

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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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 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 first quarterly report, progress has been made both in laboratory and field studies. The current report will discuss: 1) microcosm experiments; 2) analysis of field samples; and 3) analysis of commercial gasolines.

Microcosm experiments

Continuation of work with previously described material from the ARCO gas station site in Huntington Beach, California resulted with confirmation of anaerobic MTBE degradation potential. Virtually complete and stoichiometric conversion of MTBE to TBA in all live specimens was observed after 10 weeks of incubation, corresponding to accumulation of methane. No MTBE degradation was observed in control experiments (sterilized soil from the site). Due to MTBE concentration decreasing below the GCIRMS quantitation limit at the time of sampling, no isotope data were collected. Three of the “live” replicate microcosms have been reamended with MTBE and sampling is currently underway at more frequent intervals to obtain specimens throughout the biodegradation gradient. Two of the “live” replicate microcosms have been reamended with MTBE, sulfate and methanogenesis inhibitor. Finally, three of the “live” replicate microcosms with high concentrations of TBA (resulting from completed MTBE degradation) have been left in place to monitor TBA degradation.

A second set of microcosm experiments has been initiated using material (water with sediment suspension) from a gas station site (ARCO facility, Los Angeles, California). Data previously obtained on TBA in groundwater from the site suggest the possibility of in-situ TBA biodegradation. Based on groundwater geochemistry, the microcosms are set up for methanogenic degradation.

Field studies

Continuation of work on field samples was primarily focused on screening a number of potential microcosm study sites for isotopic evidence of biodegradation of MTBE and/or TBA. The sites have been selected as sites where biodegradation might be taking place based on their historical MTBE concentration data and on standard geochemical attenuation criteria. To date, a total of 8 sample sets from field sites in California have been delivered to OU. Samples from three of these have been processed. Evidence of biodegradation (“heavy” signatures of MTBE) was detected in two of those.

Additionally, in continuation of the previously performed carbon isotope work, a sample set from a BP gas station site in New York has been analyzed for hydrogen isotopes of MTBE. Combined carbon + hydrogen results supported the expected aerobic biodegradation mechanism of MTBE attenuation at this site.

Analysis of commercial gasolines

As discussed in the introductory section of the proposal one of the project objectives is to provide a database of carbon and hydrogen isotope ratios for gasoline compounds of interest. A set of 40 commercial gasolines collected from throughout the USA has been obtained from Dr. J.G. Rankin (Marshall University) and is scheduled for analysis in July 2005.

Publications/ Presentations:

1. Stable isotope analysis in remediation of gasoline oxygenates and hydrocarbons (T. Kuder and P. Philp). Abstract submitted for 2005 International Petroleum Environmental Conference, Houston, TX.

2. Compound-specific isotope analysis applied to MTBE biodegradation studies (T. Kuder, P. Philp, J. Wilson, and J. Allen). 2005 International Meeting on Organic Geochemistry, Seville, Spain.
3. Stable isotope analysis of MTBE (T. Kuder) Included in: "Evaluating Monitored Natural Attenuation of MTBE & TBA" Preconference Workshop, 2005 NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals, Costa Mesa, CA.

Future activities: Continuation of the work with the existing microcosms is planned to enable enough data to be collected for precise calculation of the magnitude of isotope effects upon MTBE biodegradation. After completing the analyses of groundwater samples already collected, selection of sites for collecting additional microcosm experiments will be made and the microcosms will be constructed. Monitoring of TBA microcosms for evidence of biodegradation will continue.

It is planned to initiate screening of the incoming field samples for stable isotope effects indicative of monoaromatic compound degradation (carbon and hydrogen). The prerequisite for data interpretation will be provided by the database of carbon and hydrogen isotope ratios in fresh gasolines discussed above.

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