

Utilization of the Carbon and Hydrogen Isotopic Composition of Individual Compounds in Refined Hydrocarbon Products to Monitor Their Fate in the Environment

Date of Report: 04-05-05

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

Since the submission of the last report, progress has been made primarily in the microcosm experiments and GCIRMS analysis of commercial gasolines. Additionally analytical GCIRMS methods have been tested on environmental samples containing alternative gasoline oxygenates, ethanol and tert-butyl ethyl ether (ETBE).

Microcosms:

This part of the study is done in collaboration with Dr. Irene Davidova from Dr. Suflita's group at OU Microbiology Department. This arrangement allows us to conduct the microcosm experiments drawing on the expertise in anaerobic biodegradation provided by our partner.

Microcosms have been prepared using the previously received sediment from MTBE and/or TBA-contaminated sites. Eight sets of replicate anaerobic microcosms for MTBE degradation were set up using sediment from six contaminated gas station sites in California obtained from BP partner (including three separate experiments set up using three spatially different sediment samples from the same contaminated site). The sites have been previously studied for isotope effects in groundwater and evidence of MTBE biodegradation was detected. MTBE degradation (conversion to TBA) was observed in six of the experiments in all or at least some of the "live" replicates, while no MTBE-TBA conversion was observed in sterile replicates. MTBE degradation was observed after repeated amendment with fresh substrate, and corresponding near-stoichiometric accumulation of TBA occurred. Degradation of MTBE resulted with strong isotope fractionation, measured by GCIRMS. One of the data sets had to be discarded, because isotope effects caused by biodegradation were obscured by the presence of ^{13}C -labeled MTBE used in-situ by a different research group. No evidence of activity was in microcosms from two study sites. Carbon isotope composition of MTBE and TBA was measured to obtain the objective value of enrichment factors characteristic of anaerobic MTBE bioconversion. The values of enrichment factor (ϵ) for MTBE degradation calculated for the data sets from all of the active microcosms are virtually identical and cluster around -17. This value implies even stronger isotope effect for this type of reaction than the values reported earlier. The difference is likely due to different experimental designs. Unlike in the previous studies, all of the microcosms discussed here were kept homogenous (culture bottles set on a shaker or turned over daily) to minimize heterogeneity of the medium and avoid underestimation of isotope effects. The consistence of the value between the individual data sets from different sediment samples, identical for the methanogenic and the sulfate reducing conditions, gives strong support for using the obtained value of ϵ in evaluation of MTBE degradation in-situ to calculate the amount of degraded MTBE. This phase of the project can be considered successfully completed. The remaining two inactive MTBE microcosm sets are being monitored on a monthly basis and if activity develops, they may be possibly included in a later report.

Three sets of anaerobic microcosms (two methanogenic, none sulfate reducing) were set up to study TBA biodegradation. Additionally, control samples of the MTBE experiments contain ppm-level concentrations of TBA and are also monitored for potential TBA-degrading activity. In one of the two methanogenic experiments, significant methane generation in TBA-amended microcosms has been observed (up to 1% methane in headspace). At present, concentration and isotope composition of TBA do not offer confirm anaerobic degradation.

Analysis of commercial gasolines:

A collection of 50 samples of commercial gasolines from Midwestern, East Coast and Southeastern states has been obtained from Dr. Graham Rankin (Marshall University, WV). Selected specimens of the set were screened by direct injection onto GCIRMS (carbon and hydrogen mode). To obtain carbon and hydrogen isotope values of the oxygenates (MTBE and TBA), aliquots of gasolines have been equilibrated with water and analyzed by purge and trap-GCIRMS method. This pretreatment step was necessary to eliminate low molecular weight

hydrocarbons of gasoline causing GC coelution upon GCIRMS analysis and assure accurate determination of $\delta^{13}\text{C}$ and δD . In particular, adequate GC separation of TBA from gasoline matrix is impractical in direct injection. At present the complete set of carbon isotope data is available. MTBE and TBA have been present in half of the samples at the method's detection limit. Carbon isotope ratios of MTBE ($\delta^{13}\text{C}$ of -27.9 to -30.3) agree with the values published elsewhere. TBA isotope compositions ($\delta^{13}\text{C}$ of -25.3 to -29.7), representing the values expected for TBA partitioning from gasoline spills, are the first data set of this type and can be used as a baseline for in-situ studies. To date, very few of the TBA-contaminated field samples analyzed by GCIRMS show values clearly different than those observed in gasolines – $\delta^{13}\text{C}$ values as positive as -21, -22 were noted at two out of over 40 sites analyzed to date at the University of Oklahoma. Microcosms are run on sediment from one of the “anomalous” TBA sites.

Publications/Presentations

Stable isotope analysis in remediation of gasoline oxygenates and hydrocarbons (T. Kuder and P. Philp). 2005 International Petroleum Environmental Conference, Houston, TX, oral presentation and abstract.

Future activities

Screening of the existing TBA microcosms and the two previously inactive MTBE microcosm sets is planned to detect the potential onset of degradation. The remaining samples of gasoline and the aqueous gasoline equilibrates will be analyzed to finish the database of hydrogen isotope composition of MTBE and the aromatic compounds.

At this stage it is planned to initiate the lab-scale experiments of isotope fractionation upon abiotic attenuation (volatilization and vapor diffusion-related) of MTBE.

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