Pathways and Kinetics of MTBE Degradation

Clinton Dean Church

A dissertation submitted to the faculty of the
OGI School of Science & Engineering
at Oregon Health & Science University
in partial fulfillment of the
requirements for the degree
Doctor of Philosophy
in
Environmental Science and Engineering
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The dissertation "Pathways and Kinetics of MTBE Degradation" by Clinton Dean Church has been examined and approved by the following examination committee.

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Acknowledgements

I am deeply indebted to my mentors, colleagues, and friends and family, without whom, this accomplishment would not have been possible. I owe so much to so many that mere words cannot adequately express my gratitude, and have struggled with the best way to arrange those words here. Since all the support I received was important, I decided, finally, to make my personal acknowledgements in semi-chronological order.

My mom, dad, and step dad were crucial in my achieving what I have in my life. My mom, particularly, instilled in me at an early age a love for reading and for learning. I owe her not only for this work, but for all I have achieved in my life. I appreciate her guidance during my formative years, her patience during my teen years, and her freindship today. My dad, with only a sixth grade education, would not have fully understood the achievement represented here, and yet he also was responsible for it. A few days before he passed on, when mom was out of the room, he told me that he had worked so hard in a job that he knew was hazardous so that I would not have to follow in his footsteps, and that he wanted me to go to college. I don't think he meant for me to make a career of it, but I think he would be happy nonetheless. Since entering our lives, my step dad, Jake, has always stood by my mom, my brother, and myself. His wisdom and his interest and knowledge in everything that goes on in the world has always been an inspiration to me, and I appreciate him more than I often let him know.

My eighth grade Algebra teacher, Mr. Sullivan, was the first person to convince me that I had any academic talent. His unique approach of offering to play chess with me as soon as I turned in a perfect homework assignment for the next day inspired me to finish the homework before he finished teaching about it. During that year, I slowly began to believe that I could achieve anything I set my mind to. That belief in myself led to all my academic achievements since then.

I owe Rene Dubay for her support and encouragement to return to college after I had failed miserably in my first year. I think that she, like my dad, was surprised that I stayed at it as long as I did. She often remarked that she had created a monster.

I wish to thank Wayne and Linda Zundel for their 20-year friendship and encouragement. They are the longest-term friends I have ever had and they have taught

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I owe my advisor, Paul Tratnyek, much in the way of teaching me academic discipline. His own dedication to academic excellence has made me a better scientist, and possibly even more importantly, a better writer. Jim Pankow was instrumental in securing the original funding for my work, and without his encouragement and loan of Lorne Isabelle's time to develop the analytical method; the work presented here could not have been achieved. Lorne Isabelle became much more than just a co-developer of the analytical method. He became my close friend and supporter during times when I felt like giving up. I owe him more than he will ever know. Rick Johnson was always there when I needed advise on transport and column construction issues. His comments have made the work presented here as, well as the writing presented here, better. Gwynn Johnson was new to my committee and my work, but I thank her for insightful comments that improved the quality of the dissertation.

I wish to thank all my colleagues and the staff at the OGI School of Science and Engineering, but most particularly, I wish to thank Illa Amerson. Since our research was so closely related, she and I had many long talks about MTBE issues, and I often would refer to her as my "partner in crime". But even more, I wish to thank her for her upbeat personality and her friendship.

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Dedication

This work is dedicated to Yi and Yuchen Yang. It is dedicated to Yi because she is truly my better half. It seems that she is good at all the things I am not so good at, and without her support and drive this work would probably not have been completed. It is dedicated to Yuchen to serve as an example that even someone from the most humble of beginnings can achieve great things. It is dedicated to her in the hope that she will go on to achieve all that she dares to dream of.

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Abstract

Pathways and Kinetics of MTBE Degradation

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The realization that methyl tert-butyl ether (MTBE) has become a widespread contaminant has fueled the need for an understanding of processes that control its environmental fate. The studies presented here provide a means for analyzing for MTBE and its degradation products and refine the understanding of MTBE fate in groundwater by providing a detailed assessment of the major pathways and kinetics of MTBE degradation under controlled laboratory conditions designed to simulate environmental conditions. The findings show that MTBE and its degradation byproducts are subject to both biotic and abiotic degradation and measure the kinetics of the degradation observed.

The column studies (Chapter 5) show that MTBE is subject to microbial degradation, with a rate corresponding to a 2-3 year half-life in uncontaminated soils and in the presence of oxygen. However, most of the MTBE that occurs in association with gasoline spills will not be degraded by this mechanism, since these plumes are typically anaerobic and more readily degradable compounds are usually present.

Studies with PM-1 (Chapter 4), an MTBE degrading isolate, showed that PM-1 is capable of mineralizing MTBE. They further showed that MTBE and other fuel oxygenates are degraded by similar pathways and at similar rates. Engineered treatment systems using PM-1 have since been shown to be an efficient means of treating water contaminated by MTBE.

The tert-butyl formate hydrolysis study (Chapter 3) shows that TBF is subject to neutral as well as acid and base catalyzed hydrolysis. The rates of this degradation at 22^{O}C correspond to half-lives of five days, 6 hours, and 11 minutes at pH values of 7, 2, and 11, respectively. It examines why, though TBF is the primary degradation product of many MTBE degradation pathways, it is rarely seen in field samples.

The Fenton reagent studies (Chapter 6) show that MTBE is subject to a previously undescribed environmental degradation mechanism. This mechanism involves delivery of the reactants (H_2O_2 and MTBE, in a raindrop) to a catalytic surface (iron oxyhydroxides in sediments). The subsequent degradation arises from the production of hydroxyl radical via a Fenton-like reaction, and the reaction of the hydroxyl radical thus formed with MTBE. Evidence show that this mechanism may account for as much as 8% of atmospherically deposited MTBE under ideal conditions.

All of these studies relied on the simultaneous analysis of MTBE disappearance and product appearance, analyses that could not be accomplished at environmentally relevant concentrations using conventional purge and trap techniques. Because of this analytical objective, the first task of the project was to design an analytical protocol to make the rest of the project possible. This protocol is the direct aqueous injection with detection by mass spectrometry technique discussed in Chapter 2.

Chapter 1: Executive Summary

1.1 Introduction

One of the most widely used gasoline oxygenates is methyl tert-butyl ether (MTBE). It was originally approved for use in gasoline as an octane booster in 1979, but with the introduction of the Clean Air Act Amendments of 1990, MTBE began to be used in many localities in compositions up to 15% of the total gasoline mixture [1, 2]. In 1993, production of MTBE exceeded 24 billion gallons, making it the second most manufactured organic chemical in the United States [3], and in 1997 its use was greater than 10.5 million gallons per day [4].

Ample evidence shows that MTBE has become a widely distributed environmental contaminant [5-7]. MTBE releases have resulted in detectable concentrations of MTBE in urban air [8-10], shallow groundwater [11-18], and surface water [18-20]. The conclusions of one study further suggests that in areas where MTBE use is widespread, the detection of MTBE in surface waters is ubiquitous if measurements are made with low detection limits (15 ppt) [21]. Due to the evidence that MTBE is a widely distributed contaminant, there continues to be interest in its environmental fate and effects [5-7, 22].

Assessing the exposure to MTBE and its degradation products (and thus, the risks) requires characterization of the processes controlling both transport and transformation of MTBE, and there is still a good deal of uncertainty about the processes that control its environmental fate. However, based on what is currently known about the fate of MTBE, a limited number of processes are likely to control its occurrence (and occurrence of its degradation products) in groundwater. A schematic diagram incorporating both the major degradation pathways and environmental partitioning scenarios for MTBE and its major degradation products is provided in Figure 1.1.

The most thoroughly studied MTBE degradation pathway is atmospheric photooxidation, in which attack by hydroxyl radical gives tert-butyl formate (TBF) as the major product [9, 23-26] is illustrated by Figure 1.1, Pathway A. Possible MTBE degradation pathways in surface waters, soils, and groundwater (Figure 1.1, Pathway C) involve microbially mediated hydrolysis [27] and/or oxidation [28, 29], both of which can yield tert-butyl alcohol (TBA). An alternate MTBE biotic degradation pathway, in which biodegradation of MTBE to TBA occurs via TBF, has also been reported [30]. This possibility is reflected in Figure 1.1, Pathway B.

Phase transfer also affects the environmental fate of MTBE, as has been addressed in several analyses [30-36]. MTBE can enter the environment through non-point-source releases (Figure 1.1, Pathway 1) in addition to the obvious releases from spills and leaking fuel tanks (Figure 1.1, Pathway 4). This is because, having a high aqueous solubility (50 g/L) and low dimensionless Henry's gas law constant ($H/RT = 0.011$ at 15˚C) [37], MTBE is relatively hydrophilic. This is consistent with observations that MTBE tends to be present in the dissolved aqueous phase rather than adsorbed to sediments or organic materials in ground or surface waters [31, 35, 36, 38-43]. In the case of atmospheric contamination, MTBE can partition into available rainwater and subsequently be rained out (Figure 1.1, Pathway 2).

Similar arguments can be made for the major degradation products of MTBE. The aqueous solubility and dimensionless Henry's Gas Law Constant for TBF do not appear to have been measured, and so were calculated to be 17.4 g/L and 0.024, respectively, using previously published methods [44, 45]. TBA is fully miscible over all proportions and its dimensionless Henry's Gas Law Constant is 0.0023 [46-48]. Based on these values, both TBF and TBA are also likely to partition to water. Thus, both compounds can be susceptible to atmospheric rainout, as shown in Figure 1.1, Pathway 3.

1.2 Summary of Thesis Work

1.2.1 DAI-GC/MS Analytical Method (Chapter 2)

Some of the pathways shown in Figure 1.1 involve the in situ degradation of MTBE. To assess whether this degradation actually occurs, it is necessary to have an analytical method for MTBE and its degradation compounds that is sensitive to 0.1 μg/L or below. Most analyses for MTBE in water are currently done by purge and trap techniques (P&T), using EPA Standard Method 602, 624, or some variant thereof. However, determination of most MTBE degradation products by this method is impractical due to their low Henry's Gas Law constants. Heated purge and trap methodologies show considerable promise for the detection of TBA at sub-μg/L levels [49], but simultaneously increase the rate of TBF hydrolysis [40], making it even less likely to be detected.

One way to obtain the full range of likely MTBE degradation products is by direct aqueous injection (DAI). We developed a direct aqueous injection onto a gas chromatograph with mass spectrometer detector (DAI-GC/MS) analytical technique capable of simultaneous analysis of MTBE and its expected degradation products at the sub-ppb level [50, 51]. Other researchers have since adapted this technique to perform similar functions [52, 53].

We have subsequently used the DAI-GC/MS method to perform numerous process level investigations of MTBE degradation and the degradation of its major byproducts. These investigations include MTBE and degradation product analyses of samples from a number of field sites, assessment of the degradation pathways of isolate PM1, assessment of the hydrolysis kinetics of TBF, and MTBE degradation in model column aquifers. An example of the sensitivity of the DAI-GC/MS method for detecting MTBE degradation is shown in Figure 1.2, which depicts sample chromatograms from one of the model column aquifers. Following a lag period of approximately 35 days, TBA was detected in the column effluent (44 day chromatogram) although no evidence of the degradation could yet be seen from MTBE disappearance.

1.2.2 TBF Hydrolysis Studies (Chapter 3)

Various studies on the fate of MTBE have shown that it can be degraded to tert-butyl formate (TBF), particularly in the atmosphere. While it is generally recognized that TBF is subject to hydrolysis, the kinetics and products of this reaction under environmentally relevant conditions had not been described previous to our work. In this study, we determined the kinetics of TBF hydrolysis as a function of pH and temperature.

Over the pH range of 5 to 7, the neutral hydrolysis pathway predominates, with $k_N = (1.0 \pm 0.2) \times 10^{-6}\ s^{-1}$. Outside this range, strong pH effects were observed due to acidic and basic hydrolysis, from which we determined that $k_A = (2.7\pm0.5) \times 10^{-3}\ M^{-1}s^{-1}$ and $k_B = 1.7 \pm 0.3\ M^{-1}s^{-1}$ (Figure 1.3). Buffered and unbuffered systems gave the same hydrolysis rates for a given pH, indicating that buffer catalysis was not significant under the conditions tested. The activation energies corresponding to kN, kA, and kB were determined to be 78 ± 5, 59 ± 4, and 88 ± 11 kJ mol^{-1}, respectively.

In all experiments, tert-butyl alcohol (TBA) was found at concentrations corresponding to stoichiometric formation from TBF. Based on our kinetic data, the expected half-life for hydrolysis of TBF at pH = 2 and 4˚C (as per some standard preservation protocols for water sampling) is 6 hours. At neutral pH and 22˚C the estimated half-life is 5 days, and at pH = 11 and 22˚C the value is only 8 minutes [40].

1.2.3 Degradation Pathways of PM1 (Chapter 4)

Numerous studies with laboratory microcosms have indicated that little, if any, biodegradation of MTBE can be expected in the subsurface. The persistence of MTBE, coupled with growing concern over its negative environmental effects, has created a great deal of interest in the few reported cultures of microorganisms that rapidly degrade MTBE. One of these cultures, designated PM1, is a strain of bacteria isolated from a compost biofilter at the Los Angeles County Joint Water Pollution Control Plant in Carson, CA. PM1 rapidly mineralizes MTBE over a range of laboratory conditions, and it grows with MTBE as its sole carbon and energy source at MTBE concentrations as high as 500 mg/L [54, 55].

To help characterize the pathways of MTBE degradation by PM1 (Figure 1.4), we used direct aqueous injection (DAI) GC/MS to determine the degradation products of MTBE and five related compounds: tert-amyl methyl ether (TAME), ethyl tert-butyl ether (ETBE), di-isopropyl ether (DIPE), tert-amyl alcohol (TAA), and tert-butyl alcohol (TBA). The direct aqueous injection technique was particularly useful because it allowed simultaneous quantification of reactants and products and monitoring of the reaction progress over a wide range of concentrations.

The findings of this study confirm that, under favorable conditions (aerobic conditions and in the absence of more favorable substrates), PM1 is capable of rapidly mineralizing MTBE. They also show that the rates of degradation of TAME, ETBE, DIPE, TBA, and TAA by PM1 are of the same order of magnitude as the degradation rate for MTBE. The similarity in degradation rates and consistent patterns in product formation suggest that similar enzyme systems are responsible for all of these pathways [56].

1.2.4 Degradation of MTBE in Model Column Aquifers (Chapter 5)

Convincing evidence for in situ biodegradation of MTBE is difficult to obtain from field data alone because of several distinctive characteristics. For example, the interpretation of relative plume lengths for MTBE versus other gasoline constituents is difficult due to variations in the formulation and distribution of oxygenated gasoline [13]. Decreases in MTBE concentrations over time or space (i.e., along a flow path) may be due to degradation, but they also result from dilution and dispersion [41, 57, 58] or transfers among different environmental compartments [32, 33, 36, 59, 60]. Even the discovery of likely MTBE degradation products (i.e., tert-butyl alcohol, TBA) is equivocal evidence for biodegradation of MTBE because TBA has been used as an oxygenate in some geographical locations and TBA is present as an impurity in much of the MTBE used to oxygenate gasoline [13]. These difficulties with proving in situ degradation of MTBE from field data alone are exacerbated by the fact that biodegradation of MTBE is slow under almost all circumstances. An alternative approach to investigate degradation of MTBE is to use controlled model systems that are designed to simulate typical field conditions.

In using the DAI-GC/MS method to investigate the pathways and kinetics of MTBE biodegradation in model column aquifers under controlled conditions we found that MTBE degraded to TBA after a lag period of 35 days, but only under aerobic conditions and in the absence of BTEX (the more recalcitrant constituents of gasoline: benzene, toluene, ethyl benzene, and o-, m-, and p-xylene). This conversion of MTBE to TBA in the aerobic columns eventually declined (apparently due to oxygen use by microorganisms) along with a decrease in dissolved oxygen in the column effluent. In similar columns with anaerobic or BTEX-containing influents, there was no MTBE degradation up to 120 days [61].

To investigate the kinetics of MTBE degradation the columns were subjected to influents containing MTBE at higher flow rates (to avoid oxygen limitations). The concentrations of MTBE and TBA measured by DAI-GC/MS on the column effluents are shown in Figure 1.5 (A, C, and E). These plots show steady-state concentrations of MTBE for 5-7 days after breakthrough, and a steady partial conversion of MTBE to TBA after 40 days, with essentially complete mass balance. Since the appearance of TBA was a much more sensitive indicator of degradation than was the disappearance of MTBE, TBA appearance kinetics were used to estimate degradation rates. Figure 1.4 B, D, and F show TBA concentrations at each port plotted against the elapsed contact time. The linearity of these plots suggests that the kinetics of TBA appearance might be zero-order.

Further analysis however (Figure 1.6), shows that the extent of reaction in our column was not great enough to distinguish between zero-order and first-order conversion of MTBE to TBA. To distinguish between these possibilities, one column was exposed to three different initial concentrations of MTBE (ranging over two orders of magnitude). The results (Figure 1.6, A-C), give nearly identical rate constants when fit to a first-order model for appearance of TBA. In aerobic columns containing three of the sediments, conversion of MTBE to TBA was observed to follow first-order kinetics with half-lives ranging from 1.7 to 2.7 years. In these same columns, TBA degradation was observed to follow first-order kinetics with half-lives ranging from 2.0 to 2.6 years.

In separate experiments, we saw no MTBE degradation for up to 120 days in columns containing the same and similar sediments but with anaerobic influents or in columns with aerobic influents spiked with isopropanol, hexane, isopentane, isopentanol, malate, or ethanol. Note that we had previously not seen any degradation in columns containing aquifer materials that were contaminated with a mixture of BTEX (benzene, toluene, ethyl benzene, and o-, m-, or p-xylene: typical components of gasoline) compounds [62]. Overall, these results indicate that, in situ biodegradation of MTBE and/or TBA is favorable only under aerobic conditions in the absence of significant concentrations of more readily metabolized compounds. Since the opposite conditions are typical of plumes at leaking underground storage tank (LUST) sites, this explains why significant biodegradation of MTBE and TBA usually is not observed at LUST sites.

1.2.5 MTBE Degradation by Soil Catalyzed Decomposition of Hydrogen Peroxide (Chapter 6)

While numerous studies of engineered treatment systems [63-66] and reactions with MTBE in the atmosphere [23, 25, 26, 67] have shown that MTBE is subject to rapid attack by hydroxyl radical (HO•), few studies have been performed on naturally occurring variations of catalyzed decomposition of hydrogen peroxide (CDHP). An unexplored hypothesis is that there exists a natural mechanism of MTBE degradation that may significantly reduce MTBE concentrations that would otherwise infiltrate to groundwater. This reaction is the soil CDHP reaction (H_2O_2 plus crystalline Fe(III) at environmentally relevant pH to produce the hydroxyl radical) that likely occurs when a raindrop containing H_2O_2 [68, 69] and MTBE [33] encounters Fe(III) in the raindrop [70, 71] or at the grounds surface [72-91]. As the final portion of my thesis, I designed a set of experiments to ascertain whether this reaction occurs, and if so, its likely significance in the environment.

A preliminary assessment of the efficacy of classical Fenton conditions (Fe(II) combined with liquid H_2O_2, pH = 1.8) to oxidize an initial concentration of 100 ppm MTBE revealed the promising results in Figure 1.7. This figure shows complete disappearance of MTBE in less than 20 hours, with the formation of the four intermediate products, tert-butyl formate (TBF), tert-butyl alcohol (TBA), acetaldehyde, and acetone. Of those four products, acetone was the only intermediate product detected after 20 hours, and it too disappeared prior to the 36 hour sampling point (data not shown), leaving only CO_2.

Further experiments showed that MTBE degradation also occurs under soil CDHP conditions using mineral forms of iron (III) oxyhydroxides (goethite and hematite), and naturally occurring Fe(III)-coated sands at environmentally relevant pH values, and near concentrations of MTBE (20 ppb) [33] and H_2O_2 (40 ppb) [92, 93] that might be expected to occur in rainwater or in zones of rainwater infiltration (Table 1.1). These experiments indicate that the reaction proceeds to completion in less than 30 minutes if MTBE to H_2O_2 concentration ratios are similar to what might be found in a raindrop (1:2 on a ppb scale, 1:5 on a mM scale), and may account for as much as 8% of the MTBE in the raindrop if other competing reactants are not present.

To demonstrate the degradation of MTBE during simulated infiltration into sediments, two model column aquifers were constructed using a natural iron oxyhydroxide coated sand for a catalytic surface. The pH = 7 column influents contained 20 μg/L MTBE amended with 40 μg/L H_2O_2. After exhibiting a typical breakthrough curve, steady MTBE concentrations were observed until the influent containing both MTBE and H_2O_2 exited the column. This effluent showed a decrease in MTBE concentration and the transient appearance of TBA as a degradation product. Approximately 8% of the MTBE was completely mineralized to CO_2 in the column (Figure 1.8). TBA was detected as a trace intermediate at the onset of the degradation, but appears to have been degraded thereafter. No other intermediate products were detected.

These experiments demonstrate that a previously undescribed degradation mechanism for MTBE exists in the environment. This mechanism is activated when a raindrop containing MTBE and H_2O_2 makes contact with iron oxide coated sands and clays at the earth's surface and continues during the infiltration process (Figure 1.1, Reaction E). The amount of MTBE degraded is dependent upon the concentration of H_2O_2 contained within the raindrop, the speciation of the iron, pH, and the absence or presence of competing reactants. Evidence suggests that the MTBE is mineralized to

CO_2. The addition of this CDHP degradation pathway to the model shown in Figure 1.1 completes the model of the major pathways influencing the environmental fate of MTBE.

Chapter 1 Tables

Table 1.1. MTBE Degradation by Fenton and soil CDHP Reactions
Experimental conditions and results of MTBE degradation by Fenton and soil CDHP reactions at various pH values.

Fe\pH	**2**	**3**	**4**	**5**	**6**	**7**
MTBE Degradation Under Classic Fenton Conditions (soluble ferrous sulfate)						
Soluble FeII (ferrous sulfate)	100 mg/L MTBE 200 mg/L H_2O_2 $t_{1/2}$= 2.2h	N.P.	N.P.	100 mg/L MTBE 7% H_2O_2 $t_{1/2}$=0 .16h	100 mg/L MTBE 7% H_2O_2 $t_{1/2}$=0.33h	100 mg/L MTBE 7% H_2O_2 $t_{1/2}$=2.0h
MTBE Degradation Under soil CDHP Conditions (mineral Fe(III))						
Conditions	**Percent MTBE degraded in 30minutes**					
0.5g Geothite 100 mg/L MTBE 200ppm H_2O_2	15.3%	14.1%	13.6%	11.1%	9.3%	8.6%
0.5g Hematite 100 mg/L MTBE 200ppm H_2O_2	11.4%	10.1%	9.3%	8.6%	7.5%	6.4%
1g Milford [94-96] 100 mg/L MTBE 200ppm H_2O_2	14.1%	13.1%	12.3%	10.6%	9.1%	8.2%
1g Milford [94-96] MTBE 25-50-100 μg/L 100 μg/L H_2O_2	N.P.	N.P.	N.P.	N.P.	N.P.	D-raindrop 16.1-8.4-4.3

N.P. = not performed

Chapter 1 Figures

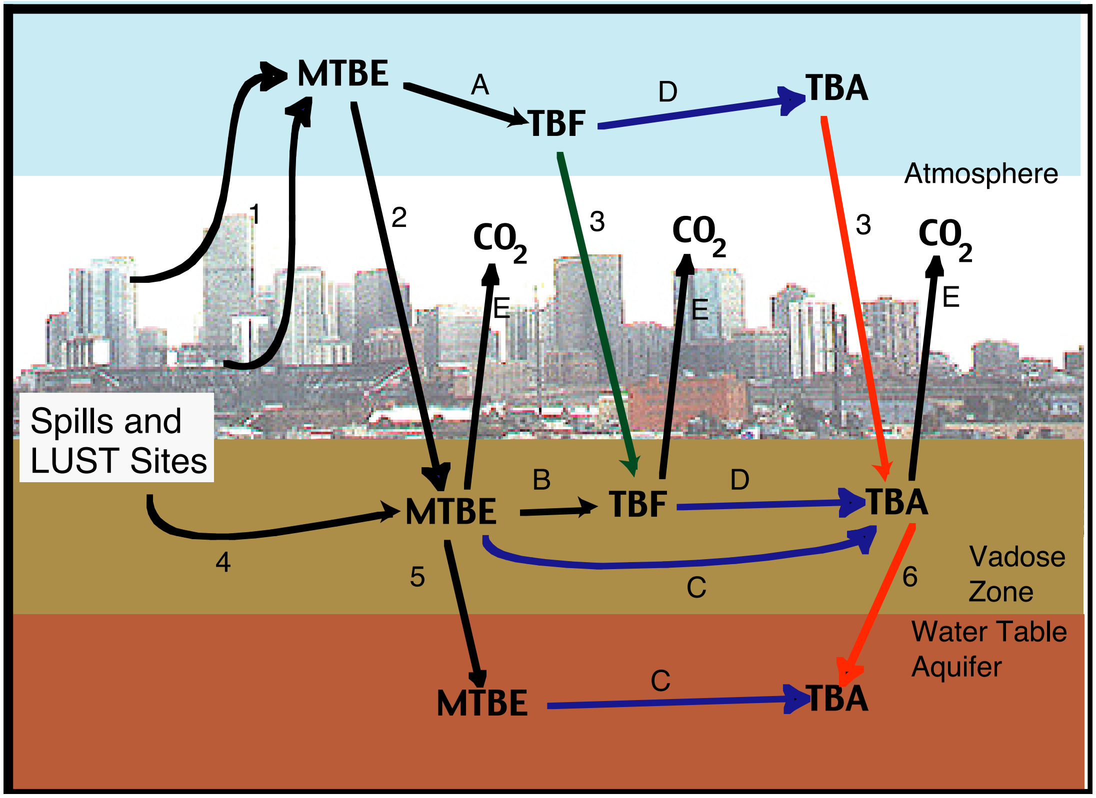

Figure 1.1. The MTBE Cycle
Summary of chemical transformation pathways and phase transfer processes for MTBE. Analogous transformations can be expected for other alkyl ethers used as gasoline oxygenates (e.g., ETBE and TAME). TBF (*tert*-butyl formate) is subject to rapid hydrolysis to TBA (*tert*-butyl alcohol). TBA is subject to further biodegradation to acetone, isopropanol, formate, and ultimately CO_2. Adapted from [40].

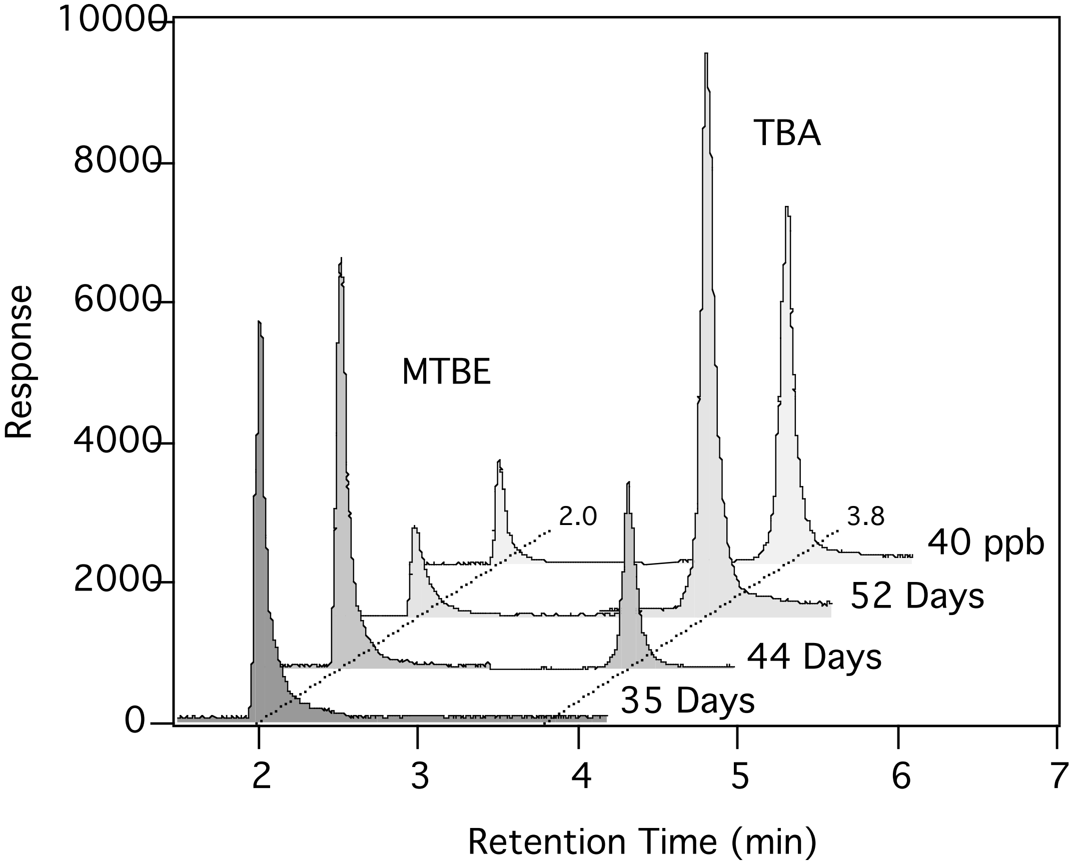

Figure 1.2. Sample DAI-GC/MS Chromatograms
Sample chromatograms from the DAI-GC/MS method (Heliflex column), showing analyses of effluent from a soil column before (front) and after (middle) the onset of biodegradation, and 40 μg L^{-1} standards (back). Note that 40 μg L^{-1} TBA corresponds to the MDL for previously reported methods. Successive chromatograms are offset by 750 response units and 0.5 min [50, 51].

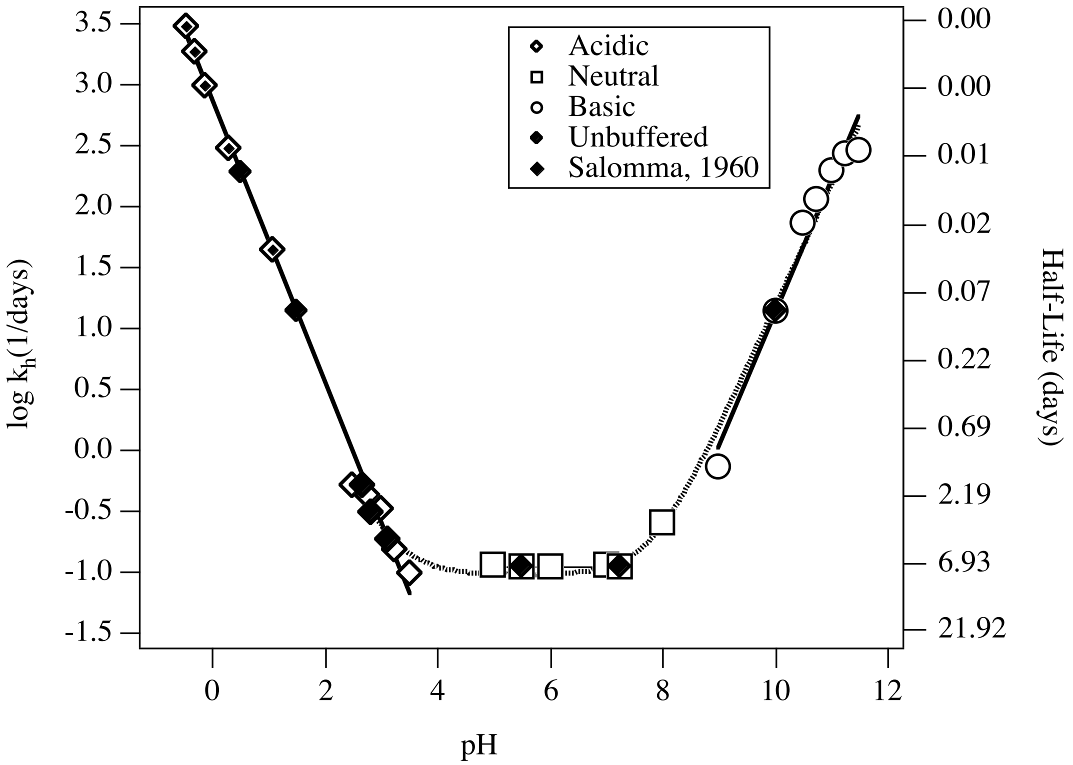

Figure 1.3. Tert-Butyl Formate Hydrolysis Kinetics
Kinetics of hydrolysis of *tert*-butyl formate (TBF) at 22 ºC, showing the effects of pH on the observed reaction rate (k_h). Solid lines are separate linear regressions on the rate constants which reflect the contributions of acidic (k_A), neutral (k_N) and basic (k_B) pathways to k_h. The smooth dashed line is a nonlinear regression on all of the rate constants at 22 ºC.

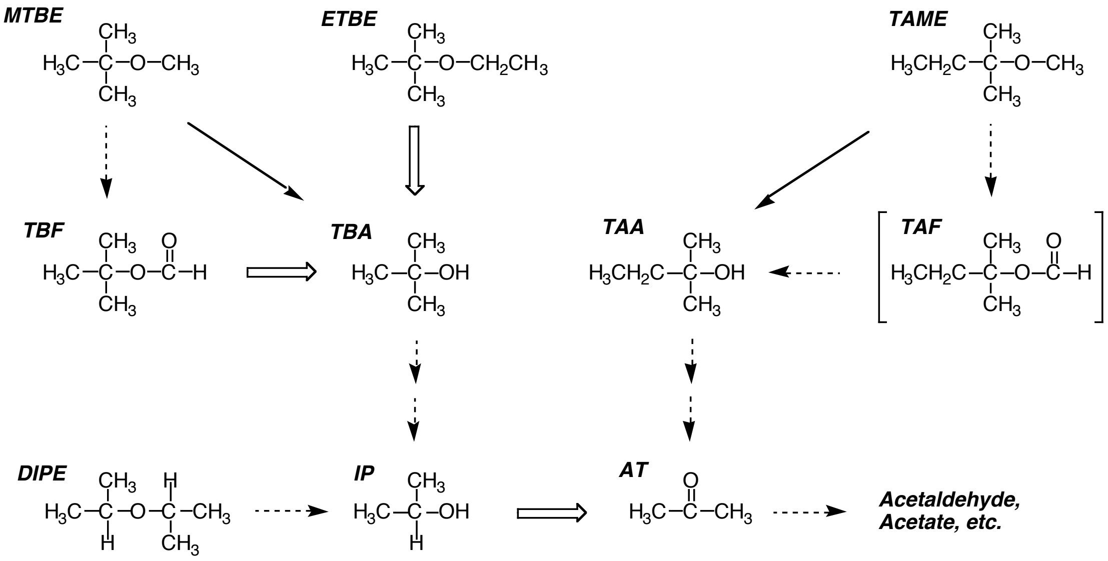

Figure 1.4. MTBE Degradation Pathways of PM1

Proposed degradation pathways of fuel oxygenates by PM1. Open arrows: transformations that were directly observed. Solid arrows: observed but may occur via intermediates. Dashed arrows: hypothesized steps. [56]

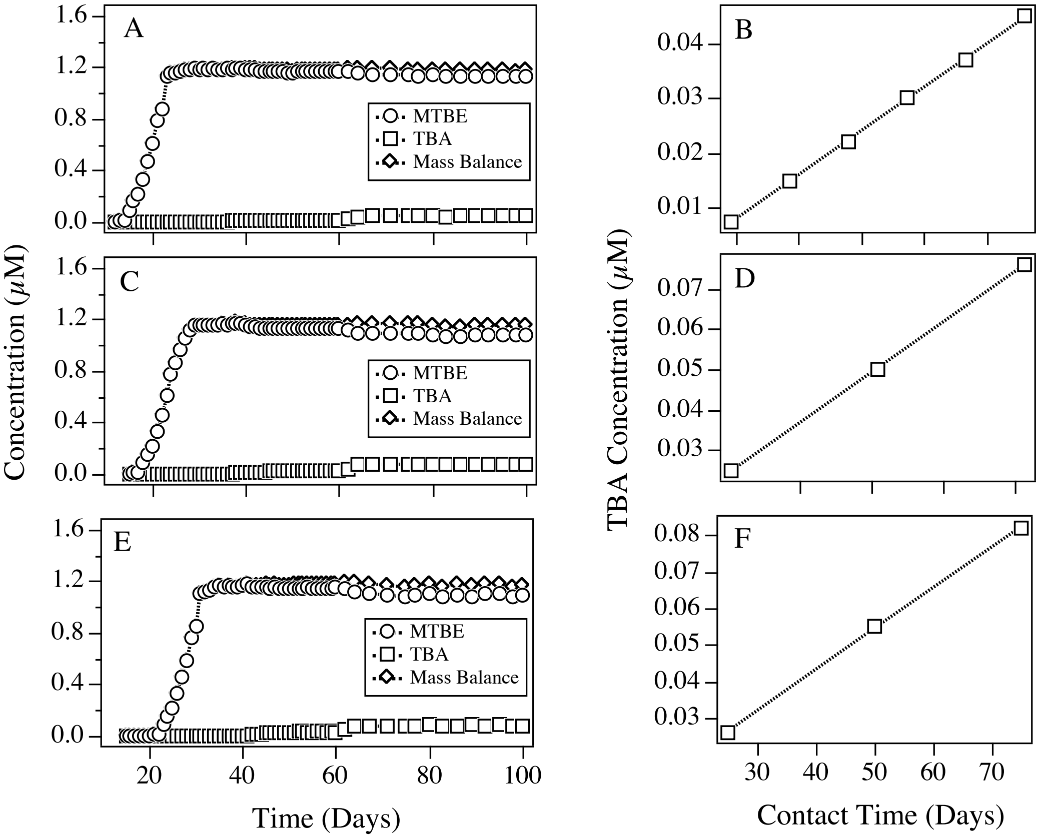

Figure 1.5. Degradation of MTBE in Model Column Aquifers
A, C, and E show MTBE and TBA concentrations in the effluents of three columns containing previously uncontaminated sediments. (A) Base Borden, (C) Lake Erie, (E) New Jersey. The columns were challenged with aerobic influent containing 1.13 μM MTBE. B, D, and F show TBA concentrations derived from sampling ports along the length of columns A, C, and E, respectively, while columns were at steady-state [62].

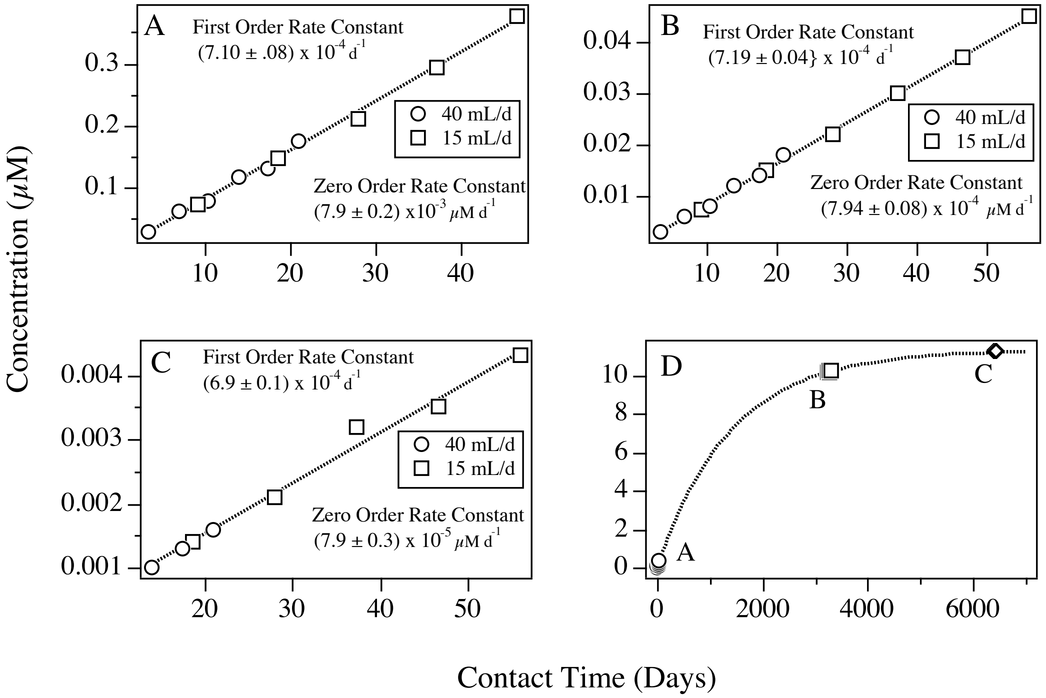

Figure 1.6. TBA Appearance Kinetics
A, B, and C show TBA appearance kinetics for three MTBE influent concentrations in Base Borden sediment. Influent concentrations were (A) 11.3 μM, (B) 1.13 μM, and (C) 0.113 μM. D is a compilation of the plots shown in A, B, and C, showing that all of the data can be placed on one first-order appearance curve for a rate constant equal to 7.1 x 10^{-4} d^{-1}.

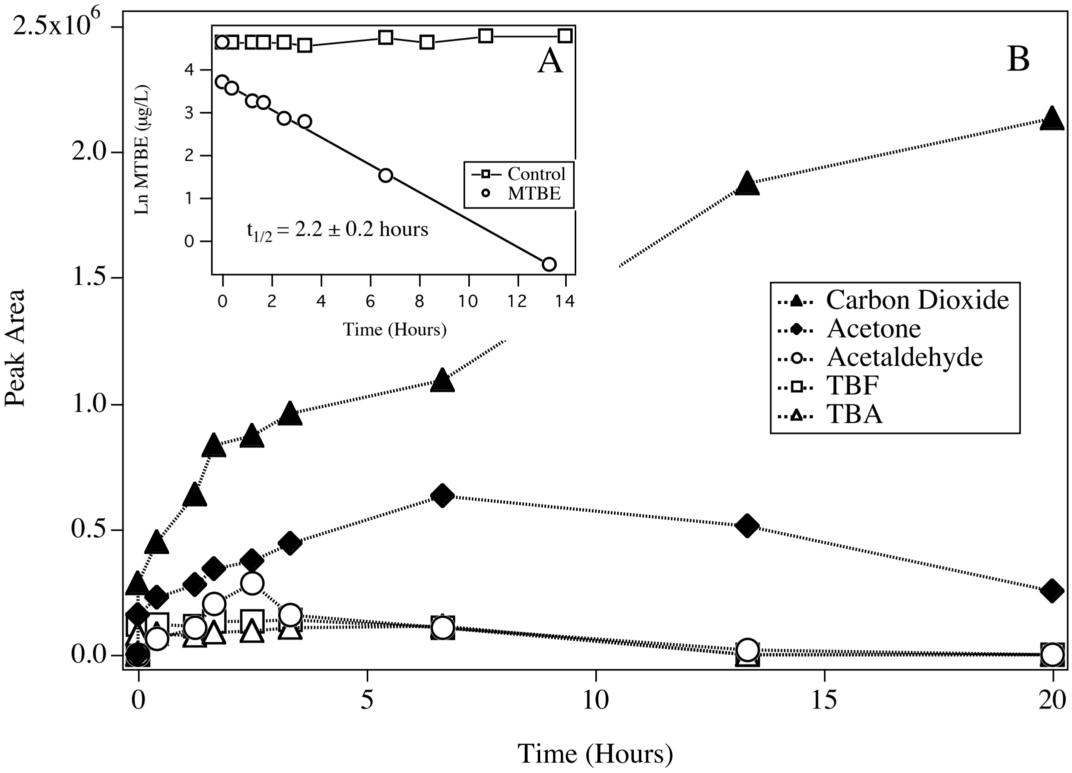

Figure 1.7. Classical Fenton MTBE Degradation
Disappearance of MTBE and formation of degradation products under classical Fenton conditions (Initial concentrations: (H_2O_2, 200 mg/L; $FeSO_4$, 1.15 mM; MTBE 100 mg/L). Inset is a plot of the first-order MTBE disappearance, which shows that after an initial rapid loss of MTBE the pseudo first-order disappearance rate constant, k, for this reaction is equal to 0.32. This corresponds to a half-life of MTBE under these conditions of 2.2 hours.

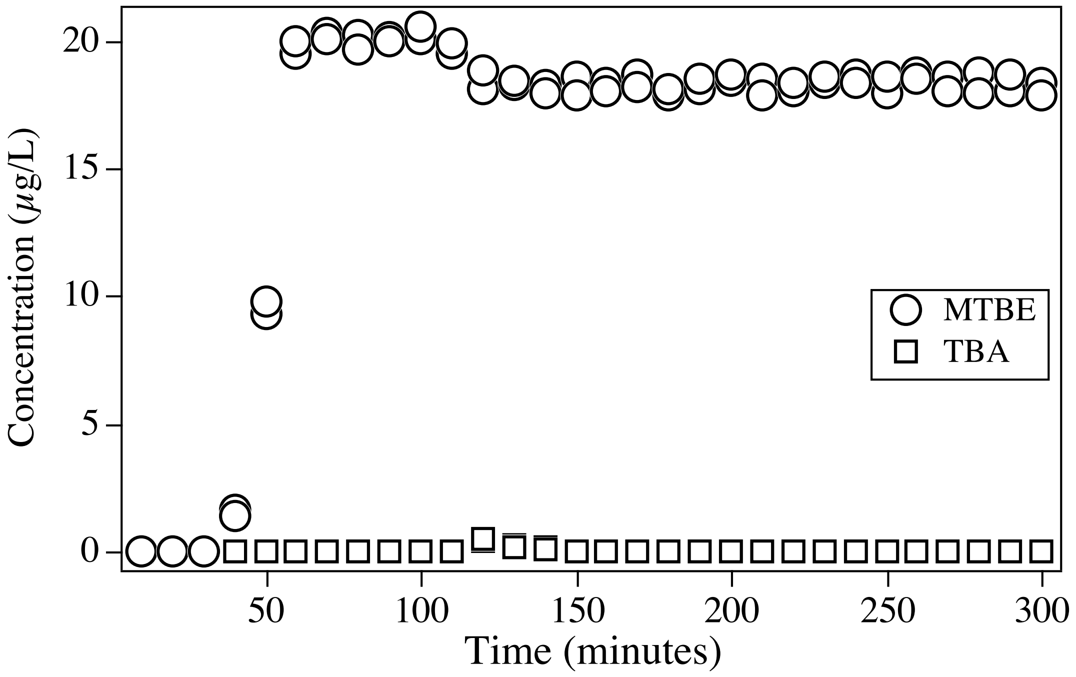

Figure 1.8. MTBE Degradation from Soil CDHP During Column Infiltration
Disappearance of MTBE and its transient degradation product TBA under soil CDHP conditions in columns packed with Milford sediment. The initial pH was adjusted to pH = 7 with NaOH. The columns received influents of 20 μg/L MTBE for one hour, and were then switched to influents containing 20 μg/L MTBE amended with 40 μg/L H_2O_2.

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Chapter 2

Method for Determination of Methyl-*tert*-Butyl Ether (MTBE) and its Degradation Products in Water

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Chapter 3

Hydrolysis of tert-Butyl Formate: Kinetics, Production, and Implications for the Environmental Impact of MTBE

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Chapter 4: Pathways for the Degradation of MTBE and other Fuel Oxygenates by Isloate PM1[3]

4.1 Introduction

Numerous studies with laboratory microcosms have indicated that little, if any, biodegradation of MTBE can be expected in the subsurface [e.g., 1, 2, 3]. The persistence of MTBE, coupled with growing concern over its negative environmental effects, has created a great deal of interest in the few reported cultures of microorganisms that rapidly degrade MTBE [4, 5]. One of these cultures, designated PM1, is a strain of bacteria isolated from a compost biofilter at the Los Angeles County Joint Water Pollution Control Plant in Carson, CA [5]. PM1 rapidly mineralizes MTBE over a range of laboratory conditions, and it grows with MTBE as its sole carbon and energy source at MTBE concentrations as high as 500 mg/L [5].

To help characterize the pathways of MTBE degradation by PM1, we used direct aqueous injection (DAI) GC/MS to determine the degradation products of MTBE and five related compounds: tert-amyl methyl ether (TAME), ethyl tert-butyl ether (ETBE), di-isopropyl ether (DIPE), tert-amyl alcohol (TAA), and tert-butyl alcohol (TBA). The direct aqueous injection technique was particularly useful because it allowed

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simultaneous quantification of reactants and products and monitoring of the reaction progress over a wide range of concentrations.

4.2 Experimental Approach

A pure culture of PM1 (250 mL) was obtained from Kate Scow at the University of California, Davis, and diluted to 500 mL with mineral salts media. MTBE was added to give a final concentration of 100 mg/L. After 24 hours incubation (22oC) on a rotary shaker (30 r.p.m.) the cells were centrifuged, washed, and resuspended in mineral salts media containing 100 mg/L MTBE, and reincubated as above until the MTBE concentration reached 10 mg/L (approximately 48 hours).

To determine the products of MTBE degradation, 75 mL aliquots of the culture were transferred to each of six serum vials and capped. MTBE, TBA, tert-butyl formate (TBF), isopropanol (IP), acetone (AT), and acetaldehyde (AA) were added to achieve final concentrations of 100 mg/L. These vials were sampled at one-half hour intervals by filtering (0.2 μm syringe filter) the culture directly into 2-mL vials, followed by analysis with DAI-GC/MS [6]. TBF samples were analyzed immediately, because TBF is labile to hydrolysis [7]. The disappearance plots from this experiment are shown in Figure 4.1A, and Table 4.1 shows the zero-order rate constants and products obtained from these experiments.

To test for analogous degradation pathways in compounds related to MTBE, 1 mL of the remaining culture was placed into each of five 2-mL vials. These vials received MTBE, TAME, ETBE, TAA, and DIPE to achieve final concentrations of 100 mg/L. The disappearance plots from this experiment are shown in Figure 4.1B, and Table 4.1 shows the corresponding zero-order rate constants and products observed.

4.3 Discussion

From the appearance of products, it is clear that TBA is an intermediate in the degradation pathways for MTBE and ETBE, and that TAA is an intermediate in the degradation pathway for TAME. This finding is in agreement with the findings of previous studies of fuel oxygenate degradation by pure cultures [4, 8, 9], and it is the expected pattern of biodegradation for ether linkages by a wide variety of microorganisms [10]. No products were observed in the degradation of DIPE, but a pathway analogous to that of MTBE and ETBE can be inferred. Proposed degradation pathways for MTBE and the other fuel oxygenates studied are summarized in Figure 4.2.

Whether or not MTBE and TAME are degraded directly to the corresponding alcohol, or by oxidization to the formate with subsequent hydrolysis of the formate to the alcohol (as suggested by others [8]), can not be unequivocally proven by the results of this study. However, the appearance of TBA as a product of TBF degradation, and the higher rate of TBF degradation (compared to the rates for MTBE and TBA), indicates that pathways with the formate as an intermediate are possible. Regardless whether degradation occurs via a formyl intermediate, the evidence presented here indicates that the initial step(s) for degradation of MTBE, TAME, ETBE, and DIPE by PM1 involve degradation of the less branched side of the ether linkage, and give the corresponding alcohol as the first stable intermediate. The resulting alcohol is then further oxidized, presumably to isopropanol or acetone, and ultimately to CO_2 (results not shown).

The findings of this study confirm that, under favorable conditions (aerobic conditions and in the absence of more favorable substrates), PM1 is capable of rapidly mineralizing MTBE. They also show that the rates of degradation of TAME, ETBE, DIPE, TBA, and TAA by PM1 are of the same order of magnitude as the degradation rate for MTBE. The similarity in degradation rates and consistent patterns in product formation suggest that similar enzyme systems are responsible for all of these reactions.

Chapter 4 Tables

Table 4.1. Kinetics and products of degradation by Strain PM-1

Compound	Zero Order Rate Constant (mM h^{-1}) *	r^2	Products Observed
MTBE	(2.16 ± 0.01) x 10^{-2}	0.9998	TBA
	(1.99 ± 0.01) x 10^{-2}	0.9991	TBA
TAME	(1.47 ± 0.01) x 10^{-2}	0.9980	TAA
ETBE	(2.87 ± 0.02) x 10^{-2}	0.9992	TBA
DIPE	(1.12 ± 0.01) x 10^{-2}	0.9981	None
TBA	(2.96 ± 0.01) x 10^{-2}	0.9996	None
TAA	(3.94 ± 0.02) x 10^{-2}	0.9996	None
TBF	(5.38 ± 0.02) x 10^{-2}	0.9997	TBA
IP	0.12 ± 0.01	0.9997	AT
AT	0.19 ± 0.01	0.9980	None
AA	1.12 ± 0.01	0.9990	None

* From the slope of concentration vs. time data in Figure 4.1. Uncertainties are 1 standard deviation of the slope of the regression lines shown.

Chapter 4 Figures

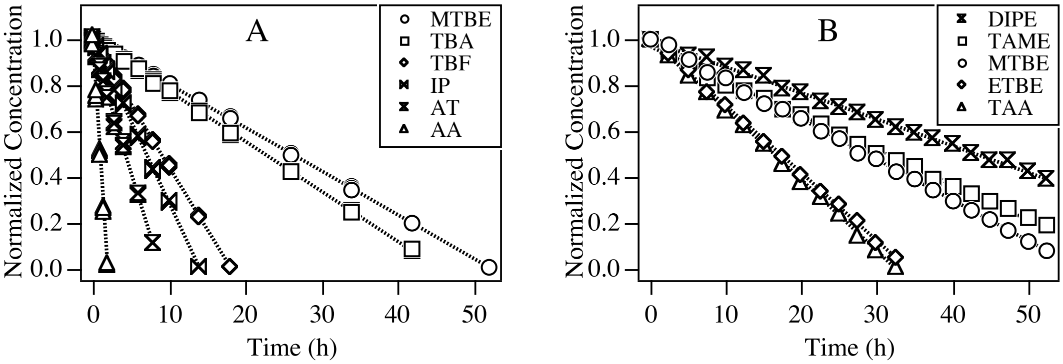

Figure 4.1 Degradation of MTBE, its products, and other oxygenates by PM1
(A) Degradation of MTBE and its expected products by PM1. (B) Degradation of MTBE and other oxygenates by PM1.

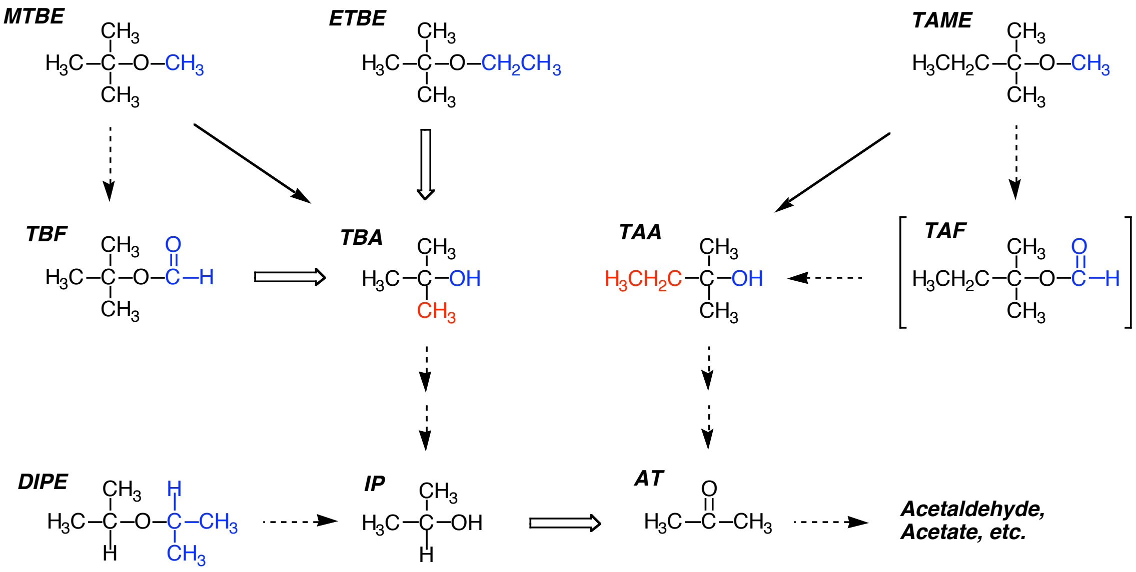

Figure 4.2. Proposed degradation pathways of fuel oxygenates by PM1
Open arrows: transformations that were directly observed. Solid arrows: observed but may occur via intermediates. Dashed arrows: hypothesized steps.

Chapter 4 References

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Chapter 5: Kinetics of MTBE and TBA Degradation in Model Column Aquifers[4]

5.1 Abstract

We performed a series of model column aquifer experiments to investigate the pathways and kinetics of MTBE (methyl tert-butyl ether) biodegradation under controlled conditions. The sediments used for these columns were collected aseptically from four geographically and geologically distinct sites. In all cases, autoclaved site ground water spiked with MTBE or TBA (tert-butyl alcohol) was used as the column influent, and the column effluent was analyzed for MTBE or TBA and their likely degradation products. Since the conversion of MTBE to TBA was small in all cases, the appearance of TBA was a much more sensitive indicator of degradation than was the disappearance of MTBE. Accordingly, the appearance kinetics of TBA were used to estimate degradation rates. In aerobic columns containing three of the sediments, conversion of MTBE to TBA was observed to follow first-order kinetics with half-lives ranging from 1.7 to 2.7 years. In these same columns, TBA degradation was observed to follow first-order kinetics with half-lives ranging from 2.0 to 2.6 years. We did not see any evidence of MTBE degradation for up to 120 days in columns containing the same and similar sediments but with anaerobic influents or in columns with aerobic influents spiked with isopropanol, hexane, isopentane, isopentanol, malate, or ethanol. We also did not see any degradation in columns containing aquifer materials that were contaminated with a mixture of BTEX (benzene, toluene, ethyl benzene, and o-, m-, or p-xylene: typical components of

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[4] **Note:** Chapter 5 has been prepared as a journal article. Joel Z. Bandstra, and Paul G. Tratnyek are co-authors.

gasoline) compounds. Overall, these results show that, in situ biodegradation of MTBE and/or TBA is favorable only under aerobic conditions in the absence of significant concentrations of more readily metabolized compounds. Since the opposite conditions are typical of plumes at leaking underground storage tank (LUST) sites, this explains why significant biodegradation of MTBE and TBA usually is not observed at LUST sites.

5.2 Introduction

The persistence and mobility of methyl tert-butyl ether (MTBE) [1-5] and its primary degradation product, tert-butyl alcohol (TBA) [6-12], coupled with concern over their potential negative environmental and health effects [2-5], have created a great deal of interest in their potential for in situ degradation [3-5, 13-18]. However, convincing evidence for in situ degradation of MTBE and TBA is difficult to obtain from field data alone because of several distinctive characteristics of these compounds coupled with their use history and environmental fate [13, 16].

The characteristics of MTBE and TBA that make assessment of their in situ degradation challenging are, at least, four-fold. First, variations in the formulation and distribution of gasoline containing MTBE and the fact that many leaking underground storage tanks (LUSTs) were leaking for an indeterminable time before oxygenated fuel was introduced make it difficult to interpret the behavior of MTBE versus other gasoline constituents [19]. Second, the fate of MTBE in groundwater depends, in part, on the rates and products of MTBE degradation and, in part, on the physical transfer of MTBE among different environmental compartments [20-26]. For this reason, measurements of MTBE concentration decreases in ground water alone are not adequate to prove whether it has biodegraded in situ, since decreases may be due to transfer to another environmental compartment [22, 24]. Third, decreases in MTBE concentrations over time or space (i.e., along a flow path) may be due to degradation, but they also result from the processes of dilution and dispersion [15, 16, 27]. Fourth, biodegradation of MTBE is slow under most natural circumstances, which exacerbates the above challenges to proving in situ degradation of MTBE from field data alone.

To demonstrate the occurrence of in situ biodegradation of MTBE convincingly, measurements of MTBE disappearance need to be accompanied by additional evidence, such as evidence that microorganisms are present at a particular site have the potential to degrade MTBE under controlled laboratory conditions and that this potential can be expressed under field conditions [28-30]. Numerous investigators have now reported that MTBE is biodegradable under favorable circumstances in pure cultures, enrichments, and batch microcosms [8, 10-12, 15, 18, 31-38]. 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 extrapolation of biodegradation rates from batch microcosms experiments to field situations is fraught with uncertainty.

Compelling evidence for in situ degradation of MTBE would be the appearance of characteristic metabolic intermediates or products [28, 29]. 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 in some pathways for aerobic microbial degradation of MTBE [34, 39-41]. TBF is a transient intermediate—so it usually does not accumulate to detectable concentrations—because it is rapidly hydrolyzed to TBA by either abiotic [7] or enzyme catalyzed mechanisms [34, 41].

A few studies have shown that TBA may be further degraded to isopropanol, acetone, and ultimately CO_2 [11, 38]. 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 [6], (ii) a demonstrated product of MTBE biodegradation [8, 10, 11, 34, 38, 41], and (iii) sufficiently resistant to further degradation that it may accumulate as an intermediate before being further degraded [8, 11, 12, 32, 38].

Unfortunately, even the detection of TBA in ground water samples does not provide unequivocal proof of MTBE degradation [15]. 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. Even if some TBA was introduced with the original contamination, it is still possible—in principle—to demonstrate MTBE degradation to TBA by showing a decrease in mass of MTBE and concomitant increase in mass of TBA using data from intensive sampling of the site over space and time. If sampling is sufficiently intensive, it may even be possible to make a case for MTBE degradation based on mass balance of MTBE data alone [14, 17, 18, 27, 42]. Such detailed site characterization is rarely available, however, so unequivocal demonstration of in situ degradation of MTBE is rarely possible. Of course, the lack of unequivocal proof of MTBE degradation from field studies does not mean that it does not occur under favorable conditions (e.g., engineered by biostimulation or bioaugmentation).

Recently, a number of recent studies have shown the potential of compound specific isotope analysis to indicate degradation of MTBE in column microcosms [43-46] and in the field [47-54], but none to date have yielded reliable estimates of in situ MTBE degradation rates. TBA was also included in a number of the studies. Most of them, however, reported little or no isotopic fractionation in TBA, possibly because the lighter isotopic TBA resulting from MTBE degradation offsets the isotopically heavier TBA remaining when TBA is further degraded [55].

To assist with interpretation of field data on the in situ degradation of MTBE, we set out to obtain complementary information using column model systems that are designed to simulate a representative range of field conditions and relatively long contact times. We constructed six model column aquifers using aseptically collected sediments from four geographically and geologically distinct sites: two USGS (U.S. Geological Survey) urban NAWQA (National Water-Quality Assessment) field sites (Detroit, Michigan and Turnersville, New Jersey); a USGS leaking underground storage tank study site (Laurel Bay, South Carolina); and a controlled release site at Base Borden, Ontario, Canada (Borden). Additional details on these sites are given in 5.3.2, below.

In our first report on work with these columns [56], we found that MTBE degraded to TBA after a lag period of 35 days, but only under aerobic conditions and in the absence of BTEX (the least biodegradable constituents of gasoline: benzene, toluene, ethyl benzene, and *o*-, *m*-, and *p*-xylene). As noted there, the conversion of MTBE to TBA in the (originally) aerobic columns became negligible and this was accompanied by a decrease in dissolved oxygen in the column effluent. In similar columns with anaerobic influents, there was no MTBE degradation up to 120 days. The apparent oxygen requirement for MTBE degradation in our columns is consistent with field studies showing increases in MTBE degradation in engineered systems where oxygen is amended [57-59]. There was likewise no MTBE degradation in columns that received either aerobic or anaerobic BTEX-containing influents.

For the new work reported here, we designed two types of experiments to further investigate the nature of the aerobic degradation observed in the studies. The first series of experiments was designed to determine whether the rate of MTBE degradation can be enhanced by the addition of a cometabolic substrate, as suggested by earlier laboratory studies [34, 41]. The second series of experiments was designed to investigate the kinetics of the observed MTBE degradation and to investigate the degradation of its primary metabolite, TBA.

5.3 Experimental Section

5.3.1 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 for MTBE and degradation products by direct aqueous injection with gas chromatography and detection by mass spectrometry (DAI-GC/MS) according to a method described previously [6]. 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.

5.3.2 Column Sediments

The sediments for the column studies were collected using either a hand auger or a split-spoon core sampler. In all cases, care was taken to use aseptic sampling techniques (alcohol flame sterilized equipment, etc.). Sediments were packaged to exclude oxygen and shipped on ice to the OGI School of Science and Engineering at Oregon Health & Science University where they were kept in a $4^{O}C$ cold-room until they were aseptically repacked in the columns. A brief description of the sediments and aquifer conditions at each site follows.

Detroit Sediments. The Detroit sediments came from an urban NAWQA Program study site in Farmington Hills, a suburb of Detroit, MI. The sediments consisted of fine sand mixed with some silt and gravel, with an organic-carbon content ranging from 0.4 to 0.7 percent. 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 [60].

Turnersville Sediments. Sediments were collected at an urban NAWQA study site in Turnersville, NJ, 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 [61].

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 downgradient from the Borden MTBE plume [17]. The Borden aquifer is relatively homogeneous and composed of clean, well-sorted, fine- to medium-grained sand. The bulk density of the aquifer material is about 1.81 g/cm^3, with a porosity of 0.33, and has a relatively low organic carbon content of 0.02 percent [62]. 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, 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, but the iron became progressively less prevalent with increases in contaminant concentration. Natural organic carbon content in these sediments was < 0.02 percent [63]. 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 [15]. Sediments used for the aerobic column experiments were collected from an aerobic (4.0 mg/L O_2) 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 O_2) part of the aquifer near the plume source that contained both MTBE and BTEX.

5.3.3 Column Construction and Operation

The columns were constructed using segments of 2.54 cm I.D. stainless steel pipe totaling 360 cm in length (Figure 5.1). Sediments were aseptically packed into autoclaved column segments using alcohol-flamed tools inside a laminar 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—which allowed samples to be taken at evenly spaced points along the column—and incubated in a 15°C cold-room.

The columns were challenged with a number of treatments in series. In all cases, column influent solutions were autoclaved site ground water, which were either equilibrated with the atmosphere or purged of oxygen by sparging with nitrogen gas. These feed solutions were pumped through the column in upflow mode for 14 days at 40 mL/day using a syringe pump. After this initial equilibration period, the column feed was switched to solutions of site water amended with MTBE or TBA in appropriate concentrations for the various treatments (described below). For the BTEX contaminated experiments and the cometabolism experiments (using either isopropanol, hexane, isopentane, isopentanol, malate, or ethanol), the ground water solutions were also amended with 100 μg/L each of the constituent being tested. In all cases, compounds used as amendments were the purest available from commercial sources (> 97%) and were used as received.

All columns were initially challenged with a concentration of 100 μg/L MTBE with a pump rate of 1.5 mL/day. The results of this initial treatment is documented in a previous paper [56], and are summarized briefly below. For the steady-state experiments discussed here, the columns in which degradation of MTBE was observed were challenged with concentrations of 100 μg/L MTBE, 10 μg/L MTBE, 1000 μg/L MTBE, and 100 μg/L TBA, sequentially.

In each case, the pump rate was maintained at 40 mL/day and daily samples of the pore water were taken at ports along the column. After steady-state concentrations of MTBE (and/or TBA) were observed for a minimum of 15 days, the flow rate was reduced to 15 mL/day and samples were collected at each of the ports for a minimum of an additional 20 days. Finally, all columns were subjected to a final challenge of 100 μg/L MTBE with a pumping rate of 40 mL/day in order to see if columns had undergone any changes in MTBE degrading ability as a result of the preceding treatments.

5.3.4 Microbial Community Studies

At the time of column packing, after the initial equilibration stage, and following each of the challenges, the column sediments were sub-sampled at the influent, effluent, and in the middle of the columns. Each sample was immediately subdivided, diluted, and subjected to plate counts for heterotrophs [64], and most probable number analyses for nitrifiers [65], and iron reducers [66], and sulfate reducers [67]. Additionally, duplicates of sediment samples taken at the end of the study were frozen and sent to the laboratories of Dr. Lisa Alvarez-Cohen (University of California, Berkeley) and Dr. Kate Scow (University of California, Davis) for deoxyribonucleic acid (DNA) molecular marker analysis.

5.4 Results and Discussion

5.4.1 Summary of Preliminary Studies

After equilibration with site groundwater, all columns were initially challenged with a concentration of 100 μg/L MTBE at a pump rate of 1.5 mL/day. Three columns containing three different sediments from uncontaminated sites (Base Borden, ON; Detroit, MI; and Turnersville, NJ) were operated with aerobic influent that contained no detectable BTEX compounds. In each of these columns, conversion of MTBE to TBA was observed after a lag period of approximately 35 days. Degradation was not sustained, however, and conversion of MTBE to TBA eventually stopped, accompanied by a decrease in dissolved oxygen measured in the effluent from approximately 9 mg/L to 1 mg/L. This correlation suggested that biodegradation of MTBE in the columns was an aerobic process, and that the mass of oxygen supplied in the influent was insufficient to sustain steady-state degradation. Further evidence for this conclusion is that an anaerobic column containing Base Borden sediments showed no conversion of MTBE to TBA over 120 days. These findings are consistent with reports of batch experiments which show that biodegradation of MTBE occurs under aerobic conditions [11, 32, 34, 36, 37, 41, 68-71], but is slow to non-existant under anaerobic conditions [10, 12, 72, 73].

Two columns were prepared with sediment from a leaking underground storage tank site (Laurel Bay Exchange, SC). These columns were operated with both aerobic and anaerobic site waters containing 100 μg/L BTEX compounds. No MTBE to TBA conversion was observed in either of these columns up to 120 days, suggesting that the BTEX compounds were serving as a preferential substrate [8, 56]. Further evidence for this conclusion is that: (i) there was an approximate 10 percent reduction of BTEX compounds in the aerobic effluent and 5% in the anaerobic effluent, (ii) there was evidence of oxygen utilization in the aerobic column (9 mg/L and 1 mg/L in the influent and effluent, respectively), and (iii) there was evidence that iron was being used as a terminal electron acceptor in the anaerobic column (Table 5.1) by the presence of Fe(II) in the effluent. This result suggests that MTBE degradation is most likely to occur in the absence of significant levels of more readily metabolized contaminants (such as BTEX).

5.4.2 Microbial Community Studies

After completion of the preliminary studies (discussed above), further studies were performed to investigate (i) changes in microbial community structure in response to being challenged by MTBE and/or TBA, (ii) possible effects of co-substrates, and (iii) the kinetics of MTBE and TBA degradation. The microbial community studies were designed to investigate whether there was significant change in microbial populations over the course of the investigations. For these studies, sediment subsamples were collected from near the influent end, in the middle, and near the effluent end of each column. These samples were examined using two methodologies: (i) plate counts and MPN (most probable number) tests for heterotrophs, and nitrate, iron, and sulfate reducers; and (ii) lipid and nucleic acid examinations. Based on the results of plate counts and MPN tests for heterotrophs [64], nitrifiers [65], and iron reducers [66], and sulfate reducers [67] there appears to have been no significant change in the various populations of bacteria tested (Figure 5.2).

Any method of microbial counting that requires removal of organisms from a natural environment and their subsequent growth on an alien substrate (such as MPN and plate techniques, discussed above) is inherently selective. Because of this, plate count and MPN techniques can lead to equivocal results [74-78]. Molecular techniques, which were well established in the medical and biochemical fields, have also been applied in the field of microbial ecology. These techniques are less selective as they rely on existing bacterial RNA, DNA, or fatty acids present in sediment, rather than relying on growth of microorganisms. To lend direct validation to the results of the MPN and plate counts, frozen duplicate sediment samples of the MPN and plate count tests were also subjected to molecular analysis.

Fluorescent in-situ hybridization (FISH) and terminal restriction fragment length polymorphism analyses (T-RFLP) were performed on the column sediments. Fatty acid methyl ester (FAME) and denaturing gradient gel electrophoresis (DGGE) analysis were performed on the sediments. The results of these studies were to be compared to known libraries to identify the groups of microorganisms present and to other column samples differentiated by time to indicate whether there had been any growth of specific groups of microorganisms as a response to MTBE exposure. Unfortunately, the sediment samples contained insufficient fatty acid methyl ester for the FAME analyses, and neither laboratory was able to extract DNA from the frozen sediments, probably because of low biomass (note results of plate counts, Figure 5.2).

5.4.3 Cometabolic Studies

In the experiments designed to investigate whether the rate of MTBE degradation might be enhanced by the addition of a cometabolic substrate, the conversion of MTBE to TBA stopped upon addition of added isopropanol, hexane, isopentane, isopentanol, malate, and ethanol (data not shown). This finding further confirmed the conclusion of the preliminary studies that MTBE conversion to TBA occurs primarily in the absence of more favorable substrates.

5.4.4 MTBE Degradation Kinetics

To avoid the onset of anaerobic conditions, as was observed in previous experiments performed at flow rates of 1.5 mL/d [56], the column microcosms were conditioned at 40 mL/d until steady-state concentrations of MTBE and TBA were observed in the effluent (40-60 days). Some data was collected at 40 mL/d, but most kinetic data was collected after the flow rate had been lowered to 15 mL/d. The concentrations of MTBE and TBA measured by DAI-GC/MS on the column effluents are shown in Figure 5.3 (A, C, and E). These plots show steady-state concentrations of MTBE for 5-7 days after breakthrough, and a steady partial conversion of MTBE to TBA after 40 days, with essentially complete mass balance.

The kinetics of MTBE degradation in these columns cannot be quantified reliably from the decrease in MTBE concentration because the proportion of MTBE degraded is less than 1 percent. The appearance of TBA is a much more sensitive indicator of MTBE degradation, however, so we have used TBA concentration data for our kinetic analyses. Note that mass balance calculations suggest loss of MTBE is accompanied by stoichiometric conversion to TBA (Figure 5.3 A, C, and E). Figure 5.3 B, D, and F show TBA concentrations at each port (under steady-state conditions, confirmed by agreement of kinetic parameters for 40 mL/d and 15 mL/d pumping rates) plotted against the elapsed contact time. The linearity of these plots suggests that the kinetics of TBA appearance might be zero-order.

However, further analysis (Figure 5.4) shows that the extent of reaction in the columns was not great enough to distinguish between zero-order and first-order conversion of MTBE to TBA. To distinguish between these possibilities, one column (the one containing Borden sediment) was exposed to three different initial concentrations of MTBE (ranging over two orders of magnitude). The results (Figure 5.4, A-C), give nearly identical rate constants when fit to a first-order model for appearance of TBA. Similar results were found for the other two columns (data not shown). The average first-order rate constant for the experiments were $(7.1 \pm 0.1) \times 10^{-4}\ d^{-1}$, $(1.1 \pm 0.1) \times 10^{-3}\ d^{-1}$, and $(9.9 \pm 0.1) \times 10^{-4}\ d^{-1}$ for the Base Borden, Detroit, and Turnersville sediments, respectively.

TBA Degradation Kinetics. TBA degradation kinetics were measured under the same conditions as the kinetics of MTBE degradation, but with the column influent containing 100 μg/L TBA. In these experiments there were no observable degradation products, presumably because the rates of their degradation were much higher than the rate at which they were being formed. Because of this, the kinetic values listed in Table 5.2 for TBA degradation are based on TBA disappearance, rather than product appearance. As expected, the error in the measurements are greater due to this method of measurement, but in general, the rates of TBA degradation appear to be slightly faster than the rates of MTBE degradation in the same columns. We observed this same general trend in the degradation kinetics of MTBE and TBA [38] by PM1, a bacterial isolate that has been shown to degrade MTBE rapidly in the laboratory [37].

Predicted Maximum TBA Concentration. If the degradation rates of MTBE and TBA, as well as the initial concentration of MTBE in a particular system are known, it is possible to predict the maximum concentration of TBA expected under ideal conditions (assuming other nutrients do not become limiting, negligible or identical retardation, etc.). Based on the results of the experiments reported here, the conversion of MTBE to TBA and the subsequent disappearance of TBA are expected to be first-order processes when occurring in the environment and, therefore, the following rate laws may be written.

$$\frac{d\left[MTBE\right]}{dt} = -k_{MTBE}\left[MTBE\right] \tag{1}$$

$$\frac{d\left[TBA\right]}{dt} = k_{MTBE}\left[MTBE\right] - k_{TBA}\left[TBA\right] \tag{2}$$

where k_{MTBE} and k_{TBA} are the first order rate constants of MTBE conversion and TBA disappearance, respectively. Taking $[MTBE] = [MTBE]_0$ and $[TBA] = 0$ as initial conditions, this system of rate laws has the following solution set.

$$\left[MTBE\right] = \left[MTBE\right]_0 e^{-k_{MTBE}t} \tag{3}$$

$$\left[TBA\right] = \left[MTBE\right]_0 \frac{k_{MTBE}}{k_{TBA} - k_{MTBE}}\left(e^{-k_{MTBE}t} - e^{-k_{TBA}t}\right) \tag{4}$$

The maximum TBA concentration may then be found to be a function of initial MTBE concentration and the first order rate constants.

$$\left[TBA\right]_{\max} = \left[MTBE\right]_o \left(\frac{k_{MTBE}}{k_{TBA}}\right)^{\left(\frac{1}{1-\frac{k_{MTBE}}{k_{TBA}}}\right)} \tag{5}$$

Equation 5 shows $[TBA]_{MAX}$ to be a surface with independent variables $[MTBE]_0$ and k_{MTBE} / k_{TBA}. This surface is represented with contours of constant $[TBA]_{MAX}$ in Figure 5.5. The asymptotic features of Figure 5.5 are intuitive: $[TBA]_{MAX}$ becomes large as $[MTBE]_0$

becomes large and vanishingly small as $[MTBE]_0$ goes to zero. Where $k_{MTBE} << k_{TBA}$, TBA is destroyed much faster than it is formed and, therefore, the maximum TBA concentration is small, vanishingly so in the limit. In the opposite case where $k_{MTBE} >> k_{TBA}$, TBA is formed much quicker than it is destroyed and the maximum TBA concentration approaches the initial MTBE concentration.

Since Equation 5 and Figure 5.5 describe the relationship between the initial concentration of MTBE, the relative degradation rates of MTBE and TBA, and the expected maximum TBA concentration, they may also be used to estimate unknown parameters in field studies if the other three parameters are known. For example, if the initial concentration and degradation rate of MTBE in a ground water system is known and TBA is observed, the concentration of TBA can be used to estimate the degradation rate of TBA.

Using the kinetic data for MTBE conversion to TBA (Table 5.2), the kinetic data for the subsequent degradation of TBA (Table 5.2), and the analysis represented by Equation 5 and Figure 5.5, we can estimate the maximum TBA concentration expected in the preliminary study [56], since it was designed to have a much longer contact time (although oxygen limited) than the kinetic studies. The predicted maximum TBA concentrations for the preliminary study are 0.53 μM (39 μg/L), 0.55 μM (41 μg/L), and 0.65 μM (48 μg/L) for the Base Borden, Detroit, and Turnersville sediments, respectively. This prediction is in relatively good (between 18 and 29 percent) agreement with the maximum TBA concentrations observed [56], which were 0.45 μM (33 μg/L), 0.77 μM (57 μg/L), and 0.85 μM (63 μg/L) for the Base Borden, Detroit, and Turnersville sediments, respectively (data not shown here). The differences observed is likely due to a number of factors, including oxygen limitation in the preliminary study or relative changes in the number or degrading efficiency of MTBE and/or TBA degrading bacteria over the two years the columns were operated.

5.4.5 Implications

From the combined results of this study, the average half-lives for MTBE conversion to TBA are 2.7, 1.7, and 1.9 years for Base Borden, Detroit and Turnersville sediments, respectively, while the respective average half-lives for the subsequent degradation of TBA are 2.6, 2.0, and 2.1 years. The similarity among these values is remarkable, and suggests that slow biodegradation of MTBE to TBA (with half-lives ca. 2.1 years) and slightly faster degradation of TBA (with half-lives ca. 2.2 years) may occur in a wide variety of aerobic aquifers. In fact, the estimate for MTBE degradation is consistent with available estimates of MTBE biodegradation rates in the field, which include half-lives of 1.8 [13] and 2.8 years [17] (Table 5.2). Such slow degradation rates are very difficult to characterize from field data, however, so the comparison with our column data should not be interpreted as more than qualitative agreement.

An apparent discrepancy between our results and some previously reported studies concerns the range of terminal electron accepting processes (TEAPs) under which MTBE degradation occurs. While our anaerobic columns displayed no degradation of MTBE, the TEAPs represented in our columns were in the nitrate to iron reducing range only, so our data is not evidence against biodegradation of MTBE under methanogenic conditions. In fact, other laboratories have reported degradation in microcosms under anaerobic conditions that might have involved methanogenesis [51, 72, 73, 79], and recent field studies have reported evidence for relatively rapid MTBE degradation under these conditions [53, 80-84] [44, 85]. It remains to be determined whether the presence of substrates more easily biodegraded than MTBE—such as are typical of groundwater conditions in and around plumes at gasoline spill sites—inhibits methanogenic biodegradation to the degree that we found these substrates inhibit MTBE biodegradation under aerobic and other anaerobic conditions.

Chapter 5 Tables

Table 5.1. Ion concentrations in column influents and effluents (mg/L)

Sample	Chloride	Iron (II)	Nitrate	Sulfate
Detroit Influent	100.0	BDL	3.0	52.0
Detroit Effluent	99.9	BDL	2.9	51.6
Turnersville Influent	36.9	BDL	4.4	13.2
Turnersville Effluent	36.9	BDL	4.3	12.9
Borden Aerobic Influent	0.9	BDL	BDL	9.6
Borden Aerobic Effluent	0.8	BDL	BDL	10.0
Borden Anaerobic Influent	0.9	BDL	BDL	9.6
Borden Anaerobic Effluent	0.9	BDL	BDL	9.5
Laurel Bay Aerobic Influent	2.6	BDL	BDL	2.6
Laurel Bay Aerobic Effluent	2.7	BDL	BDL	2.5
Laurel Bay Anaerobic Influent	2.6	BDL	BDL	2.6
Laurel Bay Anaerobic Effluent	2.6	0.7	BDL	2.5

BDL = below detection limit

Table 5.2. Kinetic parameters based on column results (this study) and field studies.

Column Sediment	MTBE k_1 (days^{-1})	MTBE $t_{1/2}$ (yr)	TBA k_1 (days^{-1})	TBA $t_{1/2}$ (yr)
Borden	$(7.16 \pm .03) \times 10^{-4}$	2.7	$(7.3 \pm .4) \times 10^{-4}$	2.6
Detroit	$(1.12 \pm .1) \times 10^{-3}$	1.7	$(9.5 \pm .7) \times 10^{-4}$	2.0
Turnersville	$(9.9 \pm .1) \times 10^{-4}$	1.9	$(9.0 \pm .8) \times 10^{-4}$	2.1
Borden Field Study [17]	1.1×10^{-3}	1.8	N.M.	N.M.
North Carolina Field Study [13]	6.8×10^{-4}	2.8	N.M.	N.M.

N.M. = not measured. Uncertainties all represent one standard deviation based on the fit to a single time series of experimental data.

Chapter 5 Figures

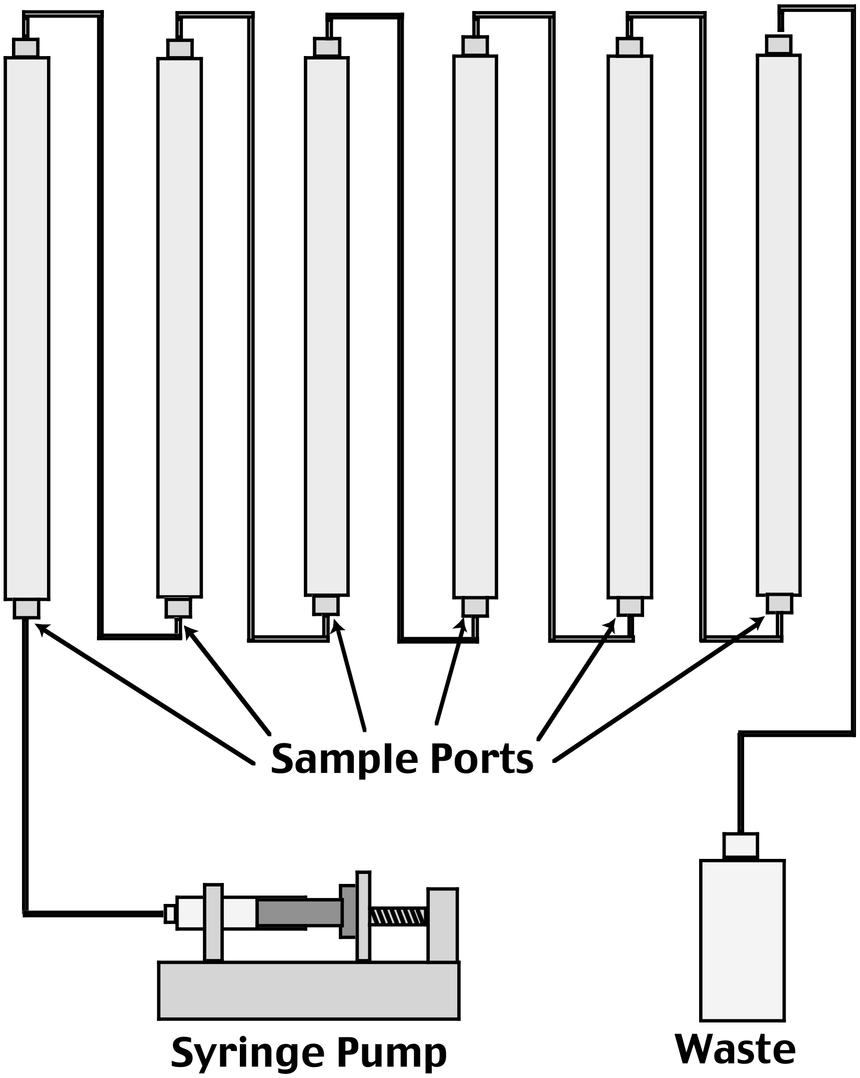

Figure 5.1. Configuration of one column model system
Each column is constructed of 60 cm long column segments (totaling 360 cm) and was fed by a syringe pump in upflow mode.

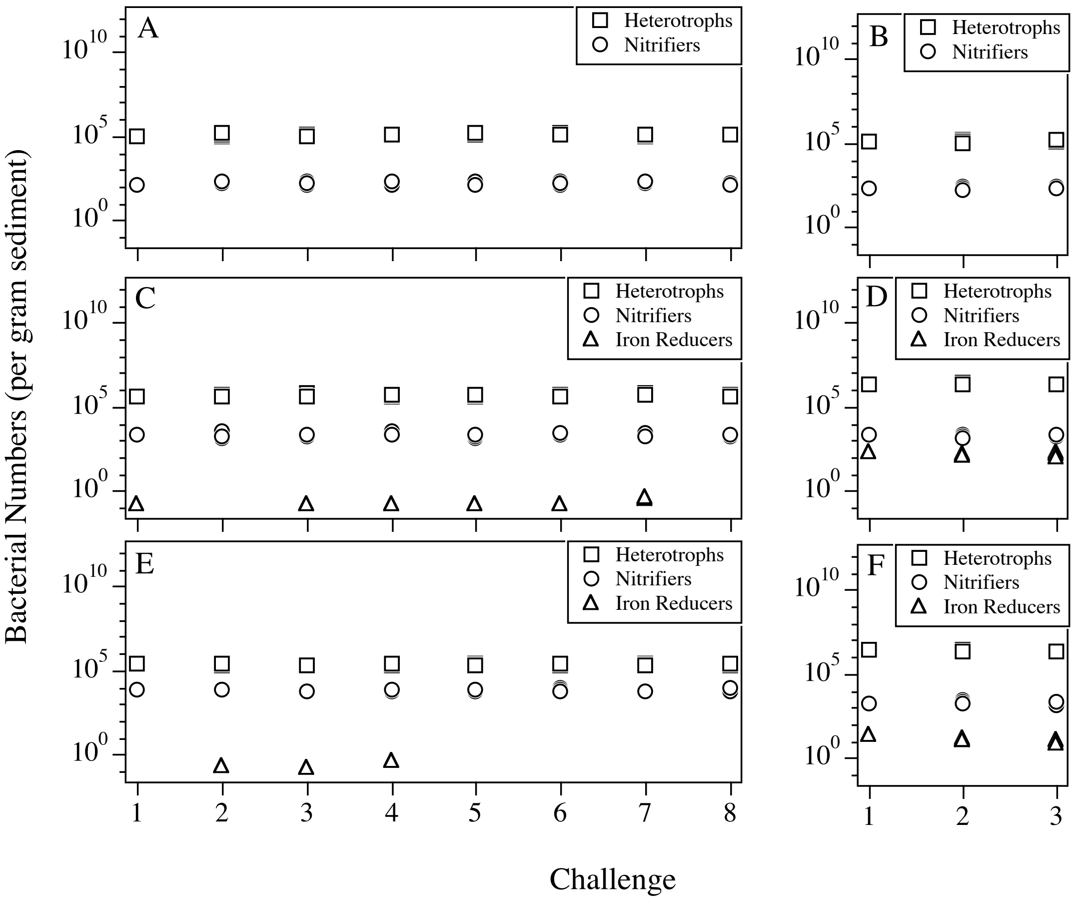

Figure 5.2. Bacterial concentrations during the course of the experiments
A through F show bacterial concentrations based on plate counts and most probable number analyses in sediment sub-samples of the six columns tested. (A) Base Borden Aerobic, (B) Base Borden Anaerobic, (C) Detroit Aerobic, (D) Laurel Bay Aerobic, (E) Turnersville Aerobic, (F) Laurel Bay Anaerobic. The sediments were sub-sampled following each "challenge", which are shown on the abscissa: (1) original sediment, (2) equilibration, (3) 100 μg/L (1.13 μM) MTBE, (4) steady state 100 μg/L (1.13 μM) MTBE, (5) steady state 10 μg/L (0.113 μM) MTBE, (6) steady state 1000 μg/L (11.3 μM) MTBE, (7) steady state 100 μg/L (1.35 μM TBA), (8) steady state 100 μg/L (1.13 μM) MTBE.

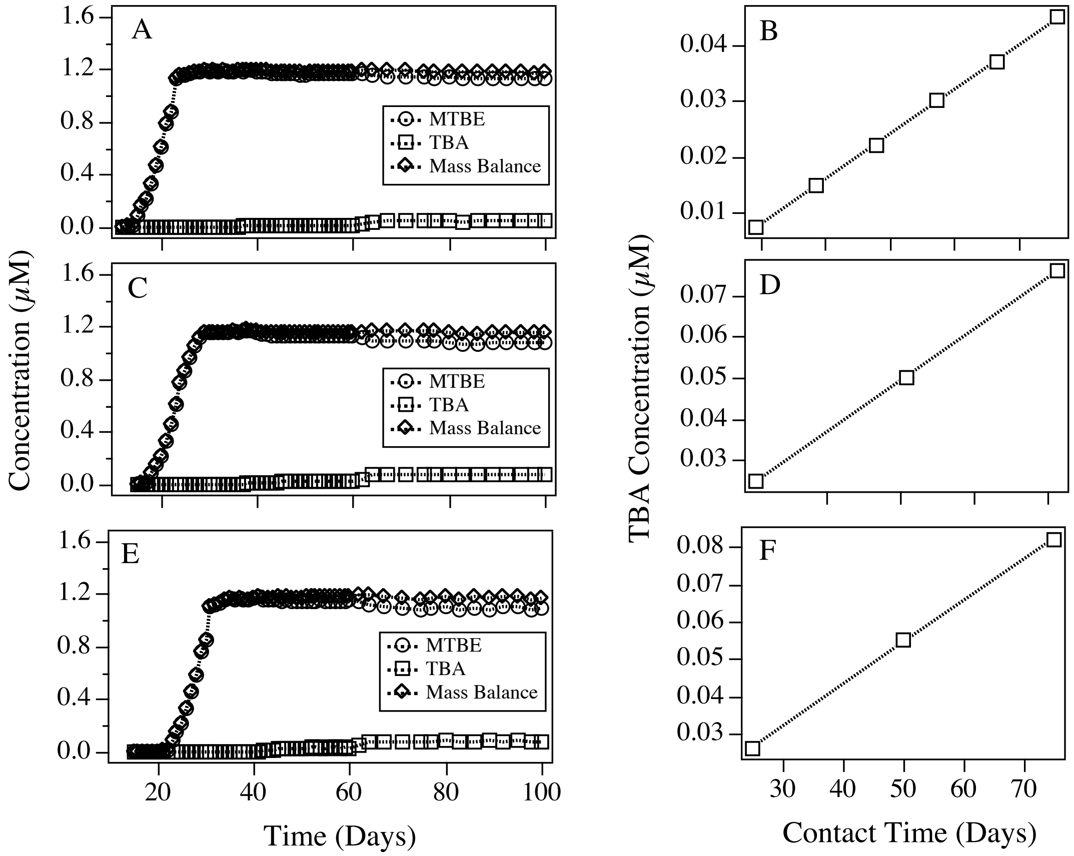

Figure 5.3. MTBE degradation and TBA Appearance in model column aquifers. A, C, and E show MTBE and TBA concentrations in the effluents of the three columns containing previously uncontaminated sediments in which MTBE degradation was observed. (A) Base Borden, (C) Detroit, (E) Turnersville. The columns were challenged with aerobic influent containing 100 μg/L (1.13 μM) MTBE at a rate of 15 ml/day. B, D, and F show TBA concentrations derived from sampling ports along the length of columns A, C, and E, respectively, while columns were at steady-state.

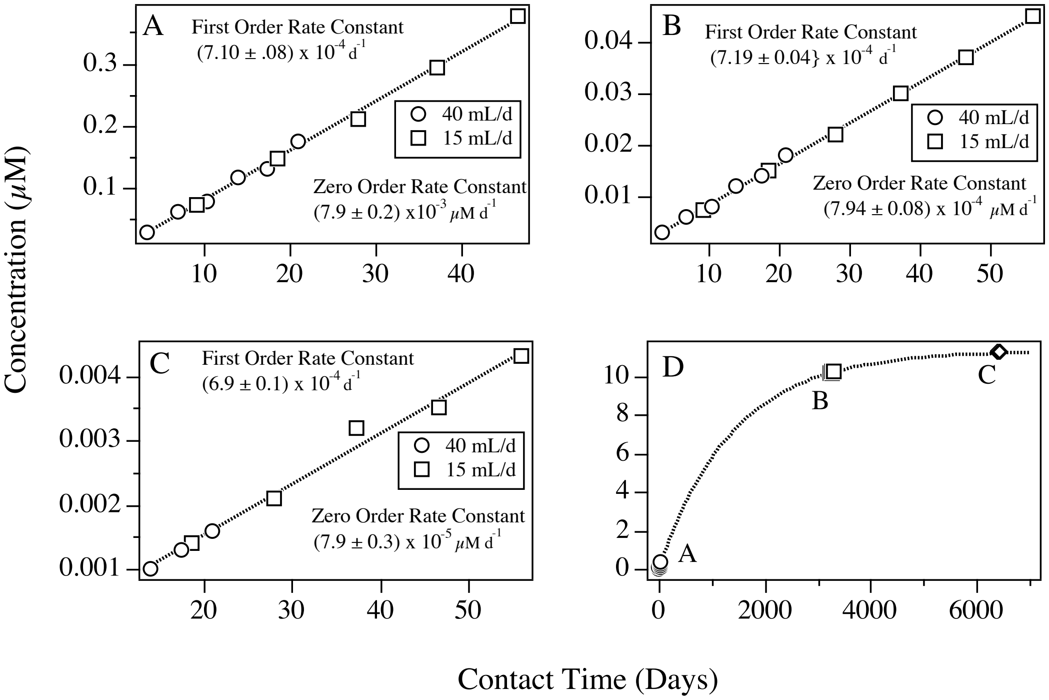

Figure 5.4. First-order TBA appearance kinetics.

A, B, and C show TBA appearance kinetics for three MTBE influent concentrations in Base Borden sediment. Influent concentrations were (A) 1000 μg/L (11.3 μM), (B) 100 μg/L 1.13 μM, and (C) 10 μg/L (0.113 μM). D is a compilation of the plots shown in A, B, and C, showing that all of the data can be placed on one first-order appearance curve with a rate constant equal to 7.1 x 10^{-4} d^{-1}.

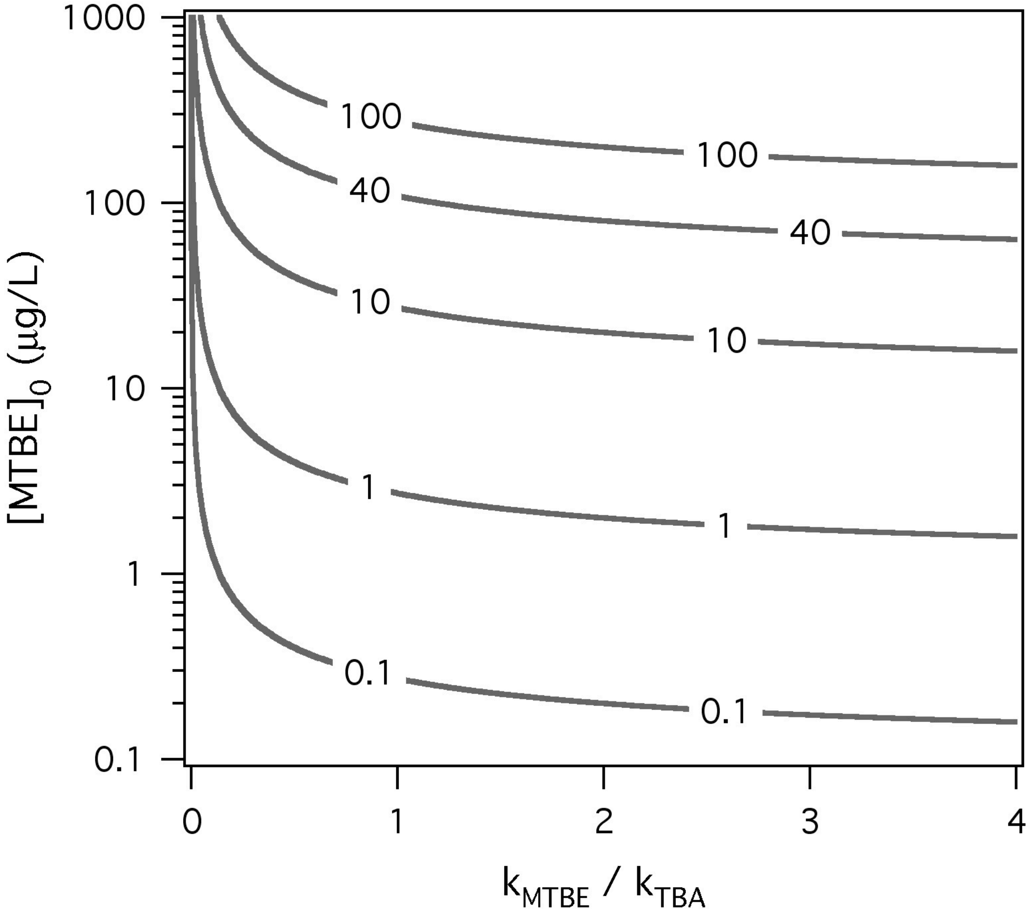

Figure 5.5. Predictive model of TBA appearance.
Contours of maximum TBA concentration versus the ratio of the first-order conversion of MTBE to TBA and the subsequent first-order disappearance of TBA (x-axis) for given initial MTBE concentrations (y-axis). Based on equation 5.

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Chapter 6: MTBE Degradation by Soil Catalyzed Decomposition of Hydrogen Peroxide

6.1 Introduction

The realization that MTBE has become a widely distributed groundwater contaminant [1] and is likely to remain a concern long after its use is discontinued [2] has created a demand for a more complete understanding of the environmental fate of this compound. Our current understanding of MTBE fate in the environment comes mainly from studies of MTBE in association with gasoline, and indicate that MTBE is highly mobile and persistent [3-8]. This is consistent with the fact that MTBE has been found in urban air [9-12], surface waters [13-16], and some shallow groundwaters [1, 13-23].

Data on the degradation of MTBE in the environment is limited in part because the rate of MTBE degradation is generally quite slow and the resulting products are not easily detected using conventional methods. In most of the studies that have reported MTBE degradation rates in the subsurface (usually based on MTBE disapearance), the rates appear to be too slow to support significant natural attenuation in contaminated aquifers [24-28]. From this argument, and from modeling studies [2], it appears that MTBE will be a persistent groundwater contaminant on time scales of years to decades.

In natural surface waters, soils, and groundwaters, the only pathways for MTBE degradation studied to date are microbially mediated hydrolysis [29] and oxidation [30, 31]. The major product of both biodegradation pathways is TBA. In active, engineered remediation situations, chemical oxidation of MTBE has been studied extensively in recent years [32-51]. Most chemical oxidation processes that degrade MTBE involve hydroxyl radical, HO•, which aggressively abstracts hydrogen from most organic molecules. For MTBE in aqueous solution, this reaction (eq. 1) has a second-order rate constant of 1.6 x 10^9 M^{-1} s^{-1} [52].

$$HO\bullet + (H_3C)_3COCH_3 \rightarrow (H_3C)_3CO\dot{C}H_2 + H_2O \qquad (1)$$

Recent studies of this reaction have generated the hydroxyl radical through the use of ozone [53, 54], ozone/hydrogen peroxide [55], and UV/hydrogen peroxide [10, 56, 57] systems, photocatalytically in TiO_2 slurries [58], and via the Fenton reaction [59]. The major products of the degradation of MTBE reported include tert-butyl formate (TBF), TBA, acetone, methanol, and acetaldehyde [10, 53-59].

In the near-subsurface, HO• may be formed via enzymatic pathways [60-65] and iron catalyzed decomposition of hydrogen peroxide [32-51, 66, 67]. One mechanism of iron catalyzed decomposition of hydrogen peroxide (CDHP) that has been studied extensively is the Fenton reaction, which begins with the oxidation of Fe(II) to Fe(III) to generate the hydroxyl radical:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO\cdot \qquad (2)$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO\cdot_2 + H^+ \qquad (3)$$

$$HO\cdot + H_2O_2 \rightarrow HO\cdot_2 + H_2O \qquad (4)$$

$$HO\cdot + Fe(II) \rightarrow Fe(III) + OH^- \qquad (5)$$

$$Fe(III) + HO\cdot_2 \rightarrow Fe(II) + O_2H^+ \qquad (6)$$

$$Fe(II) + HO\cdot_2 + H^+ \rightarrow Fe(III) + H_2O_2 \qquad (7)$$

$$HO\cdot_2 + HO\cdot_2 \rightarrow H_2O_2 + O_2 \qquad (8)$$

The second-order rate constant for equation 2 is 76 M^{-1} s^{-1} [68] (in water at 22°C, pH = 3) so even low concentrations of the reactants could give a substantial production rate of HO•. Production of HO• is balanced by its rapid destruction via a host of possible processes, including reactions with organic molecules present. Reaction with MTBE will be among these reactions, resulting in degradation of MTBE and an additional sink for HO•.

In the environment, generation of the hydroxyl radical by CDHP is limited by the amount of available H_2O_2, but H_2O_2 is relatively ubiquitous at low concentrations [69-107]. Numerous studies have shown that H_2O_2 is present in the atmosphere [69-83] and in surface waters [84-96], where it is produced primarily by photochemical processes. Measured concentrations of H_2O_2 range from < 2 to >40 *μM* levels in fog and rainwater [75, 97-106] to an average of 20 *nM* for a wide variety of groundwaters [96, 107]. Sites where H_2O_2 is pumped into the subsurface to enhance in situ bioremediation may exhibit local concentrations in the m*M* (or higher) range.

While numerous studies of engineered treatment systems [53, 54, 108, 109] and reactions with MTBE in the atmosphere [11, 110-112] have shown that MTBE is subject to rapid attack by hydroxyl radical (HO•), few studies have addressed MTBE degradation by naturally occurring variations of CDHP. One unexplored hypothesis is MTBE degradation as a result of soil CDHP (H_2O_2 plus crystalline Fe(III) to produce the hydroxyl radical at environmental relevant pH values) that likely occurs when a raindrop containing H_2O_2 [113, 114] and MTBE [115] encounters Fe^{3+} at the ground surface [32-51].

As noted by Pignatello [116], and shown by equations (2-8) there is overlap between the reactions involved in soil CDHP and the classical Fenton reaction (soluble ferrous sulfate and H_2O_2 in aqueous solution at pH < 2), but there can be differences in the rates if the initial H_2O_2 concentration is small compared to the concentration of the other reactants. Therefore, we will distinguish between the two in this discussion. The purpose of this study was to demonstrate that this process occurs under simulated environmental conditions, and to provide a preliminary assessment of its likely significance in the environment.

6.2 Experimental Section

6.2.1 Standards and Analytical Techniques

Standard solutions were made using the highest purity MTBE, tert-butyl alcohol (TBA), tert-butyl formate (TBF) and other potential degradation products (isopropanol, acetone, acetaldehyde) that were available from commercial sources (Aldrich, >97%) and Millipore water. Standards and the effluent from column experiments were analyzed for MTBE and degradation products by direct aqueous injection with gas chromatography and detection by mass spectrometry (DAI-GC/MS) according to a method described previously [117] or by direct aqueous injection with gas chromatography and detection by flame ionization (DAI-FID). DAI-GC/MS was preferred because it allowed: (*i*) simultaneous quantification of MTBE and TBA at much lower detection limits than DAI-FID; (*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. However, DAI-FID was necessary in order to collect data on the initial stages of experiments due to the recovery time (30 minutes) of the mass spectrometer.

6.2.2 Minerals and Natural Geologic Materials

Goethite was synthesized by adjusting the pH of a 0.4 M ferric chloride solution to pH 13 using 4 N NaOH and incubating the solution at 70^{O}C for 16 hours with constant stirring [118]. The precipitate was then washed with centrifugation until the chloride concentration was <0.5 mM, freeze dried, and passed through a 100 μm sieve [119]. Hematite (Fe_2O_3 powder) was purchased from Baker Chemical Company. It was heated at 750^{O}C for 2 hours, allowed to cool, and passed through a 100 μm sieve prior to use. When examined by X-ray diffraction (XRD) neither the hematite nor the goethite showed evidence of crystalline impurities, and the goethite showed slight broadening of XRD peaks consistent with the small particle size [120].

Natural soils used in the experiments were Pliocene and Pleistocene age Atlantic coastal plain sand collected from a gravel pit near Milford, Delaware. The sand consisted of iron (III) oxide (predominately goethite) coated quartzitic sands and have been described in greater detail previously [119, 121, 122].

6.2.3 Experimental Procedures

All experiments with the exception of the column infiltration tests (discussed below) were carried out in pressure tubes (Belco Glass, Vineland, NJ) sealed with butyl rubber stoppers. Solutions for the experiments were prepared in the same manner as the standards and no buffers were used. pH was adjusted with 1M NaOH (Aldrich, 95%). For the experiments shown, all reactants except H_2O_2 were sealed within pressure tubes, and sampled to determine initial MTBE concentrations and verify the initial pH. H_2O_2 (Aldrich, 7% and 30% solutions, used as received within 1 month) was then injected with a syringe to achieve the desired H_2O_2 concentration. Separate control experiments (not shown) were conducted similarly to ascertain that there was no reaction between either MTBE or TBA and H_2O_2 in the absence of an iron catalyst.

Column Construction and Operation. Two identical columns for the infiltration experiment were constructed using segments of 2.54 cm I.D. stainless steel pipe totaling 30.5 cm in length each. Milford Iron oxyhydroxide coated sand for the column studies were packed in the column and the column was then autoclaved three times on three successive days. The packed columns were connected to high performance liquid chromatograph pumps using autoclaved 1.5 mm O.D. stainless steel tubing with stainless steel fittings and placed in a 15°C cold-room where the experiments were performed.

Column influent solutions were autoclaved Millipore water equilibrated with the atmosphere. These feed solutions were pumped through the column in upflow mode at a flow rate of 1.0 mL/min for 2 hours to equilibrate the column. After this initial equilibration period, the column feed was switched to solutions of Millipore water amended with 20 μg/L MTBE for 1 hour, at which point the feed solutions were amended with 40 μg/L H_2O_2.

6.3 Results and Discussion

6.3.1 Classical Fenton

To confirm the facile mineralization of MTBE under the optimal conditions of the classical Fenton reaction, we exposed 100 μg/L MTBE to H_2O_2 in the presence of ferrous sulfate at pH = 2. The disappearance of MTBE (Figure 6.1A) showed an immediate drop of about 9 %, followed by a slower decline that appeared to be pseudo first-order with a half-life of 2.2 ± 0.2 hr (Table 6.1). The bimodal kinetics seen in Figure 6.1 is common in Fenton systems where reaction of H_2O_2 with Fe(II) (eq. 2) rapidly converts Fe(II) to Fe(III) and then the slow reaction of H_2O_2 with Fe(III) becomes dominant [116, 123, 124]. The control, which contained no H_2O_2, showed no evidence of MTBE disappearance, as expected [59].

Complete disappearance of MTBE was observed in less than 20 hours, with formation of the four intermediate products, *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), acetaldehyde, and acetone (Figure 6.1). The products observed in this experiment (Figure 6.1B) agree closely with previous experiments of MTBE degradation with hydroxyl radical [10, 53-55, 57, 58] with the exception of one study which did not observe TBF[59], although they did note that there were several other unidentified reaction products besides TBA and acetone. Another possible explanation is that TBA and TBF may have co-eluted on their 2 m packed column, since elution times are very close on even a 30 m capillary column (Church, 1997). Since they used a flame ionization instead of mass spectrometer detector, it would not have been possible to determine if the two peaks had co-eluted.

6.3.2 CDHP at Environmental pHs

In order to show that CDHP contributes to the degradation of atmospherically deposited MTBE it must be shown to occur at typical environmental pH values and with geologic materials, rather than at pH = 2 and with soluble Fe(II) as in the experiment depicted in Figure 6.1. Figure 6.2 (A and B) are the results of a set of experiments showing that the Fe(II)/H_2O_2 system does give significant MTBE degradation at relevant pH values. In these experiments, the pH of the ferrous sulfate solution used in the Figure 6.1 experiment was adjusted to an environmentally relevant pH range of 5-7 prior to the injection of H_2O_2 (7000 mg/L initial concentration). Under these conditions, the rate of MTBE degradation (Summarized in Table 6.1) is shown to vary with respect to pH (Figure 6.2B) according to:

$$k/\text{min} = (13.9 \pm 0.06) - (1.95 \pm 0.09)(\text{pH}) \qquad (9)$$

These results agree with other results of other studies which have studied the effects of pH on the CDHP. For example, it has been reported that the reaction proceeded rapidly only under the pH range of 2-4 [123-125] and that the extent of the reaction was limited by the amount of H_2O_2 [123, 124]. It is likely that this observed change in rate is due primarily to the speciation of iron and the corresponding reactivities of those species with H_2O_2 [116].

6.3.3 CDHP in Soil Slurries

Another set of experiments was performed to determine the extent of MTBE degradation under soil CDHP conditions using mineral forms of iron (III) oxyhydroxides (goethite and hematite), and naturally occurring Milford Fe(III)-coated sands. The initial pH values of the sediment/water solutions were adjusted prior to the addition of MTBE and H_2O_2 (initial concentrations: 100 mg/L MTBE and 200 mg/L H_2O_2). In all cases the reaction proceeded to completion in less than 30 min and no degradation products were observed. The percent of MTBE degraded (summarized in Table 6.1) showed that the reaction is likely to occur at environmentally relevant pH values and with natural iron oxyhydroxide coated sand, that the reaction proceeds to completion in less than 30 minutes if MTBE:H_2O_2 concentration ratios are similar to what might be found in a raindrop (1:2 on a mg/L scale, 1:5 on a mM scale) [9-12, 75], and that the amount of MTBE degraded is depended on the pH of the reaction.

To demonstrate that H_2O_2 was the limiting reactant, a batch experiment containing 20 μg/L MTBE and 0.5 g of Milford sediment (adjusted to pH 7) received respikes of 40 μg/L H_2O_2 in 30 minute intervals. The results of this experiment are shown in Figure 6.3.

Each addition of MTBE resulted in a rapid decrease in MTBE concentration. TBA was detected as a degradation product, but also rapidly degraded. Preliminary analysis of the kinetics of MTBE degradation showed that the reaction was not pseudo first-order, but rather was bi-modal with a fast step for the first minute, followed by slower MTBE disappearance. This is not unexpected and is likely due to reaction of hydroxyl radical with the products of the MTBE degradation (recall Figure 6.1B).

To simulate infiltration of a raindrop containing MTBE and H_2O_2, two columns packed with Milford oxyhydroxide coated sand received influents of 20 μg/L MTBE for one hour, and were then switched to influents containing 20 μg/L MTBE amended with 40 μg/L H_2O_2 (Figure 6.4). Both solutions were adjusted to pH = 7.

After exhibiting a typical breakthrough curve, steady MTBE concentrations were observed until the influent containing both MTBE and H_2O_2 exited the column. This effluent showed a decrease in MTBE concentration and the transient appearance of TBA as a degradation product. It is not possible to be as precise under these conditions as in the batch experiment (above) due to the effects of diffusion, but it appears that the reaction proceeded to completion in 30-35 minutes.

6.3.4 Summary and Implications

From the experiments documented here it appears that CDHP may contribute to natural attenuation of MTBE where rainfall impacts the near-surface soils. Both MTBE [115, 126] and H_2O_2 [75, 127-129] enter the atmosphere through various phase transfer and chemical transformation processes (Figure 6.5, MTBE and its degradation products shown only). Some of the MTBE degrades to TBF and/or TBA by pathways discussed earlier (Chapters 1 and 3, and [110-112, 130]). MTBE, its degradation products, and H_2O_2 are all polar compounds and thus, partition to fog and raindrops. Note that, in a separate experiment (not shown), there was no evidence of a reaction between either MTBE or TBA and H_2O_2 in the absence of an iron catalyst. Some studies have shown that iron also occurs in raindrops [131, 132] and, in fact, does react with H_2O_2. It is evident, however, that this reaction does not utilize all of the available H_2O_2, since it is readily detectable in fog and rainwater samples [75, 97-106], possibly because the rates of reaction are not fast enough to consume all of the H_2O_2. In the absence of another catalyst or other reactants, it likely that the primary reaction occurring until the reactants in the raindrop are delivered to the catalyst at the surface of the earth (for MTBE and its degradation products) is the partial hydrolysis of TBF to TBA (Chapters 1 and 3, and [110-112, 130]).

When the raindrop containing MTBE, its degradation products, and H_2O_2 subsequently reach the earth surface, the degradation mechanism is activated upon contact with iron oxide coated sands and clays and continues during the infiltration process (Figure 6.5, Reaction E). The amount of MTBE degraded is dependent upon the concentration of H_2O_2 contained within the raindrop, speciation of the iron, pH, and the presence of competing reactants. Evidence suggests that the degradation pathway proceeds completely to CO_2. Given an initial MTBE:H_2O_2 ratio of 1:2 (ppm scale), this reaction may result in decreases of the MTBE concentration by as much as 8-9%. It is important to note that the mechanism described here is not limited to MTBE and its degradation products. Due to the high reactivity of the hydroxyl radical, any organic compound which partitions similarly to water in the atmosphere and has a significant wet-deposition component in its life-cycle would likewise be subject to degradation by the same mechanism.

Chapter 6 Tables

Table 6.1. Experimental conditions and results of MTBE degradation by classic Fenton and soil CDHP reactions at various pH values.

Fe\pH	2	3	4	5	6	7
MTBE Degradation Under Classic Fenton Conditions (soluble ferrous sulfate)						
Soluble FeII (ferrous sulfate)	100 mg/L MTBE 200 mg/L H_2O_2 $t_{1/2}$= 2.2h	N.P.	N.P.	100 mg/L MTBE 7% H_2O_2 $t_{1/2}$=0 .16h	100 mg/L MTBE 7% H_2O_2 $t_{1/2}$=0.33h	100 mg/L MTBE 7% H_2O_2 $t_{1/2}$=2.0h
MTBE Degradation Under soil CDHP Conditions (mineral Fe(III))						
Conditions	**Percent MTBE degraded in 30minutes**					
0.5g Geothite 100 mg/L MTBE 200ppm H_2O_2	15.3%	14.1%	13.6%	11.1%	9.3%	8.6%
0.5g Hematite 100 mg/L MTBE 200ppm H_2O_2	11.4%	10.1%	9.3%	8.6%	7.5%	6.4%
1g Milford [94-96] 100 mg/L MTBE 200ppm H_2O_2	14.1%	13.1%	12.3%	10.6%	9.1%	8.2%
1g Milford [94-96] MTBE 25-50-100 μg/L 100 μg/L H_2O_2	N.P.	N.P.	N.P.	N.P.	N.P.	D-raindrop 16.1-8.4-4.3

N.P. = not performed

Chapter 6 Figures

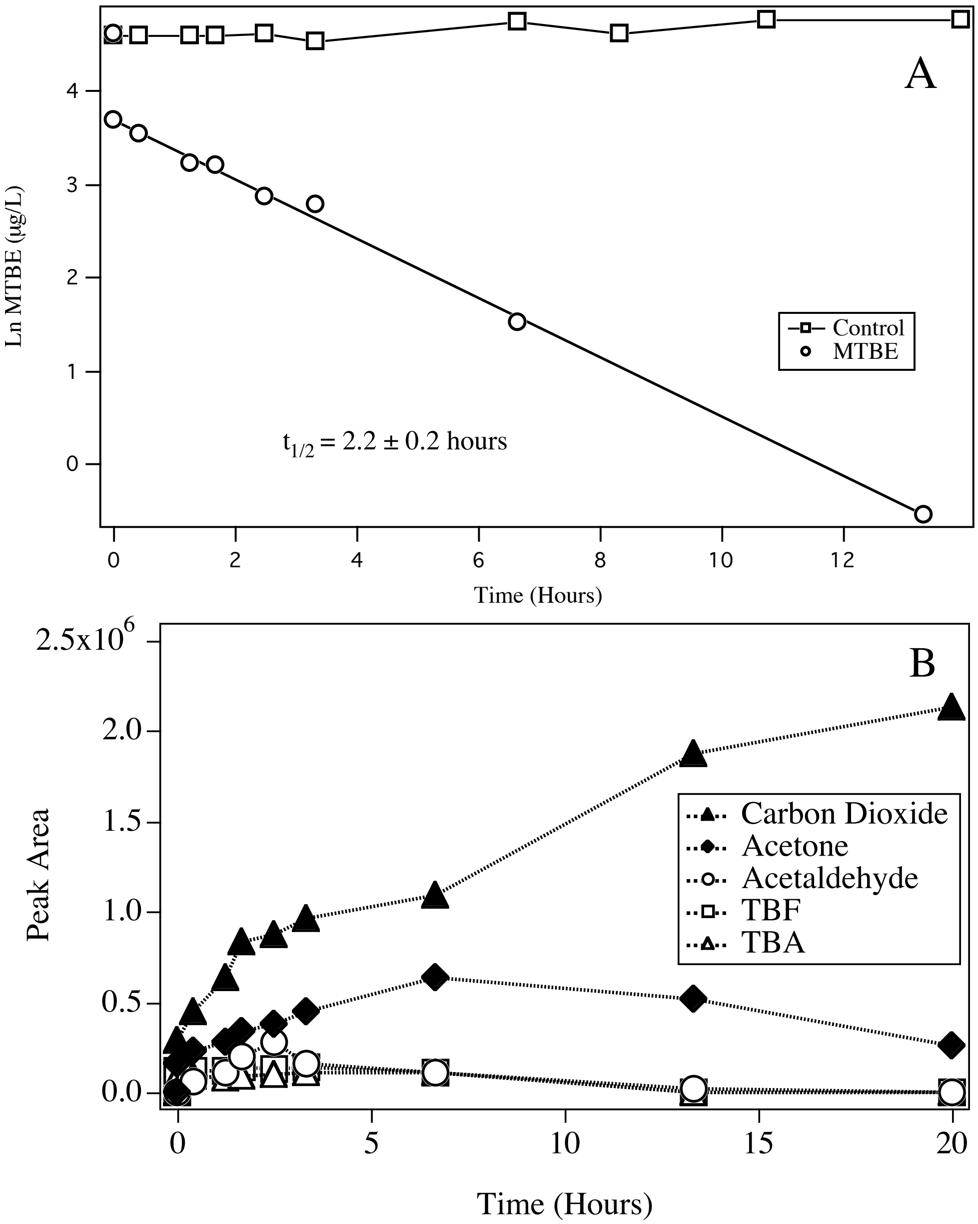
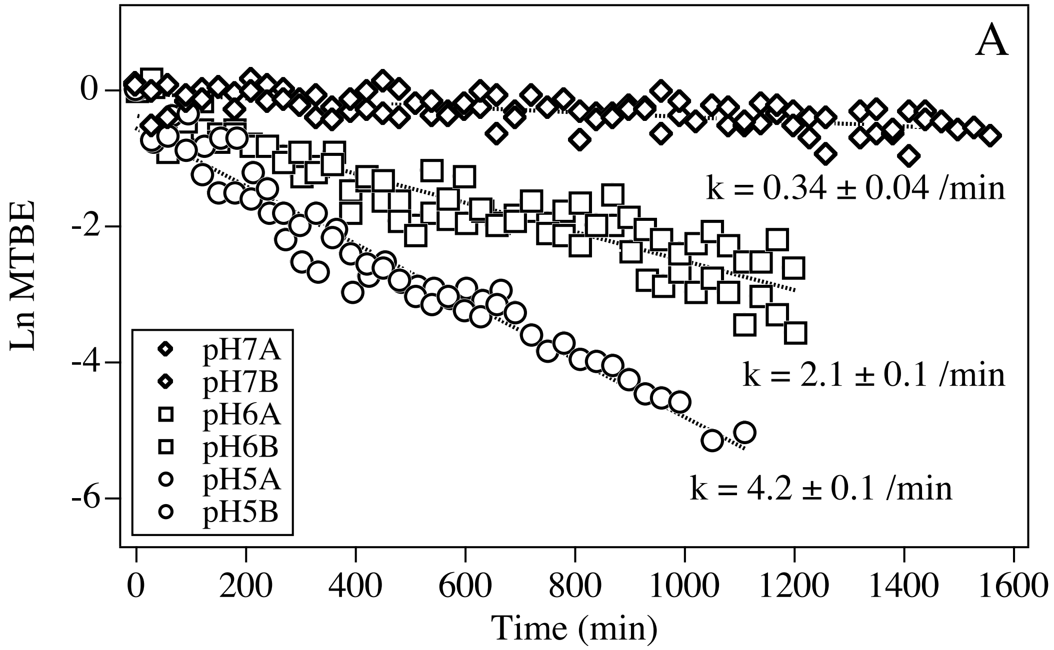


Figure 6.1. Degradation of MTBE under classical Fenton conditions.
Disappearance of MTBE and formation of degradation products under classical Fenton conditions (Initial concentrations: (H_2O_2, 200 mg/L; $FeSO_4$, 1.15 mM; MTBE 100 mg/L: initial pH = 2). (A) Plot of the first-order MTBE disappearance, which shows that after an initial rapid loss of MTBE the pseudo first-order disappearance rate constant, k, for this reaction is equal to 0.32. This corresponds to a half-life of MTBE under these conditions of 2.2 hours. (B) Appearance and subsequent disappearance of MTBE degradation products for the same experiment.



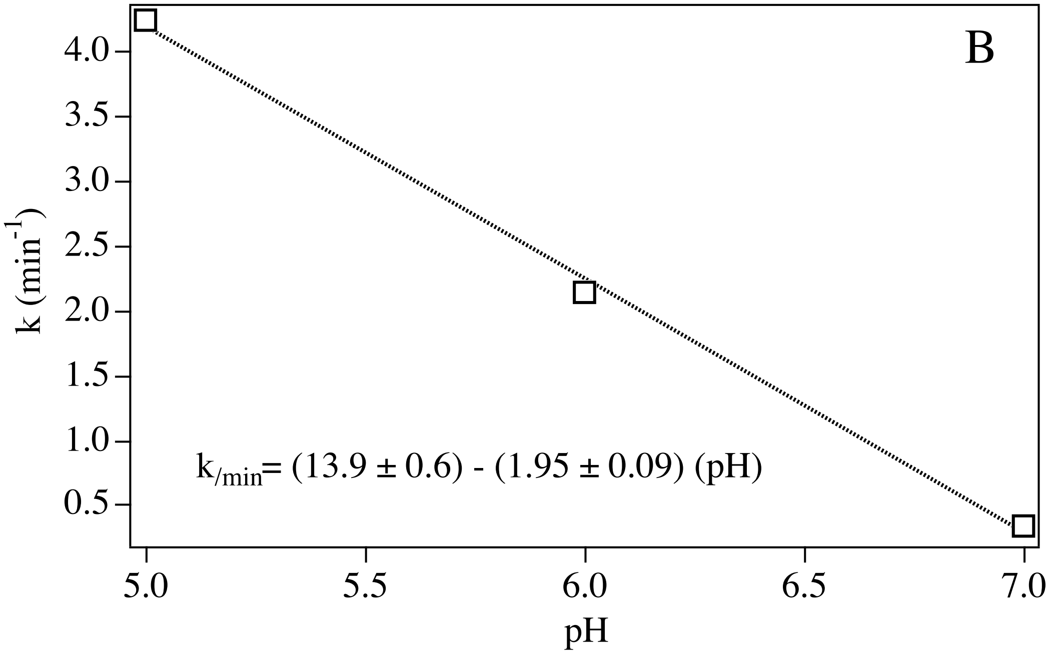


Figure 6.2. Dependence of MTBE degradation on initial pH.
A. Disappearance of MTBE under CDHP conditions at different pH values (Initial concentrations: H_2O_2, 7000 mg/L; $FeSO_4$, 500 mg/L; MTBE 100 mg/L). B. Rate of disappearance of MTBE vs pH for CDHP conditions.

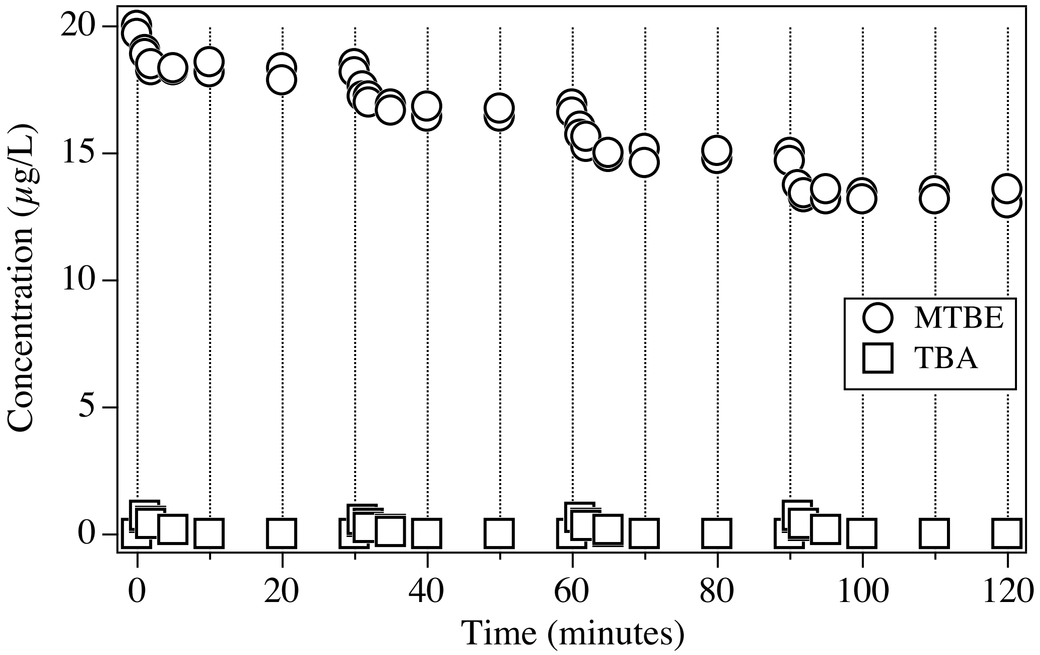


Figure 6.3. MTBE degradation under soil CDHP conditions.
Disappearance of MTBE under soil CDHP conditions in batch experiment containing 20 μg/L MTBE and 0.5g of Milford sediment (initial pH adjusted to pH 7 with NaOH). The tubes received subsequent additions of 40 μg/L H_2O_2 in 30 minute intervals.

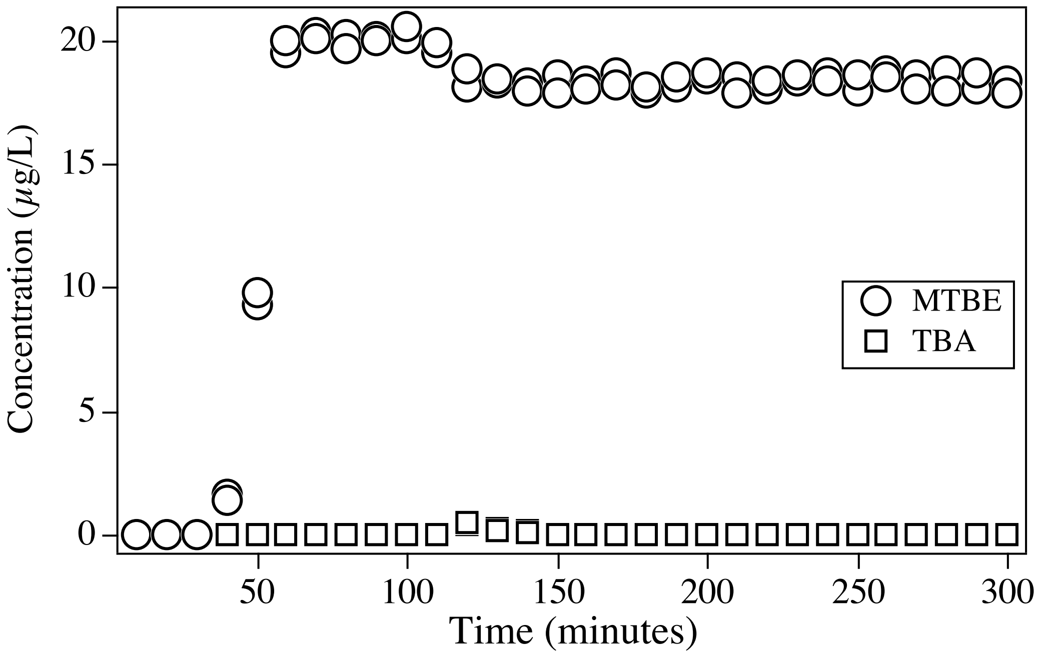


Figure 6.4. Degradation of MTBE during column infiltration.
Disappearance of MTBE and its transient degradation product TBA under soil CDHP conditions in columns packed with Milford sediment. The initial pH was adjusted to pH = 7 with NaOH. The columns received influents of 20 μg/L MTBE for one hour, and were then switched to influents containing 20 μg/L MTBE amended with 40 μg/L H_2O_2.

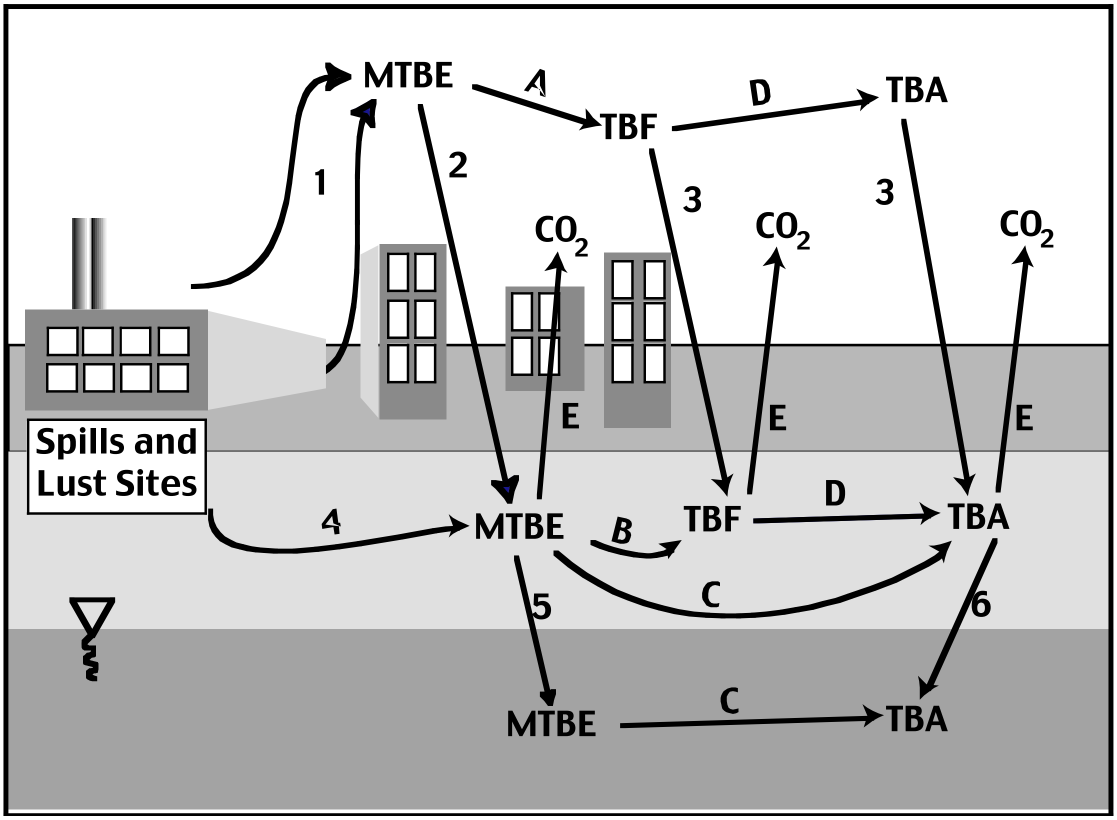


Figure 6.5. Chemical transformations and phase transfer processes for MTBE. Summary of chemical transformation pathways (designated by letters) and phase transfer processes (designated by numbers) for MTBE. Analogous transformations can be expected for other alkyl ethers used as gasoline oxygenates (e.g., ETBE and TAME). TBA is subject to further biodegradation to acetone, isopropanol, formate, and ultimately CO_2. (adapted from and described more fully in Chapter 3 and [130]).

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Appendix 1: List of Publications From This Work

1. Schirmer M., B. J. Butler, C. D. Church, J. F. Barker, and N. Nadarajah. 2003. Laboratory evidence of MTBE biodegradation in Borden aquifer material. Journal of Contaminant Hydrology 60(3-4): 229-249.

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