Project Title: "Monitored Natural Attenuation of MTBE"

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Introduction to the problem When gasoline is spilled from under ground storage tanks, Methyl Tertiary Butyl Ether (MTBE) and its degradation product Tertiary Butyl Alcohol (TBA) are among the most important contaminants that are released to ground water. The state agencies that regulate spills of gasoline from underground storage tanks need information on the behavior of MTBE and TBA in spills of gasoline.

Background: Most MTBE plumes in groundwater are anaerobic, and the organisms that naturally degrade MTBE in these plumes must be anaerobes. Unfortunately It has been very difficult to isolate anaerobic MTBE degrading microorganisms for study in the laboratory. As a consequence, risk manages often fail to consider the contribution of natural biodegradation of MTBE in groundwater in their exposure evaluation. They also fail to recognize the hazard from the accumulation of TBA that is produced from biodegadation of MTBE. Recent laboratory work has shown that the ratio of stable carbon isotopes is shifted during biodegradation. MTBE molecules with the lighter isotope (^{12} C) are preferred, and the residual MTBE accumulates more molecules with the heavy isotope (^{13}C). The extent of degradation can be predicted from the change in the ratio.

Objectives: 1) Determine the contribution of natural biodegradation of MTBE to natural attenuation of MTBE at gasoline spill sites. 2) Develop and evaluate the use of stable carbon isotope ratios as a tool to recognize natural biodegradation of MTBE when it occurs at a particular gasoline spill site. 3) Isolate microorganisms that are capable of anaerobic biodegradation of MTBE, and to characterize the pathways of MTBE metabolism and the requirements for MTBE metabolism under anaerobic conditions.

Approach: 1) Conduct detailed case studies at representative plumes of MTBE to document the rate and extent of natural attenuation of MTBE at field scale, 2) Analyze water samples from a large number of sites for the concentration of TBA and MTBE, to determine the co-distribution of MTBE and TBA, 3) Compare the ratio of concentrations of TBA to MTBE to determine if the TBA was produced by biological action on MTBE, 4) Evaluate the usefulness of the analysis of stable carbon isotope ratios to determine if MTBE has been biologically degraded in ground water.

Accomplishments to date (24 Feb 2003):

The survey data shows much higher concentrations of TBA at gasoline spill sites than would be expected from the small amounts of TBA that are present in the gasoline. In Orange County, California and in selected gasoline stations in the eastern United States, the amount of TBA in ground water is equivalent to the amount of MTBE.

At a gasoline spill site in New Jersey, the attenuation of MTBE along the flow path in ground water was directly related to an increase in the stable carbon isotope ratio in the residual gasoline in the plume. The increase in ratio of stable carbon isotope was confirmed in a microcosm study done with core material from the site.

Ground water at gasoline spills in Orange County, California has a particularly high concentration of TBA. We have completed a survey that compares the changes in the stable isotope ratio of MTBE to the attenuation of MTBE and accumulation of TBA. At most stations the high concentration of TBA was caused by natural biodegradation of MTBE. When the stable isotope ratios for MTBE were measured in at 13 gasoline spills in Orange County they revealed that there had been extensive biodegradation of MTBE in at least one well at each site. In 11 of the 13 stations, the TBA in the well with the highest concentration of TBA was produced in the ground water from biodegradation of MTBE..

The following articles have been published.

Fate and Transport of MTBE and Other Gasoline Oxygenates. 2003. John T. Wilson. In: *Handbook for Managing Releases of Gasoline Containing MTBE*. Editors: Ellen Moyer and Paul Kostecki. Amherst Scientific Publishers. pp. 9-61.

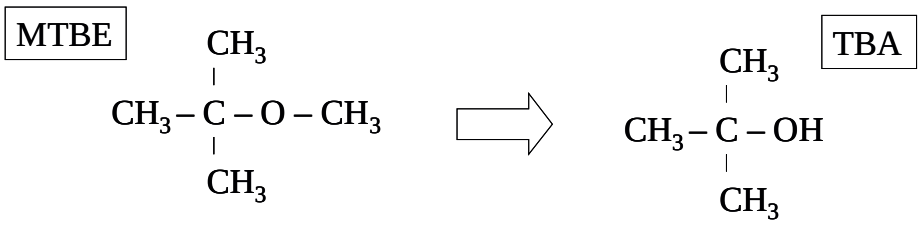
Role of Natural Attenuation in the Life Cycle of MTBE Plumes. Wilson, John T., and Ravi Kolhatkar. *Journal of Environmental Engineering*, Volume 128(9):876-882, (2002).;

Use of Compound-Specific Stable Carbon Isotope Analyses to Demonstrate Anaerobic Biodegradation of MTBE in Groundwater at Gasoline Release Site. Ravi Kolhatkar, Tomasz Kuder, Paul Philp, Jon Allen, and John T. Wilson. *Environmental Science & Technology* 26(24):5139-5146 (2002):

Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions. 2000. Wilson, J. T., J. A. Vardy, J. S. Cho and B. H. Wilson. (EPA/600/R-00/006) available at www.epa.gov/ada/pubs/reports.html

Near future tasks: A journal article is in preparation Titled *Contribution of biodegradation of MTBE to high concentrations of TBA at gasoline spills sites in Orange County.*

Graphics could also include the graphic on the cover of
Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions.



Orange County, California