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Assessment of stable carbon isotopes as a tool for assessing MTBE biodegradation at a field site

LUIS E. LESSER[1], GERARD SPINNLER[2], PAUL C. JOHNSON[1] & RAMON ARAVENA[3]

1 *Arizona State University, Department of Civil and Environmental Engineering PO Box 875306, Tempe, Arizona 85287-5306, USA.*
Luis.Lesser@asu.edu

2 *Shell Global Solutions Shell Global Solutions (US) Inc. Westhollow Technology Center, PO Box 4327, Houston, Texas 77210, USA.*

3 *University of Waterloo Earth Sciences Department, 200 University Ave. W., Waterloo, Ontario N2L 3G1, Canada.*

Abstract Stable carbon isotope techniques have been suggested as diagnostic tools for assessing hydrocarbons biodegradation. The objective of this study was to determine if isotope fractionation can be used as a reliable indicator of MTBE biodegradation, whether natural or engineered. The MTBE plume at Naval Base Ventura County (Port Hueneme, California, USA) offers a unique setting to study the fate of MTBE using stable carbon isotopes. Dramatic decreases in MTBE concentrations as a result of biodegradation have been well documented at this site. MTBE stable isotope fractionations were tracked along with MTBE concentrations. Laboratory-scale microcosms show 6‰ enrichment on MTBE-δ^{13}C under aerobic conditions. However, limited fractionation was detected in field samples.

Key words biobarrier; biodegradation; fractionation; MTBE, Port Hueneme; stable isotopes; microcosms

INTRODUCTION

Stable carbon isotope techniques have been suggested as diagnostic tools for assessing biodegradation (Van de Velde *et al.*, 1995). Galimov (1985) indicated that, for kinetic reasons, the $^{13}C/^{12}C$ ratios of a biodegradable organic compound increase when biodegradation occurs. Several studies have demonstrated a change in the stable carbon isotope ratio during biodegradation of chlorinated solvents (Hunkeler *et al.*, 1999; Sherwood Lollar *et al.*, 1999; Bloom *et al.*, 2000). BTEX compounds have been found to produce very small isotopic fractionations on carbon during biodegradation (Sherwood Lollar *et al.*, 1999; Stehmeier *et al.*, 1999; Ahad *et al.*, 2000). Polyaromatic hydrocarbons such as naphthalene have also shown small fractionation on carbon during aerobic and anaerobic biodegradation (O'Malley *et al.*, 1994; Kelley *et al.*, 1998; Lesser *et al.*, 2001).

Hunkeler *et al.* (2001) reported an enrichment of 5.1‰ to 6.9‰ on MTBE-δ^{13}C during aerobic biodegradation in microcosms experiments. The isotopic enrichment factors (ε) obtained ranged between –1.5‰ and –2.0‰. Gray *et al.* (2002) reported an enrichment of 5.2‰ to 8.1‰ on MTBE-δ^{13}C during aerobic biodegradation in microcosm experiments. The isotopic enrichment factors (ε) obtained ranged between –2.01‰ and –2.4‰. While both studies were laboratory based, no field data exits to corroborate such findings.

The objective of this study was to test stable isotope diagnostic techniques for MTBE biodegradation at the field scale, to determine if isotopic fractionation can be used as a reliable diagnostic tool to identify when biodegradation contributes significantly to natural (or engineered) MTBE attenuation.

SITE DESCRIPTION

The studied site is located at the US Naval Base Ventura County, CA (Port Hueneme). During 1984–1985, several thousands of gallons of gasoline containing MTBE were lost from subsurface transfer piping at the base gasoline station. The resultant source zone is about 250 m long × 60 m wide. Downgradient of the source zone, dissolved BTEX constituents are naturally attenuated within the first 50 m. However the dissolved MTBE plume extends over 1300 m beyond the source zone and is 150 m wide (Salanitro *et al.*, 2000; Bruce *et al.*, 2002).

At this site, several remediation system demonstrations and evaluation projects have been conducted. For each, biodegradation has been a key mechanism for MTBE attenuation. Therefore, this site was suitable for validation of the isotope technique at the field scale. It was expected that as field MTBE concentrations drop as a consequence of biodegradation, the $^{13}C/^{12}C$ ratio of the remaining dissolved MTBE would increase.

FIELD METHODS

Samples were collected using a Geoprobe®, direct push sampler. A total of 50 groundwater samples were collected at three main locations across the MTBE plume (Fig. 1) from 2.5-m and 5.5-m below ground surface. The saturated thickness of the aquifer extends from 2.5 to 6 m. The biobarrier remediation system (Location 1) is located within an area of known MTBE biodegradation. Samples collected within Location 1 were located both in the source zone upstream of the biobarrier, and within the bioactive zone where biodegradation is known to take place. Locations 2 and 3 are located downstream of the biobarrier in areas unaffected by biobarrier activity (Fig. 1). Samples collected from locations 2 and 3 are expected to have low MTBE concentrations and a non-biodegraded $\delta^{13}C$ signature.

LABORATORY METHODS

Groundwater samples with dissolved MTBE were collected with zero headspace in 40-ml VOA vials. MTBE concentrations were analysed using headspace gas chromatography (GC) analyses. The GC (SRI Model 8610C) was equipped with a 60 m, 0.53 mm ID MXT-Vol capillary column with a 2.0 μm film thickness. A flame ionization detector (FID) was used for most samples, while a photo ionization detector (PID) was used for low MTBE concentrations. Analyses were performed by injecting 0.5 ml of headspace, and the temperature programming for MTBE alone was 70°C isothermal. If

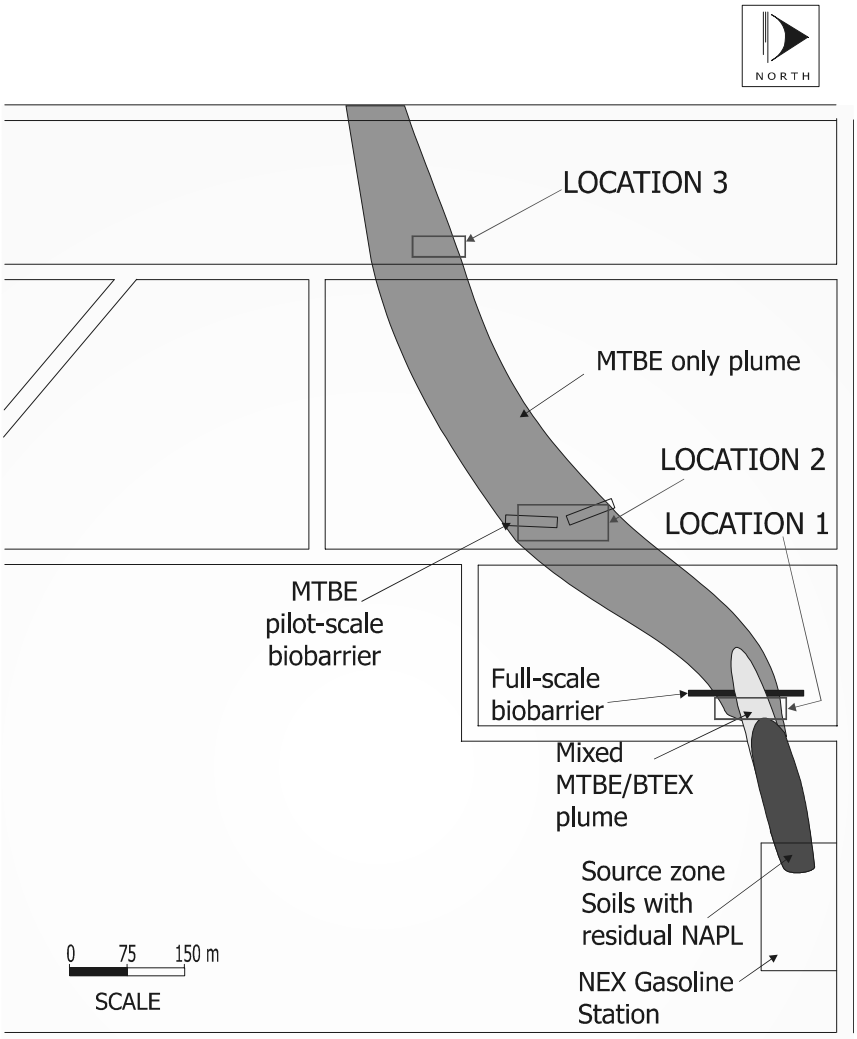

Fig. 1 Location of the MTBE plume at Port Hueneme, CA (10 μg l^{-1} contour line). The biobarrier where biodegradation takes place is in location 1. Samples at locations 2 and 3 are unaffected by biobarrier activity.

BTEX constituents were present, temperature programming included a 4-min hold at 70°C, a 15°C min^{-1} ramp to 180°C, and a 10-min hold at 180°C. QA/QC included a standard check every 10 samples.

The samples for stable carbon isotope analyses were collected in 40-ml vials, preserved with 0.2 ml of a saturated solution of mercuric chloride and sent to the Environmental Isotope Laboratory at the University of Waterloo for stable carbon isotope analyses by a GC-C-IRMS system (Hunkeler *et al.*, 2001).

Laboratory microcosms studies were also performed to complement the fieldwork. Microcosms were prepared in 1-l clear-glass narrow neck bottles, with butyl rubber screw cap septums. Each microcosm contained 320 g of sediments. Groundwater collected at each location was filtered and sparged with oxygen until saturation (40 mg l^{-1} of oxygen). Then, 650 ml of the oxygen-sparged groundwater was dispensed into each bottle leaving approximately 200 ml of headspace. The remaining headspace was purged with oxygen and the bottle was capped and taped to avoid volatilization.

The microcosms were then spiked with MTBE. Respiratory inhibited control microcosms were prepared by adding 8 g of sodium azide. The microcosms were continuously shaken and were periodically monitored for MTBE biodegradation by GC headspace analyses as described previously. Samples for stable carbon isotope analysis were also collected and preserved as previously described and sent to the University of Waterloo for isotope analysis.

MICROCOSMS RESULTS

The purpose of the microcosm experiments was to determine the maximum MTBE-carbon isotope fractionation that Port Hueneme sediments would produce under controlled conditions. These experiments were performed with starting concentrations of 6, 3.2 and 0.7 mg l^{-1} of MTBE. Initially, the MTBE-$\delta^{13}C$ was approximately –31.0‰, final MTBE-$\delta^{13}C$ ranged from –24.6‰ to –25.5‰ (Fig. 2), showing a fractionation of 5.5‰ to 6.4‰. The isotope enrichment factor (ε) from the microcosms experiments was on average –1.37‰. Control microcosms showed no biodegradation throughout the experiment. These results are similar to those reported by Hunkeler *et al.* (2001) who reported enrichments of 5.1‰ to 6.9‰, and isotopic enrichment factors (ε) from –1.5‰ to –2.0‰, and Gray *et al.* (2002) who reported enrichments of 5.2‰ to 8.1‰ and enrichment factors (ε) from –2.0‰ to –2.4‰ on MTBE-$\delta^{13}C$ on aerobic microcosms experiments.

FIELD RESULTS

In the field, we would expect high MTBE concentrations near the source zone, which would be depleted on MTBE-^{13}C. We would also expect to see a decrease in concentration from both dispersion and biodegradation; dispersion would not cause isotopic fractionation where as biodegradation would (Fig. 3).

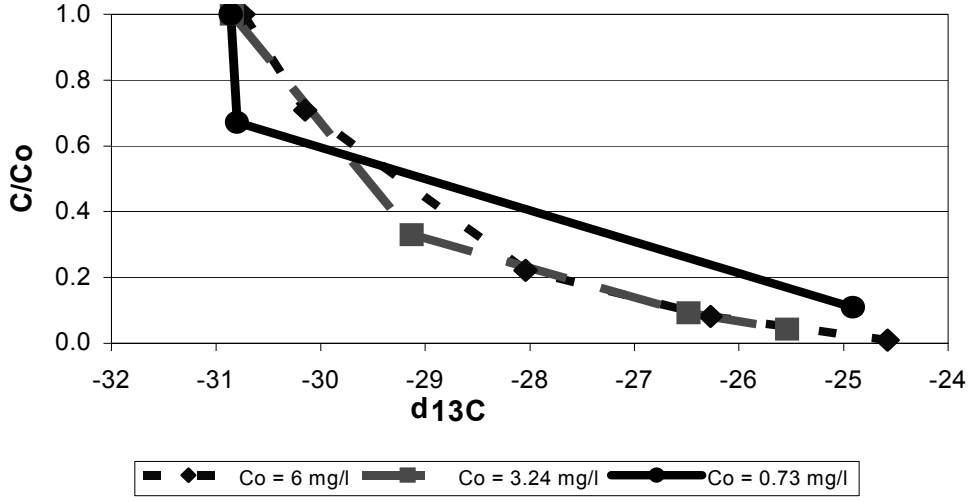

Fig. 2 Microcosm results showing an enrichment in average of 6‰ on MTBE-$\delta^{13}C$.

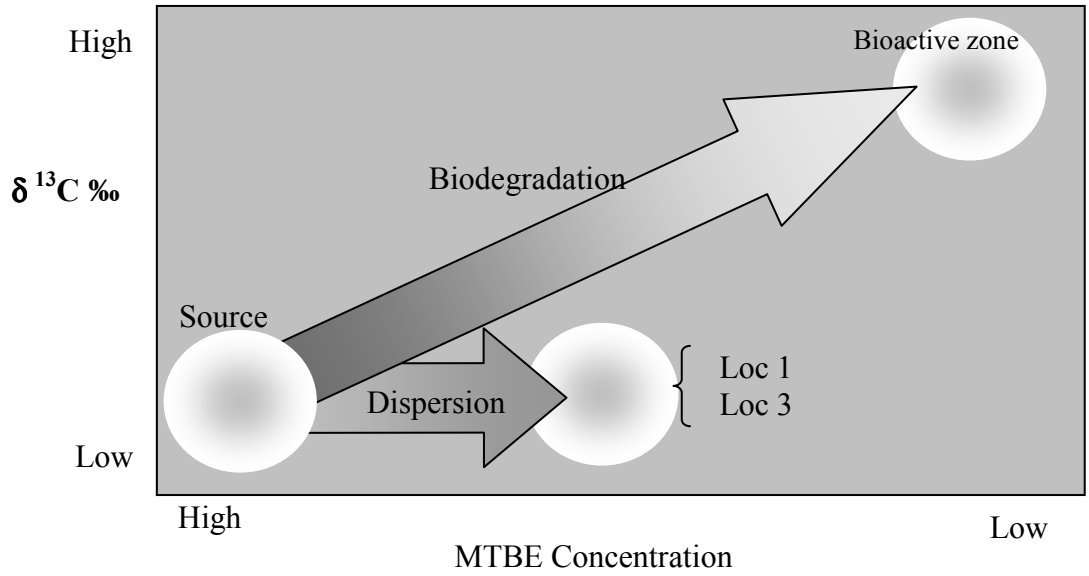

Fig. 3 Expected isotope fractionation behaviour in the field at Port Hueneme, California, USA.

In the field, the most depleted sample had an MTBE-δ^{13}C of –30.6‰, and the most enriched –27.0‰, the maximum variation observed in field triplicates was 1.1‰. For location 1 the results were divided into source area (low DO and not affected by biodegradation) and bioactive zone (high DO, where biodegradation takes place). Within the source zone, the MTBE-δ^{13}C ranged from –30.6 to –29.1‰, and within bioactive zone from –29.5 to –27.0‰ (Fig. 4).

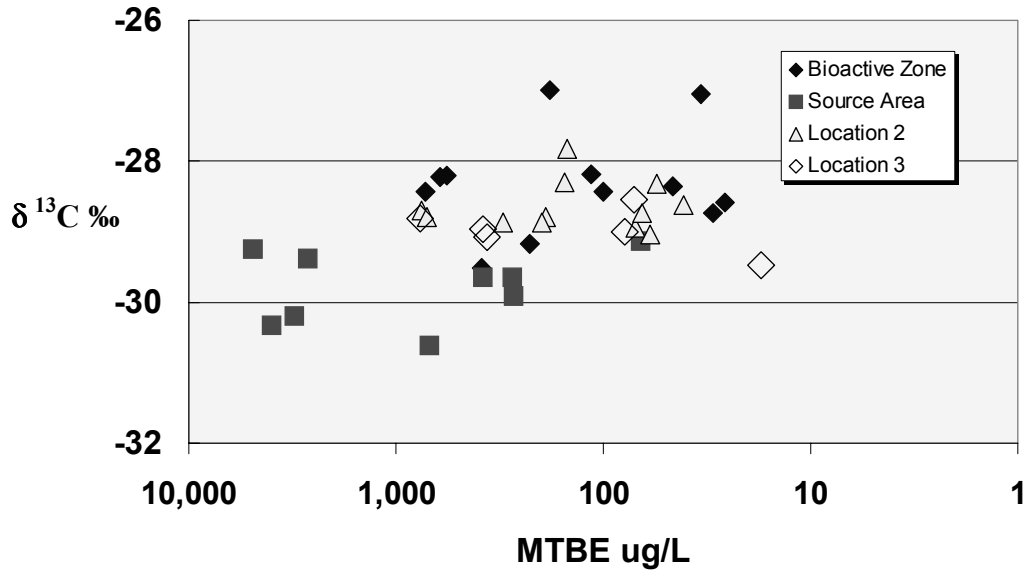

Fig. 4 MTBE-δ^{13}C results at Port Hueneme, California, USA.

These results show a very limited isotope fractionation at a field site where MTBE has biodegraded from concentrations >10 mg l^{-1} to non-detect levels. This fractionation is lower than expected from laboratory microcosm data, probably due to groundwater paths mixing in the field. Therefore, at least for this site where biodegradation is known to occur, the stable carbon isotope technique could not be employed as a conclusive tool to assess biodegradation.

At location 3, which is not been affected by the biobarrier, the MTBE-$\delta^{13}C$ ranged from –29.5 to –28.6‰, and at location 2, from –29.0 to –27.8‰. These results may be showing a wider range for the non-biodegraded MTBE-$\delta^{13}C$ signature, or a very limited MTBE biodegradation at these locations.

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