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Quantifying MTBE biodegradation in the Vandenberg Air Force Base ethanol release study using stable carbon isotopes

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Abstract

Compound-specific isotope analysis (CSIA) was used to assess biodegradation of MTBE and TBA during an ethanol release study at Vandenberg Air Force Base. Two continuous side-by-side field releases were conducted within a preexisting MTBE plume to form two lanes. The first involved the continuous injection of site groundwater amended with benzene, toluene and *o*-xylene (“No ethanol lane”), while the other involved the continuous injection of site groundwater amended with benzene, toluene and *o*-xylene and ethanol (“With ethanol lane”). The δ^{13}C of MTBE for all wells in the “No ethanol lane” remained constant during the experiment with a mean value of -31.3 ± 0.5‰ ($n=40$), suggesting the absence of any substantial MTBE biodegradation in this lane. In contrast, substantial enrichment in ^{13}C of MTBE by 40.6‰, was measured in the “With ethanol lane”, consistent with the effects of biodegradation. A substantial amount of TBA (up to 1200 μg/L) was produced by the biodegradation of MTBE in the “With ethanol lane”. The mean value of δ^{13}C for TBA in groundwater samples in the “With ethanol lane” was -26.0 ± 1.0‰ ($n=32$). Uniform δ^{13}C TBA values through space and time in this lane suggest that substantial anaerobic biodegradation of TBA did not occur during the experiment. Using the reported range in isotopic enrichment factors for MTBE of -9.2‰ to -15.6‰, and values of δ^{13}C of MTBE in groundwater samples, MTBE first-order biodegradation rates in the “With ethanol lane” were 12.0 to 20.3 year^{-1} ($n=18$). The isotope-derived rate constants are in good agreement with the previously published rate constant of 16.8 year^{-1} calculated using contaminant mass-discharge for the “With ethanol lane”.

Keywords: Carbon stable isotopes; Methyl *tert*-butyl ether; *tert*-Butyl alcohol; Biodegradation; Ethanol; Biodegradation rates

1. Introduction

Compound-specific isotope analysis (CSIA) has been successfully applied as an indicator of MTBE biodegradation in contaminated aquifers (Kolhatkar et al., 2002; Kuder et al., 2005; Wilson et al., 2005a,b; Zwank et al., 2005). The technique takes advantage of the fact that biodegradation results in a significant isotopic shift in the heavy to light isotope ratio in the degraded contaminant due to preferential breakage of bonds containing the light isotope (^{12}C) versus the heavy isotope (^{13}C). Biodegradation can therefore be documented in groundwater systems by identifying an isotopic enrichment (i.e. less negative δ^{13}C values) in groundwater samples relative to the source area. Isotopic fractionation during biodegradation of MTBE (Hunkeler et al., 2001;

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Gray et al., 2002; Kolhatkar et al., 2002; Somsamak et al., 2005, 2006) has been shown to follow the Rayleigh isotopic enrichment model (Mariotti et al., 1981) and has been used to quantify the extent of biodegradation at contaminated field sites (Kolhatkar et al., 2002; Kuder et al., 2005; Wilson et al., 2005a,b; Zwank et al., 2005). The USEPA recently issued a report outlining how CSIA can be used to calculate biodegradation rates of MTBE at contaminated field sites (Wilson et al., 2005c), attesting to the growing acceptance of this technique as a biodegradation monitoring strategy.

Concentration changes at contaminated field sites can be due to both degradative (i.e. biodegradation) and non-degradative processes (i.e. volatilization, sorption and dispersion). Methods that calculate biodegradation rate constants using concentration changes implicitly incorporate mass loss due to non-degradative processes as well as mass loss due to biodegradation, or neglect transverse dispersion (McNab and Dooher, 1998; Stenback et al., 2004). Since δ^{13}C values are only altered by biodegradation and not significantly by non-degradative attenuation processes (Harrington et al., 1999; Slater et al., 2000; Hunkeler et al., 2001; Schuth et al., 2003), biodegradation rate estimates using δ^{13}C values are more conservative and therefore less likely to overestimate the contribution of biodegradation to contaminant losses (Morrill et al., 2005; Wilson et al., 2005c; Chartrand et al., 2005). For example, Morrill et al. (2005) found that TCE biodegradation rates using δ^{13}C values were 2–4 times lower than concentration-derived estimates, and attributed the difference to sorption and dispersion which when unaccounted for artificially increased concentration-derived estimates of biodegradation. Using a modeling approach, Abe and Hunkeler (2006) also showed that the δ^{13}C approach to estimate first-order biodegradation rates is conservative and may underestimate biodegradation since it does not account for subsurface heterogeneity which can result in variations in the travel time distribution of contaminants between the source and monitoring well. Due to the high degree of uncertainty associated with concentration-based approaches, estimates based on contaminant concentration changes and isotopic values are typically within error of each other, but the isotope based errors are always the most conservative (Morrill et al., 2005; Abe and Hunkeler, 2006). In a recent multitracer test, a mixture of ring-deuterated and fully deuterated toluene and bromide (as a conservative tracer) were injected into the subsurface (Fischer et al., 2006). Since the mass of toluene and bromide injected were known, the biodegradation rates were calculated by comparing the mass and isotopic composition of toluene released to the mass, and the isotopic composition of toluene crossing two control planes. There was good agreement between toluene biodegradation rates calculated using isotopic fractionation of toluene and the Rayleigh equation, and biodegradation rates calculated using changes in toluene concentration relative to bromide across the control planes (Fischer et al., 2006).

In recent years, ethanol addition to gasoline as a fuel oxygenate has increased, as MTBE is being phased-out of gasoline (Kanaskie, 2000). There have been few studies examining what impact ethanol will have on biodegradation of gasoline constituents at contaminated field sites. Ethanol is expected to preferentially biodegrade relative to BTEX (benzene, toluene, ethylbenzene and xylene) compounds and possibly deplete the available electron acceptors or alter the microbial communities present such that a smaller proportion of BTEX degraders are present (Powers et al., 2002; Ruiz-Aguilar et al., 2002). In either case, a slower rate of BTEX biodegradation may occur. In order to test this hypothesis, two continuous side-by-side field releases (“No ethanol lane” and “With ethanol lane”) were conducted for approximately 9 months within a preexisting MTBE plume at Vandenberg Air Force Base (VAFB), California. The first involved the continuous injection of site groundwater amended with benzene, toluene and o-xylene (BTX) (“No ethanol lane”), while the other involved the continuous injection of site groundwater amended with BTX and ethanol (“With ethanol lane”). The aquifer at VAFB is normally sulfate-reducing, however the rapid biodegradation of ethanol in the “With ethanol lane” created methanogenic conditions (Mackay et al., 2006). BTX plumes in the “With ethanol lane” retracted more slowly and to a lesser extent overall than BTX plumes in the “No ethanol lane”, suggesting that ethanol reduced the rate of BTX biodegradation in the subsurface (Mackay et al., 2006).

MTBE is less susceptible to biodegradation than other fuel constituents such as the BTEX species (Schmidt et al., 2004) and hence was the focus of this study. There is significant MTBE contamination remaining in the subsurface at many fuel release sites which could be impacted by later releases of ethanol-blended fuels. Ethanol biodegradation may rapidly decrease nutrients and electron acceptors that could be used for MTBE biodegradation (Da Silva and Alvarez, 2002) and may cause contaminant plumes to extend longer distances, therefore increasing the likelihood of encountering groundwater receptors. In the present study, CSIA was used to assess the fate of MTBE in the ethanol release study at VAFB in order to verify *in situ* biodegradation and as an independent means to calculate biodegradation