Effects of Environmental Conditions on MTBE Degradation in Model Column Aquifers

Clinton D. Church, Paul G. Tratnyek, James F. Pankow, James E. Landmeyer, Arthur L. Baehr, Mary Ann Thomas, and Mario Schirmer

ABSTRACT

The current concern over point-source and non-point-source contamination of ground water by methyl tert-butyl ether (MTBE) has increased the need for a better understanding of the processes that control its environmental fate. As part of an ongoing study to characterize the potential for natural attenuation of MTBE, we have prepared a series of model column aquifers to investigate the pathways and kinetics of MTBE biodegradation under controlled conditions. The sediments used for these columns were collected aseptically from a variety of geographically and geologically distinct sites: (i) an urban site near Detroit, Michigan; (ii) an urban site in Turnersville, New Jersey; (iii) a controlled spill test site at Base Borden, Ontario, Canada; and (iv) a leaking underground storage tank site at the Laurel Bay Exchange, South Carolina. In all cases, autoclaved site ground water spiked with approximately 100 micrograms/liter MTBE was used as the column influent, and the column effluent was analyzed for MTBE and its potential degradation products. In aerobic column microcosms prepared with core materials from three sites, conversion of MTBE to TBA was observed after a lag period of approximately 35 days, but no evidence of subsequent TBA degradation was observed. This apparent MTBE to TBA conversion subsequently declined, as did measured dissolved oxygen. However, in similar columns with anaerobic influents, or with BTEX (gasoline constituents: benzene, toluene, ethyl benzene, and o-, m-, and p-xylene) contaminated aerobic influents, we have not seen any evidence of MTBE degradation up to 120 days. These results suggest that, if in situ biodegradation of MTBE occurs, it is most likely under aerobic conditions, and only in the absence of significant concentrations of more readily metabolized contaminants such as BTEX compounds.

INTRODUCTION

Evidence that methyl tert-butyl ether (MTBE) has become a widely distributed environmental contaminant has led to increased concern over its environmental fate and effects (Tratnyek and others, 1997; National Science and Technology Council, 1997; Squillace and others, 1997a; Squillace and others, 1997b). One question that has attracted a great deal of attention is the degree to which MTBE fate is determined by in situ biodegradation (for example, Borden and others, 1997; Landmeyer and others, 1998; Odencrantz, 1998; Schirmer and Barker, 1998).

The environmental fate of MTBE depends, in part, on the rates and products of MTBE degradation and, in part, on the physical transfer of MTBE among the different environmental compartments (Baehr and others, 1997; Pankow and others, 1996; Shaffer and Urchin, 1997; Squillace and others, 1997). For this reason, measurements of MTBE disappearance from ground water alone are not adequate to prove whether it has biodegraded in situ.

In order to demonstrate that in situ biodegradation of MTBE is occurring, measurements of MTBE disappearance need to be accompanied by evidence that microorganisms present at a particular site have the potential to degrade MTBE under realistic environmental conditions, and that this potential is realized in the field (Madsen, 1991; National Science and Technology Council, 1993). There is evidence that MTBE is biodegradable under favorable circumstances. Numerous investigators have reported biodegradation of MTBE in pure cultures, enrichments, and batch microcosms (Borden and others, 1997; Cowan and Park, 1996; Eweis and others, 1997; Hardison and others, 1997; Landmeyer and others, 1998; Mormile and others, 1994; Salanitro and others, 1994; Schirmer and others, 1998; Steffan and others, 1997; Yeh and Novak, 1994). However, despite evidence that MTBE biodegradation is possible, these results do not show that MTBE...
biodegradation is a significant process in the field. Nor do these results provide a means to estimate likely field degradation rates, because batch microcosms generally do not simulate aquifer conditions.

More compelling evidence for in situ degradation of MTBE would be the appearance of characteristic metabolic intermediates or products (Madsen, 1991). Of the studies that have reported MTBE degradation products, the most commonly observed products are tert-butyl alcohol (TBA) and CO_2, although tert-butyl formate (TBF) is the initial oxidation product of some aerobic microbial degradation pathways (Cain, 1981).

Recently, it has been reported that the cometabolic degradation of MTBE by a Graphium sp. produces both TBF and TBA when the mycelia are incubated under air, and exclusively TBA only when incubated in liquid culture (Hardison and others, 1997). The authors of that study concluded that TBF is the primary metabolite in both media, and that rapid hydrolysis of TBF to TBA in the liquid media is responsible for the apparent difference in product distributions. Further work has shown that Mycobacterium vaccae and a Xanthobacter strain also produce TBF as the primary degradation product (Hyman and others, 1998).

Rates of abiotic TBF hydrolysis to TBA in our laboratory support the suggestion by Hardison and others (1997) that previous studies may have underestimated the role of TBF as an intermediate in the biodegradation of MTBE. We found that TBF is hydrolyzed with half-lives (at 22°C) of 5 days, 8 hours, and 8 minutes at pH 7, 3, and 11, respectively (Church and others, 1999). Thus, TBF is unlikely to accumulate to detectable levels in groundwater, and is likely to be a poor tracer for in situ MTBE degradation.

A few studies have shown TBA to be further degraded to isopropanol, acetone, and ultimately CO_2. However, isopropanol and acetone are more biodegradable than TBA under most conditions, and so, like TBF, are unlikely to accumulate to detectable concentrations. Furthermore, isopropanol, acetone, and CO_2 may be degradation products of many other compounds, and as such, are not likely to provide characteristic evidence of MTBE degradation. Of all the products and intermediates reported in the degradation of MTBE, TBA remains the most promising indicator of degradation because it is (i) common to most MTBE degradation pathways (Church and others, 1997), (ii) a demonstrated product of MTBE biodegradation (Salanitro and others, 1994; Yeh and Novak, 1994), and (iii) sufficiently resistant to further degradation that it may accumulate as an intermediate before being further degraded (Cowan and Park, 1996; Mormile and others, 1994; Salanitro and others, 1994).

Unfortunately, even the detection of TBA in ground water samples does not provide unequivocal proof of MTBE degradation (Landmeyer and others, 1998). The reason for this is twofold: (i) TBA itself has occasionally been used as a fuel oxygenate, and (ii) TBA is often present as a contaminant in the MTBE that is subsequently blended into gasoline. Thus, unless it can be shown that TBA has never been introduced into a site, the most convincing way to demonstrate MTBE degradation to TBA is to show a mass decrease of MTBE with a concomitant TBA mass increase. This can be a difficult and costly task because it requires extensive multi-level sampling of an entire plume at multiple points in time. To the authors' knowledge, there are not yet enough data on any field site to unequivocally demonstrate the biodegradation of MTBE from the appearance of TBA. Of course, the lack of unequivocal proof of MTBE degradation from field studies does not mean that it does not occur under certain environmental conditions.

An alternative approach to investigate degradation of MTBE is to use controlled model systems that are designed to simulate typical field conditions. To perform this investigation, six model column aquifers were constructed using aseptically collected sediments from four sites and operated under various conditions. In order to compare sites that were geographically and geologically distinct, the sediments used in the columns were obtained from three US Geological Survey (USGS) projects and from a controlled release site in Ontario, Canada. The preliminary results presented here suggest that MTBE may be degraded only under aerobic conditions and only in the absence of significant levels of BTEX (gasoline constituents: benzene, toluene, ethyl benzene, and o-, m-, and p-xylene) compounds. Further studies are under way to determine (i) the kinetics of MTBE degradation, (ii) whether the observed degradation is metabolic or cometabolic, and (iii) which environmental parameters can be manipulated to enhance the degradation of MTBE.
MATERIALS AND METHODS

Standards and Analytical Techniques

Standard solutions were made using the highest purity MTBE and TBA that were available from commercial sources (Aldrich, >97%) and Millipore water. Standards and the effluent from column experiments were analyzed by direct aqueous injection with gas chromatography and detection by mass spectrometry (DAI-GC/MS) according to a method described previously (Church and others, 1997). DAI-GC/MS was particularly useful in this study because it allowed: (i) simultaneous quantification of MTBE and TBA; (ii) detection and identification of other substances that might be intermediates or degradation products, such as tert-butyl formate, isopropanol, and acetone; and (iii) monitoring of reaction progress over a wide range of concentrations.

Column Sediments

The sediments for the column studies were collected from four geographically and geologically distinct sites using either a hand auger or a split-spoon core sampler. In all cases, care was taken to use aseptic sampling techniques. Sediments were packaged to exclude oxygen and shipped on ice to the Oregon Graduate Institute where they were kept in a 4°C cold-room until they were repacked in the columns. A brief description of the sediments and aquifer conditions at each site follows.

Michigan Sediments

The Michigan sediments came from an urban National Aquifer Water Quality Assessment (NAWQA) Program study site in Farmington Hills, a suburb of Detroit. The sediments consisted of fine sand mixed with some silt and gravel, with an organic-carbon content ranging from 4 to 7 g/kg. The samples were collected from a depth interval of 1.5-4.0 m (5-13 feet), which is just below the water table in an unconfined aquifer composed of glacial outwash. The dissolved-oxygen concentration in the ground water was 1.2 mg/L.

New Jersey Sediments

Sediments from New Jersey were collected at an urban NAWQA study site in Turnersville, near the western edge of the surficial Kirkwood-Cohansey aquifer system in the coastal plain. Unsaturated zone sediment in this region is sandy and layered, as typical of marine deposition processes. Sediment used in the columns was collected at 5.7 m (18.8 feet), which is at the water table, and consisted of fine silty orange sand with intermixed clay. Organic content was not measured, but these sediments are typically low in organic content (Baehr and others, 1997).

Borden Sediments

The sediments for these columns were obtained from 3.0-4.0 m (10-15 feet) below the water table at the Canadian Forces Base Borden (Ontario, Canada) in an area that had previously been exposed to the Borden MTBE plume (Schirmer and Barker, 1998). The Borden aquifer is relatively homogeneous and composed of clean, well-sorted, fine- to medium-grained sand. The Borden aquifer has a relatively low carbon content of 0.02 percent and thus a low sorption capacity for organic compounds (Mackay and others, 1986). The dissolved oxygen content in the ground water ranged from 1-2 mg/L.

Laurel Bay Sediments

Sediments were collected at the water table from the Laurel Bay Exchange study site near Beaufort, South Carolina (SC), in the Atlantic Coastal Plain. The aquifer is comprised of silty, well-sorted sand grains. The grains are coated with Fe(III) oxides in uncontaminated areas that become progressively less prevalent with increases in contaminant concentration. Natural organic carbon content in these sediments is less than 0.02 percent. The depth to water is about 3.9 m (13 feet) near the underground storage tank (UST), and from 0.6 to 2.7 m (2 to 9 feet) nearer a concrete-lined drainage ditch, some 215 m (700 feet) downgradient of the UST source area (Landmeyer and others, 1998). Sediments used for the aerobic column experiments were collected from an aerobic (≥4.0 mg/L) part of the aquifer downgradient of the plume, where MTBE was detected but BTEX was absent. Sediments used for the anaerobic column experiment were collected from an anaerobic (<0.5 mg/L) part of the aquifer near the plume source that contained both MTBE and BTEX.
**Column Construction and Operation**

The columns were constructed using segments of 2.54 cm I.D. stainless steel pipe totaling 360 cm in length. Sediments were aseptically packed into autoclaved column segments using alcohol-flamed tools inside a linear flow hood or anaerobic glove box. The packed column segments were connected using autoclaved 1.5 mm O.D. stainless steel tubing with stainless steel fittings and incubated in a 15°C cold-room.

Column influent solutions were autoclaved site ground water which were either equilibrated with the atmosphere or purged of oxygen by sparging with N₂ prior to autoclaving. For the BTEX contaminated experiments, the ground water solutions were amended with 100 micrograms/liter (µg/L) of each of the constituents. These feed solutions were pumped through the column in upflow mode for 14 days at 40 milliliters/day (mL/day) using a syringe pump. After this initial equilibration period, the column feed was switched to identical solutions amended with approximately 100 µg/L (1.13 micromoles/liter) MTBE delivered at 40 mL/day. This pump rate was maintained and daily samples were taken until MTBE breakthrough was observed. After steady concentrations of MTBE were observed for five days, the flow rate was reduced to 1.5 mL/day to achieve a linear flow velocity between 0.67 and 1.0 cm/day (depending upon column porosity).

**RESULTS AND DISCUSSION**

**Columns with MTBE Degradation**

Three columns containing three different sediments from pristine sites were operated with aerobic influent that contained no detectable BTEX compounds. In each of these columns, TBA appeared in the effluent after a lag period of approximately 35 days (Figure 1, A and B and Figure 2, A). This was followed by a concomitant decrease in the concentration of MTBE.

Accompanying a decrease in conversion of MTBE to TBA was a decrease in measured dissolved oxygen in the effluent from approximately 9 mg/L to 1 mg/L. This correlation suggests that biodegradation of MTBE is favored by aerobic conditions, and will be investigated in subsequent experiments.

No evidence of TBA degradation (through product appearance) was observed in any of the columns. This suggests that, under the conditions tested, either TBA is recalcitrant or MTBE is a more favorable substrate. The mass balances, with the exception of as yet unexplained "spikes" at the onset of TBA appearance in the effluent, suggests a stoichiometric conversion of MTBE to TBA.

**Columns without MTBE Degradation**

One column had an anaerobic influent free of BTEX compounds. In this column, no MTBE to TBA conversion was observed up to 120 days (Figure 2, A, same sediment as in Figure 2, B). Two of the columns were fed with both aerobic and anaerobic site waters containing 100 µg/L BTEX compounds. No MTBE to TBA conversion was observed up to 120 days (Figure 3, A and B). The mass balances in these columns were equal to the MTBE concentrations, and so, were not included.

**Conclusions**

The preliminary results discussed above suggest that, if in situ biodegradation of MTBE occurs, it is most likely under aerobic conditions and in the absence of significant levels of more readily metabolized contaminants (such as BTEX). This finding is consistent with reports of batch experiments which show that biodegradation of MTBE can occur under aerobic conditions (Cowan and Park, 1996; Eweis and others, 1997; Hardison and others, 1997; Salanitro and others, 1994; Steffan and others, 1997) and that it is generally not observed or slow under anaerobic conditions (Mormile and Suflita, 1994; Yeh and Novak, 1994). Additional studies are being performed in the model column aquifers described here to determine (i) the rates of the MTBE degradation observed, (ii) whether the observed degradation is metabolic or cometabolic, and (iii) whether environmental parameters can be manipulated to enhance the degradation of MTBE.
Figure 1. MTBE and TBA concentrations in effluents from two columns containing previously uncontaminated sediments. The columns were challenged with aerobic influent containing MTBE. (A) Michigan Sediments, USGS urban NAWQA Study Site, Detroit, MI. (B) New Jersey Sediments, USGS urban NAWQA Study Site, Trenton, NJ.
Figure 2. MTBE and TBA concentrations in column effluents from a previously contaminated sediment operated with both aerobic and anaerobic influent containing MTBE. (A) Base Borden Sediments with aerobic influent, University of Waterloo Study Site, Ontario, Canada. (B) Base Borden Sediments with anaerobic influent, University of Waterloo Study Site, Ontario, Canada.
Figure 3. MTBE and TBA concentrations in column effluent from MTBE- and MTBE- plus BTEX-contaminated sediment. Influent for both columns contained both MTBE and BTEX compounds. (A) Laurel Bay MTBE-contaminated sediments, USGS Toxic Substances Study Site, Laurel Bay Exchange, Beaufort, SC. (B) Laurel Bay MTBE- and BTEX-contaminated sediments, USGS Toxic Substances Study Site, Laurel Bay Exchange, Beaufort, SC.
REFERENCES


National Science and Technology Council, 1993, In Situ Bioremediation: National Science and Technology Council, Committee on In Situ Bioremediation.

National Science and Technology Council, 1997, Interagency Assessment of Oxygenated Fuels: National Science and Technology Council, Committee on Environment and Natural Resources.


Schirmer, M., Barker, J.F., Butler, B.J., Church, C.D., and Schirmer, K., 1998, Natural


ACKNOWLEDGEMENTS

This work was supported primarily by the United States Geological Survey Toxic Substances Program through Cooperative Agreement No. 1434-WR-96-AG-00003. Collaboration with the University of Waterloo on the MTBE plume at Base Borden, Ontario, was supported by the American Petroleum Institute. In addition, Clinton D. Church was supported by an EPA STAR Graduate Fellowship.

AUTHOR INFORMATION

Clinton D, Church, Paul G, Tratnyek, and James F. Pankow; Oregon Graduate Institute, Portland, Oregon

James E. Landmeyer, U.S. Geological Survey, Charleston, South Carolina

Arthur Baehr, U.S. Geological Survey, Trenton, New Jersey

Mary Ann Thomas, U.S. Geological Survey, Columbus, Ohio

Mario Schirmer, University of Waterloo, Waterloo, Ontario, Canada