

6th Quarterly Report

Date of Report: 7-4-07

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

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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 2nd quarter 207, the focus of the project was evaluation and synthesis of the existing experimental data. Additional field sites have been sampled and subjected to CSIA.

Field sites

Two more benzene plumes and new sample sets from the air sparging site in Illinois have been collected and analyzed by CSIA. As for the previously reported sample sets, 2D-CSIA trends were indicative of biodegradation of benzene.

Data evaluation

A number of manuscripts based on the produced experimental data is in progress and will be submitted for publication. The titles listed below are tentative.

1. “Carbon and hydrogen isotope effects in anaerobic biodegradation of MTBE” – a summary of the microcosm experiments. The main deliverable is the exact determination of the carbon and hydrogen enrichment factors and demonstration that isotope effects caused by various soil consortia are identical, improving the strength of quantitative application of CSIA for field site assessment.
2. “Stable isotope fingerprinting of gasoline components” – a summary of the survey of the isotope ratios in the oxygenate and aromatic gasoline compounds. The main deliverable is defining the reference points (source isotope ratios) for CSIA in attenuation studies.
3. “Stable isotope effects in volatilization-mediated attenuation of MTBE” – a summary of the experiments with abiotic processes. The main deliverable is defining the potential of interference from isotope effects caused by abiotic attenuation processes and validating the utility of CSIA for the sites subject to attenuation techniques such as air sparging and soil vapor extraction.

Publications/Presentations

Kuder, T.; Philp, P.; Allen, J. “Stable Isotope Fractionation Resulting from Biotic and Abiotic MTBE Attenuation Processes”. Submitted for The 23rd International Meeting on Organic Geochemistry, 9–14 September 2007, Torquay, United Kingdom.

Kuder, T.; Philp, P.; Allen, J. “Stable Isotope Fractionation Resulting from Biotic and Abiotic MTBE Attenuation Processes”. Submitted for AEHS Annual International Conference on Soils, Sediments & Water, 15–18 October 2007, Amherst, Massachusetts.

Kuder, T.; Philp, P.; Allen, J. “Forensic geochemistry– stable isotope fingerprinting of gasolines”. Submitted for The 14th Annual International Petroleum Environmental Conference, 6–9 November 2007, Houston, Texas.

Kuder, T.; Philp, P.; Yang, X; Allen, J. “Monitoring of MTBE attenuation by stable isotope analysis”. Submitted for The Stable Isotope Conference – Stable Isotope Tools for the Assessment of Chemical and Microbial Transformation Reactions in Complex Natural and Contaminated Environments, 18 - 23 November 2007, Mt. Verità, Switzerland.

Future activities

For the following quarter, the focus of activities is to process and interpret the existing experimental data. It is planned to conduct several wrap-up experiments on MTBE fractionation. Microcosms constructed with one of the sediment samples exhibited slightly lower isotopic fractionation than the remaining microcosms. A series of experiments is in preparation to identify the probable cause of the difference. Several of the archived microcosms will be amended with fresh MTBE and used to test the effect of various experimental parameters on the isotope fractionation magnitude. The next screening event is planned to test whether biodegradation of TBA (and MTBE in the one previously inactive sediment) has been initiated. Work with field sites (benzene plumes) and optionally the Illinois MTBE/TBA plume with air sparging project will continue.

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