

## **Fifth Quarterly Report**

**Date of Report:** 4-4-07

**EPA Grant Number:** R83-0633-010

**Title:** Utilization of the carbon and hydrogen isotopic composition of individual compounds in refined hydrocarbon products to monitor their fate in the environment

**Investigators:** R. Paul Philp and Tomasz Kuder

**Institution:** University of Oklahoma

**EPA Project Officer:** Bala Krishnan

**Project Period:** 9-1-04 to 12-31-06 (extended to 8-31-07)

**Project Amount:**

**Research Category:** Petroleum Environmental Technology - Natural attenuation

### **Objective(s) of the Research Project:**

The major goal of this work is to develop a cost-effective method, which can be successfully applied to contaminated sites, to demonstrate the onset of natural attenuation of contaminants and monitor the extent and progress of this attenuation. The compounds of primary interest in this study are MTBE, TBA and volatile hydrocarbons associated with refined hydrocarbon products. Successful demonstration of the method with these compounds will readily permit its extension to other common contaminants such as PCE and TCE. Furthermore, although the matrix of interest is primarily groundwater, soil samples from selected sites will also be investigated (the soil matrix study may be more relevant to BTEX and especially TMB contamination).

The objectives to be investigated in order to meet this goal can be summarized: (1) extend existing results that indicate variations in carbon and hydrogen isotopic compositions of MTBE, TBA and BTEX compounds can be used to monitor the onset and extent of natural attenuation; (2) establish that stable carbon and hydrogen isotopes can be used to evaluate mechanisms of MTBE degradation and relationship to other oxygenates, such as TBA possibly derived from MTBE; (3) determine major environmental affects controlling the rate of MTBE degradation; (4) determine the major isotopic shifts associated with TBA transformation; (5) differentiate aerobic and anaerobic degradation mechanisms; (6) investigate the use of isotopic fractionation to monitor abiogenic degradation with the expectation to improve understanding of the fractionation resulting from biogenic degradation; (7) determine whether results can be extrapolated to MTBE and TBA sites also containing BTEX components; and (8) determine whether soil analysis contributes to site characterization beyond information obtained on waterborne contaminants.

### **Progress Summary/ Accomplishments**

In the 1st quarter 2007, the focus of the project was the continuation of work on the isotope fractionation in MTBE caused by volatilization-related processes (abiotic attenuation). Additionally, the archived anaerobic microcosms have been screened for methane production and the previously studied commercial gasoline samples have been reanalyzed to obtain TBA carbon isotope ratios. Work has been continued on the MTBE plume undergoing air sparging (Illinois site).

Isotope effects due to air sparging and soil vapor extraction

Benchtop-scale sediment column experiments have been conducted to simulate air sparging and soil vapor extraction. The two techniques are common site remediation techniques and unlike the natural (passive) volatilization are likely to result with significant attenuation of MTBE. Large MTBE mass fluxes driven by these processes can potentially result with more measurable isotope fractionation, therefore an experimental assessment of the isotope effects of this type will strengthen the utility of CSIA data for attenuation studies. Carbon and hydrogen isotope compositions of MTBE have been measured over a range of concentration decrease during the air sparging and soil vapor extraction. The patterns of isotope fractionation resulting from the two processes were distinctly different from those of anaerobic biodegradation and the magnitude of the carbon isotope enrichments was negligible. The experimental results on air sparging are directly relevant to the field site (Illinois) where an actual MTBE plume is treated by this technique.

#### CSIA of TBA in gasoline

Decomposition of MTBE during purge and trap desorption has been observed previously. TBA produced at the expense of MTBE “diluted” the original TBA present in gasoline and the measured isotope ratios were inaccurate. The purge and trap method has been optimized to allow analysis of TBA in the presence of high concentration of MTBE in the sample matrix. The resulting  $\delta^{13}\text{C}$  values of TBA from the gasolines were from  $-26.6$  to  $-21.7$ . This range of  $\delta^{13}\text{C}$  is “heavier” than the previously reported values for MTBE at field sites. The implication of this finding is that all carbon isotope ratios in TBA measured previously at field sites are within the normal range of fresh gasoline source.

#### **Publications/Presentations**

Kuder, T.; Philp, P.; Allen, J. “Stable isotope fractionation resulting from biotic and abiotic MTBE attenuation processes”. Presented at EGU General Assembly 2007, Vienna, Austria, 15 – 20 April 2007.

#### **Future activities**

For the following quarter, the focus of activities is to process and interpret the existing experimental data. It is expected that samples from additional field sites (benzene plumes) and optionally the Illinois MTBE/TBA plume with air sparging project will be collected and analyzed by CSIA.

**Supplemental Keywords:** Water, groundwater, sediments, bioavailability, metabolism, VOC, organics, bioremediation, cleanup, environmental chemistry, analytical, EPA Regions (1 through 10), petroleum industry

**Relevant Web Sites:** None