

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 compounds described above 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) existing results indicating variations in the carbon and hydrogen isotopic compositions of MTBE, TBA and BTEX compounds can be used to monitor the onset and extent of natural attenuation will be extended; (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.

Laboratory microcosm experiments will be undertaken in parallel with the field studies to obtain information on the intermediates involved in the degradation of the MTBE. TBA is a particularly important compound whose origin is unclear and also another contaminant which is of great concern. It is known that a certain amount of TBA is commonly associated with the

production of MTBE and therefore will be added to the gasoline at the same time as the MTBE. However TBA is also a degradation product of MTBE. Hence it is anticipated that the use of stable isotopes may permit these two sources of TBA to be differentiated.

Progress Summary/ Accomplishments:

Due to a variety of bureaucratic problems there were some delays in getting this research program started. However the problems have now been resolved and the work is underway as planned. The majority of effort to date has been directed towards the laboratory microcosm experiments and a brief summary of the progress in this area is given below.

Microcosm experiments

In the initial stage of the project, several industrial partners were contacted for soil samples necessary to construct MTBE-degrading microcosms. Soil was obtained from a gas station site (ARCO 1888, Huntington Beach, California) and used to construct the microcosms for an anaerobic (methanogenic) biodegradation experiment. MTBE-amended, control (no MTBE amendments) and lactate + MTBE amended replicate microcosms were set up in January 2005. Methane concentration has been analyzed twice since the start of the experiment. To date the observed accumulations of methane in the MTBE amended microcosms are small (highest in the lactate microcosms). Aliquots of microcosm water were collected at time zero and analyzed for MTBE concentration and isotope composition. The next MTBE sampling period and analysis of isotope ratios is scheduled for mid-April. Field samples from this site have been analyzed and strong isotope enrichment effects observed. Additional microcosm data on the same site are available confirming MTBE biodegradation potential. The current microcosm experiment is intended to provide quantitative measure of the extent of isotope fractionation during anaerobic MTBE biodegradation by the microbial association from this specific location.

It is anticipated, based on a verbal communication from the cooperating BP industrial partner, that another soil sample for MTBE/TBA degradation experiment will be collected at a gas station site from Vinal, California, this spring, along with water samples. Three sets of water samples from three sampling events in 2002-2004 have been analyzed in the past, indicating a strong possibility of TBA biodegradation. The new set of water samples will extend the existing monitoring data. TBA biodegradation is of particular interest as far less is known in this area than in the case of MTBE biodegradation.

Additional soil samples from cooperating partners from Shell and Exxon are expected later in the season. These samples will be used in similar microcosm studies to verify the numerical range of isotope effects in MTBE and TBA degradation.

Field studies

Except for the sample set discussed above (TBA-contaminated water from Vinal, CA), four field sample sets (Chevron, Exxon and two sets from BP) have been analyzed recently and at least 1 more is scheduled for sampling in the near future for carbon isotopes in MTBE and TBA. The sites have been selected based on their historical MTBE concentration data and on

standard geochemical attenuation criteria, as sites where biodegradation might be taking place. Isotope data offered confirmation of biodegradation in some of the samples analyzed for at least two sites. One of the sites is scheduled for hydrogen isotope analysis as it was proposed that aerobic biodegradation might have been active there (hydrogen isotope analysis is better suited for characterization of aerobic biodegradation on MTBE samples).

Water samples from other gas station sites will be collected for isotope analysis throughout the year 2005, and results will be generated as the samples show up.

Publications/ Presentations: List the citations for all publications and presentations arising from this project, including those submitted, in press, or published.

Future activities: Describe the major objectives and focus for the subsequent reporting period, including any expected changes in the project schedule.

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