposure to air, shipped overnight on ice to the laboratory, and stored at 4 °C.

Soil was removed from the acetate sleeves in an anaerobic chamber (Coy Laboratory Products, Inc., Grass Lake, MI) and the first 10 cm of the core ends that may have been exposed to oxygen were discarded. Collected soil consisted of silty sand with some gravel and larger stones. The soil was passed through a 0.95 cm sieve, homogenized, and then stored in amber glass jars with Teflon-lined caps at 4 °C until microcosm setup was complete. Baseline soil and groundwater data are presented in Table 1.

2.2. Microcosms

The overall approach for the microcosm experiments was to evaluate the biodegradation of BTEX and *iso*-butanol at both "high" and "low" concentrations in soil–groundwater slurries. For purposes of this study, "biodegradation" refers to primary transformation of the compound of interest, as final transformation products were not determined. For comparison, one treatment was prepared using ethanol instead of *iso*-butanol. The experimental treatment matrix is shown in Table 2. BTEX and alcohol concentrations were selected to represent plausible groundwater concentrations that would be observed within a source area and in the near downgradient plume. The greater ethanol concentrations relative to the *iso*-butanol concentrations used in this study were intended to reflect effective solubilities of *iso*-butanol and ethanol in groundwater. Ethanol has an aqueous solubility approximately 10-times that of *iso*-butanol, and the octanol–water partition coefficient of *iso*-butanol is approximately 10-times that of ethanol (OECD, 2004a,b). So an ethanol molar concentration approximately 3-times greater than *iso*-butanol was conservatively selected for the testing in this study. The SET 1 treatments were prepared within 4 d of sample collection whereas SET 2 treatments were prepared after approximately 2 months of soil and groundwater storage.

Table 1
Groundwater and soil parameters.

Parameter	Groundwater (mg L^{-1})	Soil (mg kg^{-1})
Total organic carbon	22	1700
Gasoline range organics	5.7	NA
Phenol	0.008	<0.084
Bis(2-ethylhexyl) phthalate	0.003	<0.084
Total iron	490	NA
dissolved iron	<0.1	NA
Nitrate (as N)	1.5	NA
Sulfate (as SO_4^{2-})	105	NA
Alkalinity (as $CaCO_3$)	391	NA
Methane	<0.005	NA
pH	7.2[a]	NA
Dissolved oxygen	0.8	NA

NA = Not analyzed.
[a] Standard units.

Table 2
Experimental design. Target BTEX concentrations for each BTEX compound (benzene, toluene, ethylbenzene, and total xylenes) are listed under the BTEX column. Controls were amended with mercuric chloride and formaldehyde. H = high concentration, L = low concentration, IBA = *iso*-butanol.

Treatment	BTEX (μM)	*Iso*-butanol (μM)	Ethanol (μM)
SET 1			
Control	180/38/38/75	–	–
H IBA control	180/38/38/75	3400	–
L IBA control	15/3.8/3.8/7.5	68	–
L BTEX	15/3.8/3.8/7.5	–	–
H BTEX	180/38/38/75	–	–
L BTEX + L IBA	15/3.8/3.8/7.5	68	–
H BTEX + H IBA	180/38/38/75	3400	–
SET 2			
Ethanol control	180/38/38/75	–	11 000
H BTEX + H IBA 2	180/38/38/75	3400	–
H BTEX + ethanol	180/38/38/75	–	11 000

Microcosms were prepared by placing 40 g of site soil into each of 54 glass serum bottles (approximate volume 160 mL each). BTEX and alcohol (*iso*-butanol or ethanol, 99.5% purity, Sigma–Aldrich, St. Louis, MO) were added to the treatment bottles to attain the target concentrations shown in Table 2. Bottles were filled with groundwater so as to leave 10 mL of headspace. Controls were amended with mercuric chloride (700 mg L^{-1} in bottles) to inhibit microbial activity, and were also subsequently amended with formaldehyde (1 vol.% in bottles) after 4 d to limit microbial activity. Treatments were prepared with a minimum of three and up to eight replicates each.

The prepared microcosms were incubated on a rotary shaker operating at 100 rpm in a temperature controlled walk-in incubator at 15 °C. Headspace in each of the bottles was monitored for BTEX and oxygen. Aqueous BTEX concentrations were calculated by applying Henry's Law. Samples of the aqueous phase were analyzed for *iso*-butanol and ethanol, as well as potential *iso*-butanol degradation products (*iso*-butylaldehyde and *iso*-butyric acid).