

2-nd quarterly report 2006

Date of Report: 07-05-06

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 effects 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 abiotic 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

The work in the second quarter was focused on completing the database of carbon and hydrogen isotope ratios of gasoline oxygenates (MTBE and TBA) and gasoline aromatics. Experiments have been initiated to determine the potential range of isotope fractionation due to abiotic attenuation processes to better understand the uncertainties of the isotope-based biodegradation studies. Additionally, several field sample sets – case studies – from gasoline contaminated sites have been added to the database. Biodegradation status of MTBE, TBA, benzene and/of TAME was investigated.

Analysis of commercial gasolines:

Carbon and hydrogen isotope ratios of MTBE, TBA (carbon isotope ratio only), benzene, toluene, ethylbenzene, xylenes and 1,2,4-trimethylbenzene (the oxygenates and the major aromatic compounds) have been measured for 25 samples of commercial gasolines from Midwestern, East Coast and Southeastern states obtained from Dr. Graham Rankin (Marshall University, WV). Carbon isotope ratios of additional aromatic compounds (a number of tri- and tetramethylbenzenes and naphthalene) were measured for an additional 25 gasolines (these samples did not contain detectable amounts of MTBE). All samples have been analyzed by purge and trap-GCIRMS after equilibration with water to improve GC separation of target analytes and to increase the precision of isotope ratio determination (the effective concentration of a number of interfering compounds, e.g., of the aliphatic fraction of gasoline, was greatly reduced by this treatment). 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 (as reported in the previous quarter). Hydrogen isotope ratios of MTBE fall between δD of -80 and -106. Carbon isotope ratios of gasoline aromatics (22 different compounds) range from $\delta^{13}\text{C}$ of -23 to -28. Hydrogen isotope ratios of gasoline aromatics range from δD of -35 to -100.

Isotope effects in abiotic attenuation processes:

Isotope fractionation caused by various abiotic non-degradative processes is normally considered small and negligible for the purpose of field site evaluation. In fact the number of reference data to substantiate this claim is not large and the present study is intended to fill this gap.

Experimental determination of carbon and hydrogen fractionation upon phase equilibrium partitioning (water-headspace, NAPL-headspace and neat MTBE-headspace) of MTBE yielded small but measurable carbon effects and relatively significant hydrogen effects (approximately 10 permil δD difference between the equilibrated pools). Kinetic fractionation of aqueous MTBE by volatilization diffusion of MTBE vapor through a porous medium resulted with a measurable carbon isotope effect (the enrichment factor of -0.7 was measured). The latter is of similar magnitude as some of the values determined in aerobic MTBE biodegradation studies, but lower by a factor of 20-30 than the values obtained in our anaerobic microcosms.

Case studies – field sites

As a part of this study, CSIA method has been applied to study benzene contamination. 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, in particular with old or complex contaminant plumes where it is difficult to determine the accurate value of the initial isotope composition of the contaminant.

Additionally, a site with TAME contamination was studied. While no evidence of isotope fractionation was detected, the analytical utility of PT-GCIRMS was demonstrated for this compound.

Publications/Presentations

None

Future activities

Screening of the existing TBA microcosms and the previously inactive MTBE microcosm sets is planned to detect the potential onset of degradation. An additional round of MTBE degradation experiments will be performed with the active microcosms and combined carbon and hydrogen data will be collected (the former to improve the precision of the calculated enrichment factors, the latter to confirm the initial conclusions on hydrogen isotope fractionation based on our 2004 data). It is planned to continue the lab-scale experiments of isotope fractionation upon abiotic attenuation (volatilization and vapor diffusion-related) of (kinetic fractionation) and also benzene, toluene and p-xylene (equilibrium and kinetic fractionation). More sites with BTEX contamination are sought for analysis, to demonstrate the utility of 2-D CSIA analysis for this class of compounds.

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