

Third Quarterly Report 2006

Date of Report: 10-05-06

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

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 3rd quarter, the focus of the project was application of CSIA to characterization of MTBE and benzene attenuation at field sites. Additionally, the status of biodegradation of MTBE and TBA in the microcosm experiments initiated previously has been monitored.

Field application of CSIA:

Two topics have been pursued in this section – effects of sampling strategy on the outcome of CSIA and application of CSIA to benzene contamination. The first of the two objectives refers to the influence of plume heterogeneity on the results of CSIA. While MTBE biodegradation may

locally reduce MTBE concentration and cause a corresponding isotopic effect, water recovered from the radius of a monitoring well can be dominated by the parts of the plume with none or limited biodegradation. CSIA performed on such a sample would be inconclusive. Pre-sampling purging of well volume can magnify this effect. On the other hand, sampling of discrete narrow intervals of a plume, with no purging, should increase the probability of diluting of the biodegraded contaminant. A site with independent evidence of in-situ biodegradation potential has been selected based on the following criteria: 1) there has been historical presence of TBA in strong excess of MTBE in parts of the plume, suggesting a possibility of in-situ MTBE to TBA biotransformation; 2) Bio-Sep (in-situ microcosms) indicated that there is microbiological potential for anaerobic degradation of MTBE (the Bio-Sep experiments were performed by a different research group and were not part of the current project). On the other hand, a previous round of CSIA work has shown MTBE isotope values within the normal range of undegraded gasoline. Samples from four monitoring wells (selected for high TBA/MTBE concentration ratios) were collected from two discrete depth intervals each without well purging and subjected to CSIA. The results were negative/inconclusive (MTBE isotope values within the normal range of undegraded gasoline). All of the analyzed samples were essentially identical in their isotope ratios. At this site, either the plume heterogeneity was not picked up at the spatial resolution of sampling or the isotope fractionation had not occurred.

Additionally, CSIA has been applied to study benzene contamination at two field sites. The results agreed with the earlier data set – two-dimensional CSIA analysis (carbon and hydrogen) visualized a fractionation pattern consistent with benzene biodegradation. On the other hand, due to relatively low magnitude of isotope fractionation in the case of benzene, carbon CSIA alone seems to be insufficient to confirm in-situ biodegradation.

Microcosm experiments:

The previously constructed sets of microcosms have been screened for evidence of TBA and/or MTBE biodegradation and for accumulation of methane. No evidence of TBA biodegradation was apparent in concentration data in any of the samples. No evidence of MTBE biodegradation was apparent in concentration data of microcosm set that were inactive at the time of the former screening.

Publications/Presentations

None

Future activities

For the following quarter, it is planned to continue work with determination of stable isotope enrichment factors in the MTBE-degrading microcosms, including the analysis of hydrogen isotope fractionation, for validation of 2D-CSIA approach in MTBE attenuation studies. The second aspect of work will be continuation lab experiment on isotope fractionation upon abiotic attenuation of MTBE. Finally, more field sites (MTBE and/or benzene plumes) will be studied.

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