

UNIVERSITY OF MISSOURI-ROLLA
ENVIRONMENTAL RESEARCH CENTER
DEPARTMENT OF CIVIL ENGINEERING

FINAL REPORT

**COMPARATIVE TREATMENT STUDY OF
MTBE AND ALTERNATIVE
FUEL OXYGENATES**

Submitted to

Mr. Jerry Lane

*Director, Public Drinking Water Program
Missouri Department of Natural Resources*

Ms. Carol Eighmey

*Executive Director
Missouri Petroleum Storage Tank Insurance Fund (PSTIF)*

Mr. Terry Timmons

*Chemical Monitoring Coordinator
Missouri Department of Natural Resources*

Mr. David Pate

*PSTIF Claims Manager for the Third Party Administrator
Williams & Company Consulting*

by

Craig D. Adams, Ph.D., P.E.

*Principal Investigator
Director, Environmental Research Center
University of Missouri-Rolla
220 Civil Engineering Bldg
Rolla, MO 65409
573-341-4041 adams@umr.edu*

Justin Sutherland, EIT

*Doctoral Candidate
University of Missouri-Rolla*

Jamshid Kekobad

*Masters Candidate
University of Missouri-Rolla*

December, 2002

REPORT ORGANIZATION

ACKNOWLEDGEMENTS

CHAPTER I–INTRODUCTION

CHAPTER II– COMPARATIVE TREATMENT OF MTBE AT PILOT SCALE

Chapter Summary

II-1. Introduction

II-2. Experimental

II-3. Results and Discussion

II-4.0 Conclusions

CHAPTER III– TREATMENT OF ALTERNATIVE OXYGENATE ETHERS AND ALCOHOLS

Chapter Summary

III-1. Introduction

III-2. Materials and Methods

III-3. Results and Discussion

III-4. Conclusions

III-5. Notation

III-6. References

CHAPTER IV–ANCILLARY STUDIES – ONGOING WORK

ACKNOWLEDGEMENTS

The fuel oxygenates pilot study was conducted for and jointly funded by the Missouri Department of Natural Resources (MDNR) and the Missouri Petroleum Storage Tank Insurance Fund (MPSTIF). The authors would like to thank Mr. Jerry Lane (Director of Public Drinking Water Div., MDNR), Mr. Terry Timmons (Chemical Monitoring Coordinator, MDNR), Mr. David Pate (Claims Manager: MPSTIF), and Ms. Carol Eighmey (Executive Director: MPSTIF) for their assistance throughout the study especially with respect to experimental design, and selection and coordination with study sites.

The authors would like to thank the Civil Engineering technical staff—Mr. Jeff Bradshaw, Mr. Steve Gabel, Mr. Bill Frederickson, and Mr. Gary Abbott—for their assistance in constructing the pilot-plant trailer and treatment processes. We would also like to thank the undergraduate students—Allison Ludlow and Valerie Metroff—for their assistance in conducting this research.



Figure A. Staff and students responsible for building mobile water treatment pilot plant. (Mr. Steve Gable, CPT R. Jacob Emerson, and CPT David Acker not shown.)

I. INTRODUCTION

I-1 – Overview

Methyl-*t*-butyl (MTBE) is commonly used as a fuel oxygenating agent in gasoline in Missouri and elsewhere. In groundwater, MTBE is particularly difficult to treat due to its high water solubility and low volatility. The most effective treatment processes include air stripping, carbon adsorption, hydrogen peroxide/ozone advanced oxidation, and hydrogen peroxide/UV advanced oxidation. Each of these processes can be significantly affected by water quality parameters (e.g., organic carbon, alkalinity, etc.) and process conditions (e.g., treatment flowrate, etc.).

The purpose of this study was to compare in pilot-scale processes each of the aforementioned treatment processes for a variety of treatment conditions. Specifically, pilot testing was used to develop key design parameters which were in turn used to calculate estimated treatment costs. These tests were conducted in five groundwaters with widely varying water quality characteristics. The experiments and results for treatment of MTBE by air stripping, carbon adsorption and advanced oxidation treatment are presented in Chapter II.

A second purpose of this study was to compare the treatability and associated costs of treating alternative fuel oxygenating agents that are currently used (e.g., ethanol and *t*-amyl methyl ether (TAME)) or are available to the petroleum industry (e.g., ethyl-*t*-butyl ether, diisopropyl ether (DIPE), and *t*-butyl alcohol (TBA)). The experiments and results for treatment of alternative fuel oxygenating agents are presented in Chapter III.

Ancillary studies pertinent to this core work on MTBE and alternative fuel oxygenating agents is still ongoing. While this work is funded internally within UMR, the results provide insight into the advanced oxidation processes and will be provided to MDNR and MPSTIF once completed this year.

I-2 – Mobile Water Treatment Pilot Plant

A mobile water treatment pilot plant was designed and constructed to conduct this research (Figures I-1 to I-6). The pilot plant included equipment for UV/H₂O₂ and O₃/H₂O₂ AOPs in addition to air stripping, carbon adsorption, reverse osmosis and laboratory facilities. This equipment is discussed in more detail in Chapter II.



Figure I-1. Mobile water treatment pilot plant in transit.



Figure I-2. Students at work in pilot plant.



Figure I-3. Interior of pilot plant.



Figure I-4. Rear of pilot plant.



Figure I -5. Unit operations in pilot plant.



Figure I -6. Mobile water treatment plant on site.

Chapter II.

Comparative Treatment of MTBE at Pilot Scale

Chapter Summary

An investigation was made of the treatability of methyl *tert*-butyl ether (MTBE) in five groundwaters with highly varied water quality characteristics. Air stripping, granular (GAC) activated carbon adsorption, and the O₃/H₂O₂ and UV/H₂O₂ advanced oxidation processes were compared in a mobile water treatment pilot plant under a variety of process conditions. Air stripping was shown to have the lower unit treatment costs for higher flowrates (i.e. 3800 L/min), although relatively tall towers were required for greater treatment requirements. At low flowrates (i.e. 38 L/min), advanced oxidation provided the lowest treatment costs for four of five waters (but was ineffective for a high COD water). Both the O₃/H₂O₂ and UV/H₂O₂ processes were more efficient at pH 7 versus 9 due in part to increased scavenging at higher pH. GAC was effective at most conditions, although it was also the most costly alternative for most waters. The results of this study can help provide specific guidance into process selection for treating MTBE in contaminated groundwaters.

II-1. Background

The Clean Air Act Amendments of 1990 mandated that fuel oxygenates be used in gasoline to reduce carbon monoxide emissions in non-attainment regions across the United States [1]. Methyl *tert*-butyl ether (MTBE) is the most commonly used fuel oxygenate currently in use with 70 percent of all gasoline in the U.S. containing MTBE in 1997 [2]. This widespread use has led to MTBE being frequently detected in groundwater across the United States with contamination occurring from both point- (e.g., leaking underground storage tanks, spills, etc.) and non-point (e.g., urban runoff, water craft, etc.) sources [3, 4].

MTBE is mobile and persistent in the environment due to its high water solubility (43,000 – 54,300 mg/L) [5], low Henry's law constant (0.023-0.12; dimensionless) [5], and relative biorecalcitrance under common conditions [3]. These same properties make MTBE relatively difficult and expensive to treat.

The most common treatment processes for MTBE include air stripping, granular activated carbon (GAC) adsorption, and advanced oxidation processes in addition to soil vapor extraction. The effectiveness and associated costs of each of these processes can be significantly affected by both water quality characteristics (e.g., organic carbon, alkalinity, etc.) and process parameters (e.g., design flowrate, treatment objective, etc.) [6, 7, 8, 9, 10, 11, 12]. Several studies have looked at individual treatment processes, treatment of single groundwaters or drinking waters, or used design model application [10, 11, 12]. Few studies, however, have looked at each of these key treatment processes in pilot-scale processes for a set of groundwaters with widely varying characteristics.

In this study, the treatment of MTBE was examined for five groundwaters from across Missouri with highly varied water characteristics. Key design parameters were determined from pilot experiments which were in turn used to estimate treatment costs for a variety of process conditions and treatment objectives. Process comparison based on technical and unit treatment costs for all four processes are included within this paper.

II-2. Materials and Methods

2.1 Materials

All chemicals used were at least reagent grade. Hydrogen peroxide (30% solution) was certified ACS grade and used as received from Fisher Scientific (Pittsburgh, PA). Two activated carbons were examined in this study. Calgon F-400 is a bituminous-coal-based carbon commonly used for drinking water treatment. The second GAC, Calgon F-600, is manufactured from “superior” bituminous coal and is designed to enhance removal of trace level organics (e.g., MTBE) from water [13].

To examine the effects of water quality on the effectiveness and associated costs for treating MTBE in groundwater, five different groundwaters from sites in Missouri with varying characteristics were included in this study (designated Sites A – E) (Table II-1). These waters were all used as pumped from the ground except for site A which was fortified with MTBE.

Table II-1. Chemical characteristics of groundwaters included in study.

	Groundwater Site				
	A	B	C	D	E
Total alkalinity (mg/L as CaCO ₃)	214	152	432	390	106
pH	7.0	7.1	7.6	7.7	7.3
Total Hardness (mg/L as CaCO ₃)	267	238	408	259	140
Ca Hardness (mg/L as CaCO ₃)	112	168	166	214	94
Mg Hardness (mg/L as CaCO ₃)*	156	70	242	45	46
Fe(II) (mg/L Fe (II))	0.01	0.01	0.01	0.00	0.01
Total (mg/L Fe)	0.09	0.02	0.05	0.01	0.15
NH ₃ (mg/L NH ₃)	0.00	0.00	0.00	0.00	0.03
NO ₂ ⁻ (mg/L NO ₂ ⁻)	0.00	0.05	0.00	0.00	0.01
NO ₃ ⁻ (mg/L NO ₃ ⁻)	0.40	2.50	0.30	0.30	0.40
Turbidity (NTU)	0.23	0.47	1.11	0.31	1.73
TDS (ppm)	250	273	424	298	169
COD (mg/L O ₂) [†]	1	29	61	5	5
Influent MTBE (mg/L)	5.03-5.31 [‡] (spiked)	0.963-1.26	0.023-0.029	0.198-0.224	0.033-0.039
Influent BTEX (mg/L)	<0.0005	<0.0005	1.28-1.86	0.012-0.115	0.013-0.019

* by difference

† COD for Site A waters was non-detect. COD was set to the MDL of 1 mg/L for calculational purposes.

‡ Influent MTBE was non-detect in unspiked sample.

2.2 Mobile Water Treatment Pilot Plant

A mobile water treatment pilot plant was constructed for this project enclosed in a 2.2 x 5 m (internal dimension) trailer that contained an externally-mounted packed-tower for air stripping, activated carbon adsorption (via rapid small-scale column tests), and UV/H₂O₂ and O₃/H₂O₂ advanced oxidation processes (AOP) systems. Additionally, the trailer contained analytical lab facilities, a computer for data recording and analysis, refrigeration for sample storage, and a reverse osmosis system. The trailer had heating and cooling to allow operation in any season.

2.3 Air Stripping

Packed towers are commonly used in groundwater treatment for stripping volatile organic chemicals (VOCs), ammonia (NH₃), hydrogen sulfide (H₂S), and carbon dioxide (CO₂) from water. Mass transfer in a packed tower can be modeled by a mass balance on the liquid side of the gas-liquid interface using the equation:

$$\frac{dc}{dt} = K_L a \cdot (c_t - c_s)$$

where $K_L a$ is the overall mass transfer coefficient (s⁻¹), t is time (s), c_t is the bulk liquid concentration (M) at time, and c_s is the liquid saturation concentration (M) in equilibrium with the gas phase. The $K_L a$ parameter incorporates chemical properties (e.g., Henry's constant, solubility, and diffusivity), properties of the packed tower (e.g., interfacial area, and liquid and gas loading), and the properties of the liquid being decontaminated (e.g., temperature and quality of liquid). While estimates of the $K_L a$ can be made using correlations [14, 15, 16, 17], experimentally derived $K_L a$ from pilot plant data allow better parameter estimation, especially for chemically complex groundwaters.

The insulated packed tower was 0.30-m diameter, contained 2.9-m of Jaeger 2.54-cm polypropylene Tri-Pack (Jaeger Products, Inc.; Houston, TX), and was operated in countercurrent mode using a method described by Hand *et al.* [18] (Figure II-1). The tower was a forced draft system with air blown into the tower at up to 0.033 m³/s with a 0.75 kW DR404 Regenerative Blower (Ametek Rotron TMD, Saugerties, NY). Additional photos of the packed tower systems are shown in Figures II-2 to II-5.

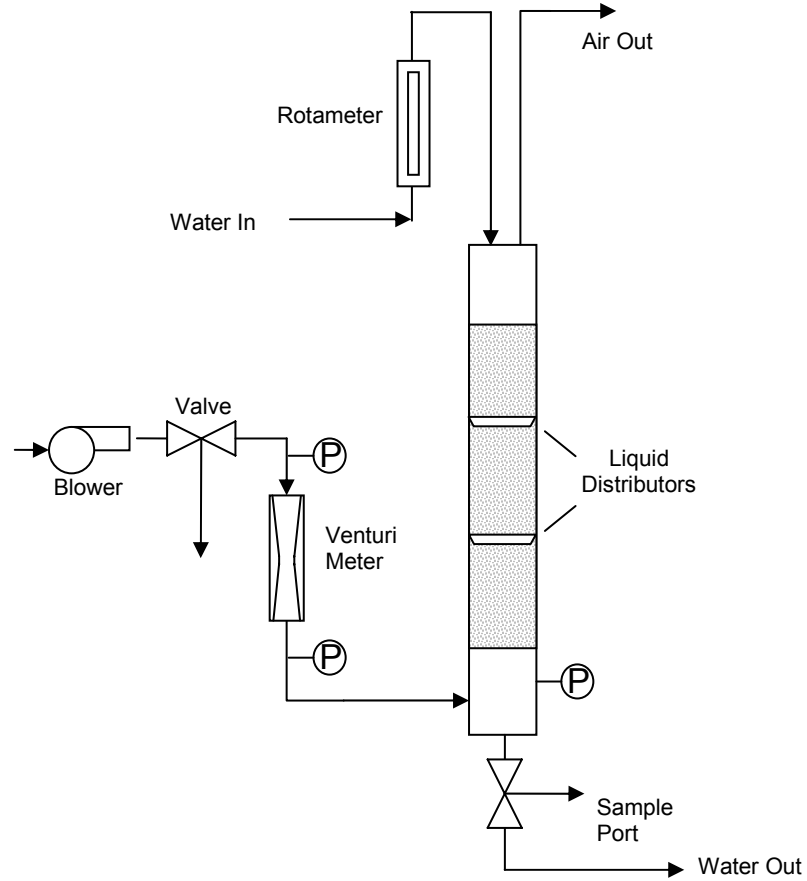


Figure II-1. Schematic diagram of packed tower system used in treatment study.



Figure II-2. Packed tower system being set up at site.



Figure II-3. Blower system for packed tower.



Figure II-4. Air and water connections at base of packed tower.



Figure II-5. Packed tower mounted on trailer.

2.4 Activated Carbon Adsorption

The rapid small scale column test (RSSCT) methodology was developed by Crittenden *et al.* [19] as a means to estimate the performance of large GAC contactors with a small-scale test. Groundwater containing MTBE was pumped through a pulse dampener to two or three glass columns in series (30×1.1-cm I.D.; Ace Glass) using 0.32-cm stainless-steel tubing or fluorocarbon tubing. Samples were periodically collected from the effluent of each column for analysis. Computational adjustment in the volume fed to the second (and third) columns was made to account for the amount of water collected from preceding columns. The breakthrough curves for MTBE for each column in series overlay each other when plotted versus bed-volumes, which checked that premature exhaustion or the preloading effect was not significant [20].

While the basic implementation of the RSSCT is fairly straightforward, grinding and sieving for a specific size fraction is an important aspect of conducting the tests. Ultimately a dry blending technique was utilized for sizing the carbon using a blender and small blender beaker. The GAC was ground using 25 second cycles. After each grinding cycle, the GAC was sized with a set of sieves, specifically 80, 100, 120, 140, 200, and 325 mesh. Any GAC retained on the top sieve (80 mesh) was reblended and resized. Carbon was ground for the RSSCT experiments using a dry blend technique detailed elsewhere [21]. The columns contained 3.0 or 5.8 g of either pulverized Calgon F-400 or F-600 GAC sieved to provide a 80×140-mesh fraction (0.18×0.11 mm). The water temperature was held at 21.5(±2)°C during the experiments. The columns were loaded at a flowrate of 7 mL/min (4.4 m/hr). Photos of the RSSCT system are shown in Figures II-6 to II-8.

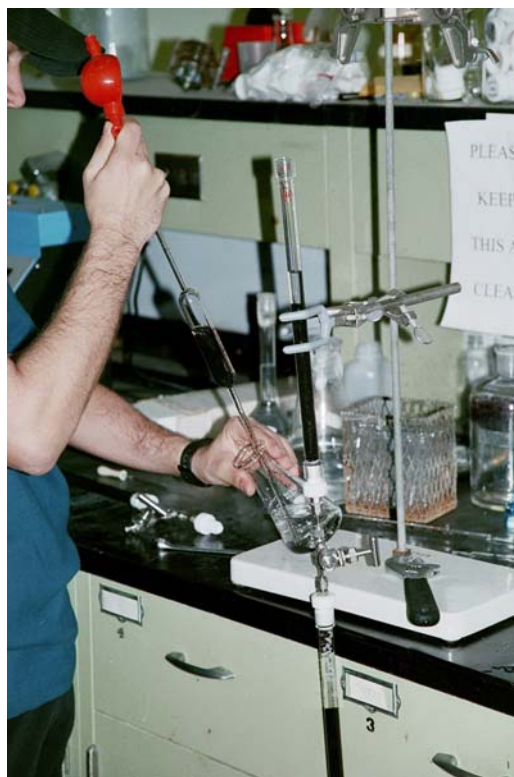


Figure II-6. Columns being loaded with ground and sieved GAC.



Figure II-7. Two RSSCT systems set up with two columns each in series.



Figure II-8. Acquiring a sample from top column during experiment.

2.5 UV/Peroxide AOP

The UV/H₂O₂ system was continuous flow with treatment rates maintained between 3.8 – 7.6 L/min. The system used a 1-kW medium-pressure, mercury vapor arc lamp

(Hanovia UR, #C002716-001) controlled by an ARC Power/Control Cabinet (Aquionics) (Figure II-9 and II-10). The reactor was a 0.050-m long by 0.015-m I.D. 316L passivated stainless steel chamber (Aquionics Model AMD150B1/1P) with an annular volume of 8.7 L. Hydrogen peroxide, sodium hydroxide, and MTBE were metered into the system as necessary with Masterflex L/S positive displacement (peristaltic) pumps.

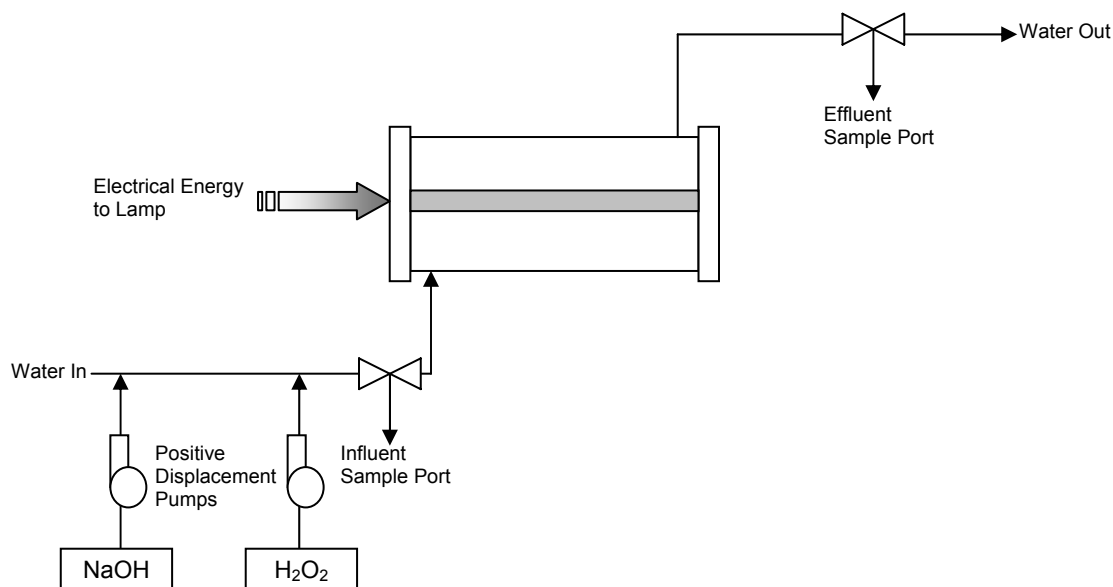


Figure II-9. Schematic of the UV/H₂O₂ system housed in the mobile water treatment pilot plant.



Figure II-10. 1.0 kW-UV reactor.

2.6 Ozone/peroxide AOP

The O_3/H_2O_2 system was continuous plug-flow configuration with treatment rates maintained at 3.8 L/min using centrifugal pumps (Figure II-11 and II-12). Oxygen for the ozone generator was produced with an oxygen generator (AirSep AS-12). Ozone was generated in an Ozat-0 ozone generator (Ozonia Model CF-0B) and was introduced into the system with an in-line Venturi injector system (Mazzei Model 484). The rate of ozone injection was controlled using a mass flow controller (Tylan DFC2900 with RO-28 readout). Gas-phase ozone concentrations were monitored using a PCI HC-12 UV-absorbance-based ozone monitor. Hydrogen peroxide, sodium hydroxide, and MTBE were metered into the system with Masterflex L/S peristaltic pumps. Ozone gas mass transfer to solution, excess entrained gas removal, and offgas destruction was achieved using a compact injection, centrifugal degas system with thermal-catalytic ozone destruct process system (GDT DS-100-WM).

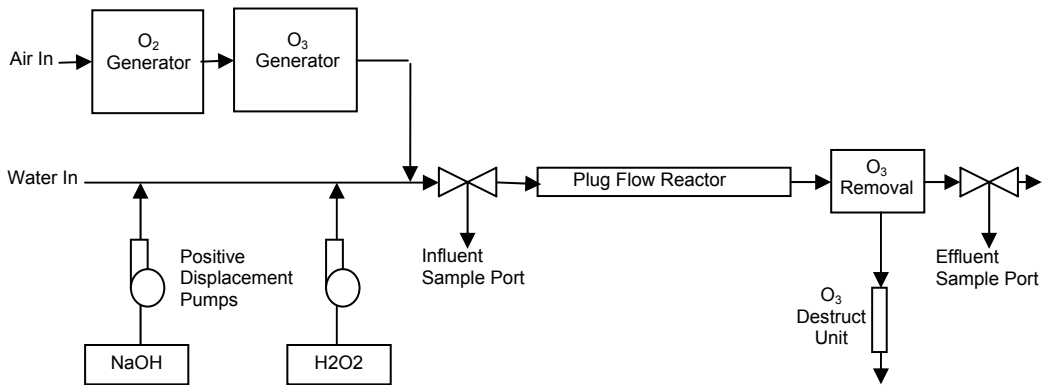


Figure II-11. Schematic of the O₃/H₂O₂ system housed in the mobile water treatment pilot plant.



Figure II-12. Ozone/peroxide advanced oxidation process.

2.5 Methods

Analysis of MTBE as well as benzene, toluene, ethylbenzene and *o*-, *m*-, and *p*-xylene (BTEX) was performed using an Agilent 6890 gas chromatograph/mass spectrometer (GC/MS) system with an 5973 mass selective detector and a DB-624 column (J&W Scientific; 25 m × 0.25 mm, 0.25 μm film thickness) (Figure II-13). Sample concentration/injection utilized a purge-and-trap system (Tekmar Dohrmann 3100 Sample Concentrator). When BTEX were not present in a source water, the column conditions were: 40°C for 2 minutes, ramp to 85°C at 10°C/min, and 85°C for 1 minute. When BTEX were present in a source water, the column conditions were: 40°C for 2 minutes, ramp to 180°C at 10°C/min, and 180°C for 1 minute.



Figure II-13. GC/MS used in study operated by Mr. Justin Sutherland.

pH was measured using a Corning 400 meter and combination probe. Hach spectrophotometric methods were used with a Hach DR 2010 spectrophotometer to measure free chlorine (Method 8021/DPD), total chlorine (Method 8167/DPD), monochloramine and free ammonia (Method 10045), nitrate (Method 8171), nitrite (Method 8507), ferrous iron (Method 8146), total iron (Method 8112/TPTZ), and chemical oxygen demand (COD) (Method 8000) with low range COD digestion reagent vials. Titrametric methods using a Hach digital

titrator were used to measure total hardness (Method 8213), calcium hardness (Method 8204), and alkalinity (Method 8203).

II-3. Experimental Results and Analysis

3.1 Air Stripping

Packed tower stripping experiments were conducted in duplicate at $20(\pm 1)^{\circ}\text{C}$ for each site water with a liquid loading rate of 0.25 L/s and a gas-to-liquid ratios (G/L; air-to-water) of 75:1, 100:1, and 150:1 (v/v). From the observed MTBE removal, $K_{L}a$'s were determined for MTBE stripping from each groundwater. In this experiment, low mass transfer coefficients were observed for each groundwater at each flowrate due to a low Henry's constant and high water solubility of MTBE. For each groundwater, greater G/L ratios ($\alpha=0.05$) correlated with increased mass transfer (Table II-2). No significant correlation ($\alpha=0.05$) was observed between observed $K_{L}a$ at a given G/L and COD, influent MTBE, influent BTEX, or alkalinity. It should be noted, however, that process temperature would be expected to have a significant effect with lower removal efficiency resulting from lower process temperature.

Onda *et al.* [16] discussed the relationship between $K_{L}a$ and system parameters including the observation that as the wetted surface area in the column increases, mass transfer coefficient ($K_{L}a$) also increases. Factors that can increase the wetted surface area (and concurrent increase in $K_{L}a$) within a column include reduction in surface tension, viscosity, and density. Thus, because certain natural or synthetic organic surfactants can have the effect of lowering surface tension, they may also enhance mass transfer. Alternatively, it is well known that surfactant accumulation can also depress mass transfer coefficients by congregation at and stabilization of the gas-liquid interface (e.g., Wagner and Popel, 1996). Determination of the detailed effects of system parameters was not possible in this pilot study.

These results indicate that MTBE removal in a packed tower is relatively independent of COD, MTBE concentrations, BTEX concentration, and alkalinity. It should be noted, however, that process temperature would be expected to have a significant effect with lower

removal efficiency resulting from lower process temperature. Furthermore, fouling of the packing is a concern especially for groundwaters that contain significant ferrous iron (which is oxidized to ferric hydroxide precipitate), high hardness (which leads to carbonate scaling as carbon dioxide is stripped), or nutrients (which may lead to biofouling).

Table II-2. Treatment costs for air stripping of each groundwater as function of air/water (G/L) ratio and flowrate for low removal percentage (100→20 ppb) and high removal percentage (1000→5 ppb)

Site	Flow		C_{in} (ug/L)	C_{eff} (ug/L)	Removal (%)	Tower Height (m)	Unit Cost (\$/1000 L)
	G/L	(Lpm)					
A	150	38	100	20	80	2.5	1.5
A	150	38	1000	5	99.5	9.2	1.7
A	75	38	100	20	80	5.4	1.6
A	75	38	1,000	5	99.5	23.9	2.2
A	150	3800	100	20	80	2.5	0.1
A	150	3800	1000	5	99.5	7.9	0.2
A	75	3800	100	20	80	5.4	0.1
A	75	3800	1,000	5	99.5	23.9	0.3
B	150	38	100	20	80	2.0	1.4
B	150	38	1,000	5	99.5	7.3	1.6
B	75	38	100	20	80	3.8	1.5
B	75	38	1,000	5	99.5	16.6	1.9
B	150	3800	100	20	80	2.0	0.1
B	150	3800	1,000	5	99.5	7.3	0.2
B	75	3800	100	20	80	3.8	0.1
B	75	3800	1,000	5	99.5	16.6	0.3
C	150	38	100	20	80	2.0	1.4
C	150	38	1,000	5	99.5	7.4	1.6
C	75	38	100	20	80	4.1	1.5
C	75	38	1,000	5	99.5	18.2	2.0
C	150	3800	100	20	80	2.0	0.1
C	150	3800	1,000	5	99.5	7.4	0.2
C	75	3800	100	20	80	4.1	0.1
C	75	3800	1,000	5	99.5	18.2	0.3
D	150	38	100	20	80	2.0	1.5
D	150	38	1,000	5	99.5	7.4	1.6
D	75	38	100	20	80	3.0	1.5
D	75	38	1,000	5	99.5	11.2	1.8
D	150	3800	100	20	80	2.0	0.1
D	150	3800	1,000	5	99.5	7.4	0.2
D	75	3800	100	20	80	3.0	0.1
D	75	3800	1,000	5	99.5	11.2	0.2
E	150	38	100	20	80	2.0	1.5
E	150	38	1,000	5	99.5	7.4	1.6
E	75	38	100	20	80	3.2	1.5
E	75	38	1,000	5	99.5	11.8	1.8
E	150	3800	100	20	80	2.0	0.1
E	150	3800	1,000	5	99.5	7.4	0.2
E	75	3800	100	20	80	3.2	0.1
E	75	3800	1,000	5	99.5	11.8	0.2

To estimate costs for the packed tower option, a cost ratio (\$/m of tower height) for the packed tower was determined using the method described by Peters and Timmerhaus [22]. Multiplying the height by the cost ratio for a packed tower, the cost of the tower and ancillary equipment were determined in 1979 dollars, and adjusted to 2001 values using Marshall and Swift's Equipment Cost Index [23,24]. The total capital cost of a packed tower system was calculated taking into account additional costs (piping, electrical, site work, engineering costs, contractor fees, etc) as outlined by Keller *et al* [25]. The total capital cost was depreciated over a 10-year period at a rate of 4 percent.

The packed tower diameter was estimated by dividing the desired liquid flowrate by the appropriate liquid loading rate. The packed tower height was estimated by calculation of the height of a transfer unit (HTU) where:

$$\text{HTU} = \frac{L}{K_L a}$$

and the required number of transfer units (NTU) where:

$$\text{NTU} = \frac{R}{R-1} \ln \left(\frac{(c_i/c_e)(R-1)+1}{R} \right)$$

and

$$R = \frac{H \cdot G}{L}$$

and R is the stripping factor (dimensionless), G is the gas loading rate ($L^3 \text{ air}/L^2/T$), H is Henry's constant, and c_i and c_e are the initial and final contaminant concentrations, respectively [26].

For purposes of analysis, the required tower heights and overall (capital plus O&M) unit treatment costs (\$/1000 L) were determined for each groundwater assuming a lower (i.e., $100 \rightarrow 20 \mu\text{g}/L$, or 80 percent) and higher (i.e., $1000 \rightarrow 5 \mu\text{g}/L$, or 99.5 percent) MTBE removal requirement.

The results showed that required packing heights for a 75:1 G/L ratio were 1.5 to 3.0 times greater than for a 150:1 G/L ratio (Table II-2). For equivalent MTBE removals, the

75:1 G/L ratio resulted in higher unit treatment costs (\$/1000 L) by a factor of from 1.03 to 2.1. Thus, the higher G/L (150:1) resulted in both shorter towers and lower estimated treatment costs. Required MTBE removals had a significant effect on tower height and estimated costs. Tower heights for 99.5 percent MTBE removals were estimated to be 3.2 to 4.4 times greater than for 80 percent removal (Table II-2). Unit treatment costs for 99.5 percent removal were from 1.2 to 2.5 times greater than for 80 percent removal. Therefore, it is clear the a packed tower design should take into account potential variability in influent MTBE and treatment objectives in terms of required effluent concentrations.

3.2 Carbon Adsorption

Using the RSSCT method, breakthrough curves were used to determine the breakthrough capacity ($C/C_0=0.05$) (mg MTBE / g carbon), ultimate capacity ($C/C_0=0.95$) (mg MTBE / g carbon), and carbon usage rates (CUR; g carbon / L water treated) for each groundwater for two different carbons—Calgon F-400 and F-600. Several specific observations were apparent from these experiments. For all groundwaters, the F-600 carbon had significantly greater breakthrough and ultimate capacities for MTBE than F-400 by a factor of from 1.5 to 2.2 times (Table II-3).

Table II-3. Capacity and carbon utilization rate results for five groundwaters with both Calgon F-400 and F-600 as function of flowrate. Required GAC dosages and costs for treatment of five groundwaters with Calgon F-400 and F-600.

Site	GAC	COD [†] (mg/L)	MTBE (mg/L)	BTEX [#] (mg/L)	Ult. Cap. (mg/g)	CUR (g/L)	Flow (Lpm)	Carb Cost (\$/1000 L) [‡]	Unit Cost (\$/1000 L) [‡]
A	F-400	1	5.03	0.0005	9.3	0.44	38	2.39	4.6
							3800	2.39	2.8
A	F-600	1	5.31	0.0005	19.94	0.26	38	1.54	3.4
							3800	1.54	1.8
B	F-400	29	0.963	0.0005	2.52	0.31	38	1.69	3.7
							3800	1.69	2.0
B	F-600	29	1.265	0.0005	5.52	0.15	38	1.32	3.3
							3800	1.32	1.6
C	F-400	61	0.029	1.284	0.11	0.26	38	1.17	3.2
							3800	1.17	1.3
C	F-600	61	0.023	1.86	0.17	0.24	38	0.78	4.1
							3800	0.78	1.4
D	F-400	5	0.198	0.012	0.86	0.16	38	1.02	3.2
							3800	1.02	1.3
D	F-600	5	0.224	0.115	1.9	0.08	38	0.68	2.7
							3800	0.68	0.9
E	F-400	4.5	0.033	0.013	0.25	0.11	38	0.58	3.7
							3800	0.58	1.1
E	F-600	4.5	0.039	0.019	0.46	0.05	38	0.49	3.1
							3800	0.49	0.8

[†] Total Soluble COD; COD of Site A water was non-detect and was set to the MDL of 1 mg/L for calculation

* M. Wt of toluene as basis.

[#] Non-detection listed at detection limit (0.0005 mg/L)

[‡] Ultimate capacity basis

The results indicated that there was a strong correlation between influent MTBE concentration and capacity on both F-400 ($r>0.99$) and F-600 ($r>0.99$) (Figures II-13). Because the carbon in a GAC column comes to approximate equilibrium with the influent stream, Figures 4a are essentially sorption isotherms. Thus, it is expected that low influent (equilibrium) concentrations should yield lower capacities than higher influent (equilibrium) concentrations (with other factors constant).

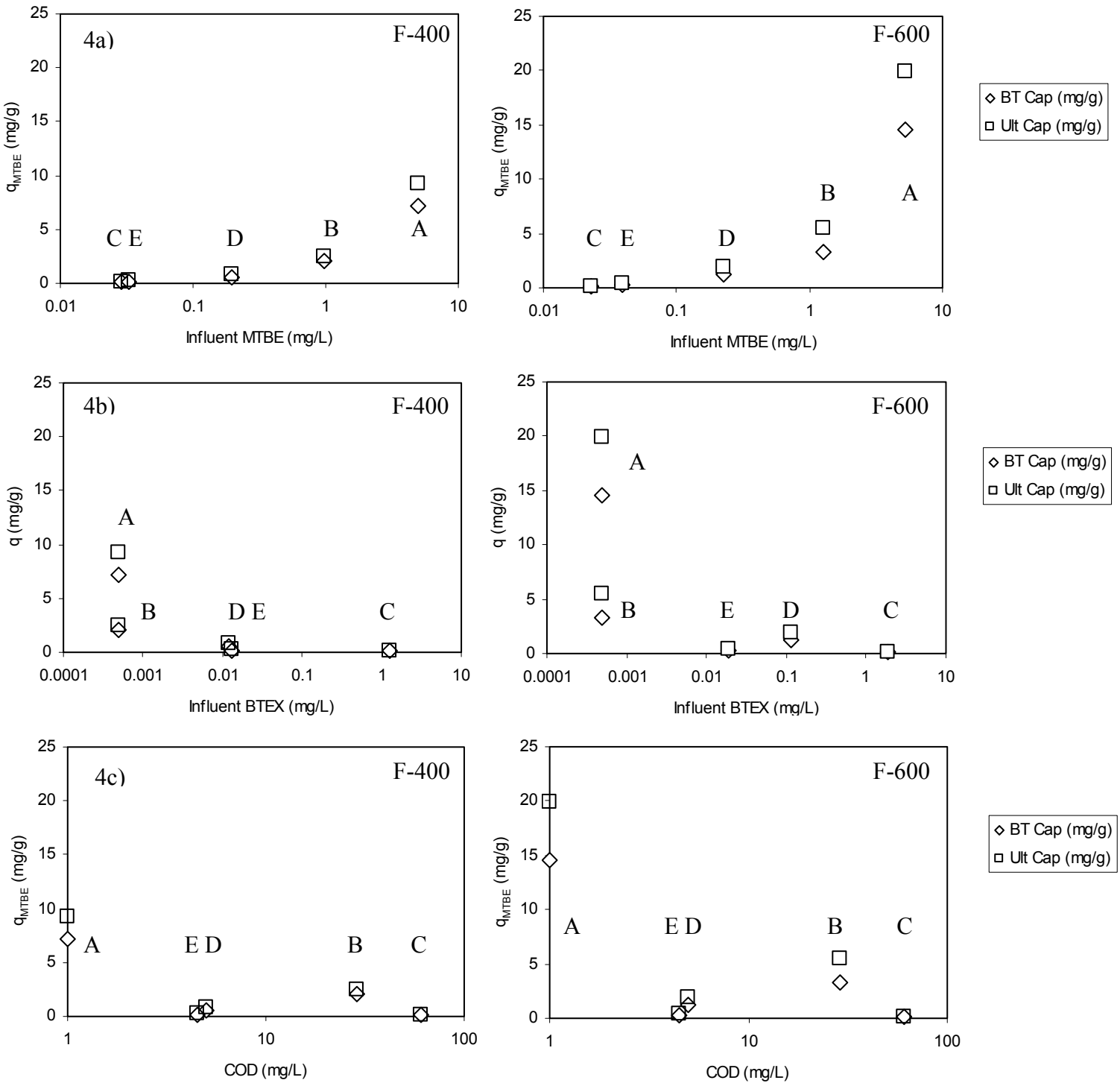


Figure II-13. GAC capacities for five groundwaters as a function of influent MTBE concentration, influent BTEX, BTEX/MTBE ratio, and COD (from top to bottom) for F-400 (left) and F-600 (right)

The RSSCT data showed that BTEX compounds were preferentially retained compared with MTBE as expected based on relative water solubility, K_{OW} values, and Freundlich coefficients [7, 27]. The result of this preferential adsorption of BTEX was to displace MTBE on the carbon thereby significantly reducing the capacity of the carbons for MTBE (Figure II-13b).

The results showed that there was no correlation between capacity and COD of ($\alpha=0.05$) (Table II-3, Figure II-14c). In all groundwaters, the COD attributable to BTEX was less than 1.1 percent of the total COD. Overall, these data suggest that GAC sorption capacities for MTBE is enhanced in situations where the MTBE concentration is relatively high (e.g., > 1 ppm) and competitive adsorption effects are low.

GAC costs were calculated based on carbon, O&M and capital costs. Carbon costs were calculated for each water and carbon based on experimentally determined capacity, the corresponding influent MTBE concentration, and carbon price (\$/kg) provided by the manufacturer (\$4.40/kg and \$6.72/kg for F-400 and F-600, respectively [28]). The results showed that carbon costs (\$/1000 L treated) were independent of assumed flowrate on a per volume basis. Capital costs for the carbon adsorber process were dependent on flowrate and were calculated based on equipment costs provided by the vendor [28] for design flows of 38 and 3800 L/min (and were optimized with respect to the number of units and the number of carbon changeouts per year). The transportation cost used to account for carbon change-out was \$1.25 per kg carbon [11] and was included as part of the operation and maintenance of the system. The total capital cost of a GAC system included the equipment cost and additional capital expenses outlined by Keller and coworkers [25] and was depreciated over a 10-year period at a rate of 4 percent.

A relatively narrow range of CUR were observed for a wide range of capacities and influent concentrations. This result is due the fact that higher capacities are achieved with higher influent concentrations (per a standard isotherm), but higher influent concentrations require a greater mass of MTBE to be removed (Table II-3). The associated carbon costs required to treat each groundwater ranged from \$0.58–2.39/1000 L for F-400 and \$0.49–1.54 /1000 L for F-600 (Table II-3). The treatment costs for the lesser expensive carbon (F-400) were greater than for F-600 (in all waters except Site C) due to the lower capacity of the F-

400. Although carbon costs are essentially independent of flowrate on a per volume basis (\$/1000 L), unit treatment costs were significantly higher for the low flow system (38 L/min) compared with the high flow system (3II-1300 L/min) by a factor of from 1.6 to 3.9.

3.3. UV/Peroxide AOP

The primary design parameter for UV/H₂O₂ systems is EE/O (kWh/1000 L/order), that is, the energy (kWh) required to reduce the concentration of a compound in 1000 L by an order a magnitude (i.e., 90 percent):

$$\text{UV Dose (kWh /1000 L)} = \text{EE/O} \cdot \log (C_i/C_e)$$

Thus, EE/O for each groundwater was determined by taking the inverse of the slope ((EE/O)⁻¹) of the plot of UV dose versus log (C_i/C_e) for a set of experiments at otherwise equivalent conditions [29]. The UV dose was varied generally to 2.2 or 4.4 kWh/1000 L by adjusting the influent flowrate to the process, that is:

$$\text{UV Dose(kWh/1000L)} = \frac{1000 \cdot \text{LampPower(kW)}}{\text{Flowrate(Lpm)} \cdot 60}$$

. pH was controlled to 7 and 9 (±0.1) in these experiments to examine the influence of pH on hydroxyl radical scavenging and overall process efficiency.

EE/O values for the suite of UV/H₂O₂ experiments ranged from 1.2 – 8.6 kWh/1000 L/order for 4 of the waters (and 13-247 kWh/1000 L/order for Site C water) (Table II-4). These values compare with “typical” EE/O values of 0.5 to 1.3 for BTEX, 2.6 to 7.9 for atrazine, and 0.5 to 1.6 kWh/1000 L/order for 1,4-dioxane [29]. Under only the most efficient conditions in the study did the EE/O values for UV/H₂O₂ treatment of MTBE fall within typical ranges for other groundwater contaminants. Thus, it is important to examine the factors that affect the process efficiency.

Table II-4. Influent concentrations, hydroxyl radical consumption, and EE/O results for UV/H₂O₂ process.

Site	COD [†] (mg/L)	MTBE+BTEX		Total BTEX (mg/L)	pH	Total H ₂ O ₂ (mg/L)	ALK (mg/L as CaCO ₃)	Percentage of OH radicals reacting						EE/O (kWh/1000 L/order)
		COD (%)	MTBE (mg/L)					MTBE	BTEX	H ₂ O ₃	HO ₂ ⁻	HCO ₃ ⁻	CO ₃ ²⁻	
A	1	85%	2.34	0.0005	7.0	25	214	41.7	0.0	27.4	0.5	29.7	0.7	1.4
	1	85%	2.34	0.0005	9.0	25	214	19.9	0.0	13.0	23.1	13.4	30.5	4.8
	1	85%	2.34	0.0005	7.0	50	214	32.6	0.0	42.8	0.8	23.2	0.5	1.2
	1	85%	2.34	0.0005	9.0	50	214	14.6	0.0	19.2	34.0	9.9	22.4	3.8
B	29	1%	0.963	0.0005	7.0	25	152	25.8	0.1	41.1	0.7	31.7	0.7	3.9
	29	1%	0.963	0.0005	9.0	25	152	9.2	0.0	29.5	26.1	10.8	24.4	8.2
	29	1%	0.963	0.0005	7.0	50	152	18.2	0.0	57.9	1.0	22.3	0.5	3.9
	29	1%	0.963	0.0005	9.0	50	152	7.3	0.0	23.4	41.4	8.5	19.4	5.5
C	61	1%	0.029	1.284	7.0	25	432	0.3	51.6	14.8	0.3	32.3	0.7	17.9
	61	1%	0.029	1.284	9.0	25	432	0.1	24.8	14.2	12.6	14.8	33.5	246.6
	61	1%	0.029	1.284	7.0	50	432	0.2	44.9	25.7	0.5	28.1	0.6	12.9
	61	1%	0.029	1.284	9.0	50	432	0.1	22.0	12.6	22.3	13.1	29.8	40.3
D	5	2%	0.198	0.012	7.0	25	390	4.0	1.0	31.2	0.6	61.8	1.4	3.0
	5	2%	0.198	0.012	9.0	25	390	1.3	0.3	19.8	17.6	18.7	42.3	8.6
	5	2%	0.198	0.012	7.0	50	390	3.1	0.8	47.4	0.8	46.9	1.1	2.1
	5	2%	0.198	0.012	9.0	50	390	1.1	0.3	16.9	29.9	15.9	36.0	5.4
E	4.5	0%	0.033	0.013	7.0	25	106	1.3	2.2	61.6	1.1	33.1	0.7	1.7
	4.5	0%	0.033	0.013	9.0	25	106	0.4	0.6	36.4	32.3	9.3	21.0	7.4
	4.5	0%	0.033	0.013	7.0	50	106	0.8	1.3	75.7	1.4	20.3	0.5	1.2
	4.5	0%	0.033	0.013	9.0	50	106	0.3	0.5	27.5	48.8	7.0	15.9	5.3

[†] Total Soluble COD, COD for Site A samples were non-detect and were set to the MDL of 1 mg/L for calculation purposes

^{*} M.Wt of toluene as basis.

[#] Non-detection listed at method detection limit (0.0005 mg/L)

- k_{MTBE} = 1.6(10⁹) Eibenberger (1980)
- k_{BTEX, ave} = 7.0(10⁹) calculated
- k_{benzene} = 7.8(10⁹) Buxton et al (1988)
- k_{toluene} = 5.1(10⁹) Wojnarovits and Foldiak (1990)
- k_{ethylbenzene} = 7.5(10⁹) Sehested and Holcman (1979)
- k_{p-xylene} = 7.0(10⁹) Sehested et al (1975)
- k_{H2O2} = 3.8(10⁷) Merenyi and Lind (1980)
- k_{HO2-} = 6.8(10⁹) Merenyi and Lind (1980)
- k_{bicarbonate} = 8.5(10⁶) Buxton et al (1988)
- k_{carbonate} = 3.9(10⁸) Buxton et al (1988)

In interpreting UV/H₂O₂ process efficiency, it is necessary to consider such important factors as the absorbance efficiency of applied UV by the H₂O₂ in solution, the fraction of generated hydroxyl radicals reacting with MTBE versus scavenging species, and the effect of pH on these processes. UV energy must first be absorbed by the H₂O₂ to allow the generation of •OH radicals via the reaction:



The fraction (f) of UV light absorbed by H₂O₂ in solution can be estimated by comparing the absorbance of H₂O₂ to the absorbance of the total solution, and integrating over the medium-pressure lamp's broad spectrum:

$$f_{\text{UV absorbed, H}_2\text{O}_2} = \int_{\lambda=200\text{nm}}^{280\text{nm}} \frac{\epsilon_{\lambda, \text{H}_2\text{O}_2} \cdot [\text{H}_2\text{O}_2]}{\sum \epsilon_{\lambda, i} \cdot [j]} \cong \sum_{\lambda=200\text{nm}}^{280\text{nm}} \frac{\epsilon_{\lambda, \text{H}_2\text{O}_2} \cdot [\text{H}_2\text{O}_2]}{\sum \epsilon_{\lambda, i} \cdot [j]}$$

where $\epsilon_{\lambda, j}$ is the molar absorptivity ($\text{M}^{-1}\text{cm}^{-1}$) of the j^{th} component, and brackets denote molar concentrations. Thus, from the known absorptivity of H₂O₂ and a measured background absorbance of the groundwater, the percentage of lamp energy absorbed by H₂O₂ for specific concentrations of H₂O₂ was estimated and plotted versus COD for each groundwater (Figure II-14). For the groundwaters in the study, greater COD concentrations were associated with greater absorbance in the UV spectrum which leads to decreased UV absorption efficiency by H₂O₂. Nonetheless, calculations indicated (not shown) that accounting for the UV absorption efficiency alone does not entirely explain the differences in the EE/O values observed for the different waters and process conditions (e.g., pH, H₂O₂ dosage, etc.). This leads to consideration of the reactions of •OH formed in solution.

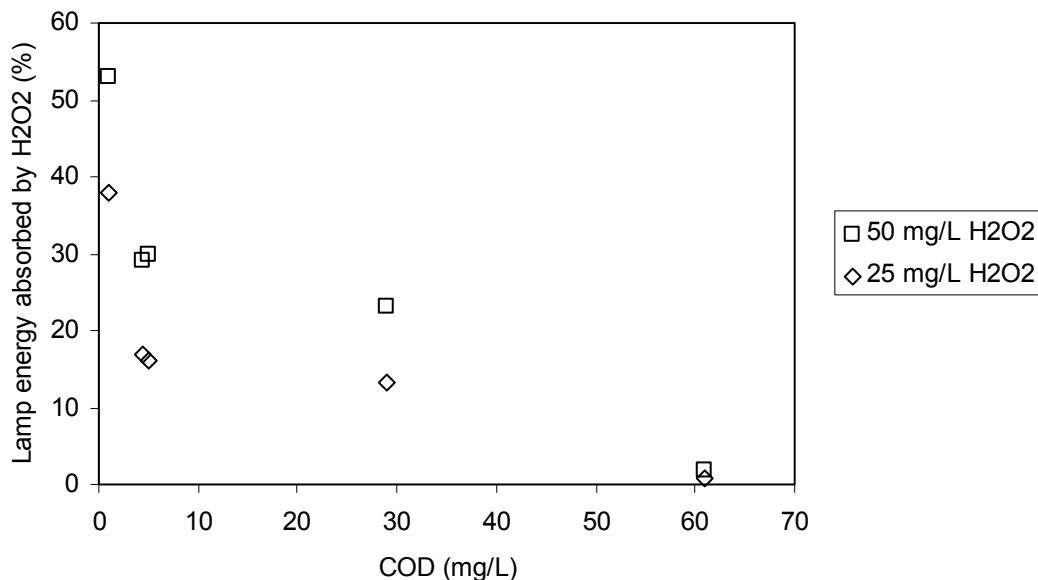


Figure II-14. Percent absorbance of H₂O₂ at 25 and 50 mg/L concentrations versus COD for the five study waters.

Once generated, hydroxyl radicals ($\bullet\text{OH}$) are free to react with the target species (i.e., MTBE) or may be scavenged by other constituents in the water. The fraction of $\bullet\text{OH}$ generated that reacts with compound “ij” can be estimated by:

$$f_{\bullet\text{OH},i} = \frac{k_{\bullet\text{OH},i} \cdot [\bullet\text{OH}] \cdot [i]}{\sum k_{\bullet\text{OH},j} \cdot [\bullet\text{OH}] \cdot [j]} = \frac{k_{\bullet\text{OH},i} \cdot [i]}{\sum k_{\bullet\text{OH},j} \cdot [j]}$$

where $k_{\bullet\text{OH},j}$ are second-order $\bullet\text{OH}$ rate constants for the j^{th} species ($\text{M}^{-1}\text{s}^{-1}$), and brackets denote molar concentrations. The percentage of $\bullet\text{OH}$ radicals reacting with each species in each groundwater was calculated and tabulated in Table II-4 including MTBE, BTEX, $\text{H}_2\text{O}_2/\text{HO}_2^-$, and $\text{HCO}_3^-/\text{CO}_3^{2-}$. (Scavenging by other constituents in solution (e.g., background COD) were neglected for this analysis and would further decrease the calculated percent of $\bullet\text{OH}$ reacting with MTBE.) The results show that $\bullet\text{OH}$ radical scavenging by BTEX, carbonate alkalinity, and peroxide itself can all be significant depending on the chemical makeup of a particular groundwater (Table II-4). Additionally, due to the pH-

dependent couples between $\text{H}_2\text{O}_2/\text{HO}_2^-$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$, pH exerted a strong effect on process efficiency (Table II-4). Overall, the effect of increasing pH from 7 to 9 was to decrease the fraction of $\bullet\text{OH}$ reacting with MTBE by a factor of from 2 to 3 (Table II-4). This loss in efficiency at increased pH was directly reflected in the much higher EE/O values at higher pH (Table II-5).

Table II-5. Treatment costs for MTBE removal in UV/H₂O₂ process at a H₂O₂ dose of 50 mg/L for both pH 7 and 9.

Site	pH	EE/O (kWh/1000L /order)	Flow (Lpm)	C _{inf} (ug/L)	C _{eff} (ug/L)	Unit Cost (\$/1000 L)
A	7	1.2	38	100	20	1.1
A	7	1.2	38	1,000	5	1.4
A	9	3.8	38	100	20	1.4
A	9	3.8	38	1,000	5	2.3
A	7	1.2	3800	100	20	0.2
A	7	1.2	3800	1,000	5	0.5
A	9	3.8	3800	100	20	0.5
A	9	3.8	3800	1,000	5	1.4
B	7	3.9	38	100	20	1.4
B	7	3.9	38	1,000	5	2.3
B	9	5.5	38	100	20	1.5
B	9	5.5	38	1,000	5	2.8
B	7	3.9	3800	100	20	0.5
B	7	3.9	3800	1,000	5	1.4
B	9	5.5	3800	100	20	0.7
B	9	5.5	3800	1,000	5	1.9
C	7	12.9	38	100	20	2.3
C	7	12.9	38	1,000	5	5.3
C	9	40.3	38	100	20	5.1
C	9	40.3	38	1,000	5	14.6
C	7	12.9	3800	100	20	1.4
C	7	12.9	3800	1,000	5	4.5
C	9	40.3	3800	100	20	4.2
C	9	40.3	3800	1,000	5	13.7
D	7	2.1	38	100	20	1.2
D	7	2.1	38	1,000	5	1.7
D	9	5.4	38	100	20	1.5
D	9	5.4	38	1,000	5	2.8
D	7	2.1	3800	100	20	0.3
D	7	2.1	3800	1,000	5	0.8
D	9	5.4	3800	100	20	0.7
D	9	5.4	3800	1,000	5	1.9
E	7	1.2	38	100	20	1.1
E	7	1.2	38	1,000	5	1.4
E	9	5.3	38	100	20	1.5
E	9	5.3	38	1,000	5	2.8
E	7	1.2	3800	100	20	0.2
E	7	1.2	3800	1,000	5	0.5
E	9	5.3	3800	100	20	0.6
E	9	5.3	3800	1,000	5	1.9

Treatment costs for the UV/H₂O₂ process were calculated based on estimated capital and operating costs. Equipment costs for an UV/H₂O₂ process were estimated as a function of the UV power required using the equations [29]:

$$\text{UV Power(kW)} = \frac{\text{EE/O} \cdot 60 \cdot \text{Flow(Lpm)} \cdot \log(C_i / C_e)}{1000}$$

and

$$\text{Equipment cost (\$)} = [0.9875 \cdot \text{UV Power (kW)} + 55] \cdot 1000 .$$

The total capital cost of a UV/H₂O₂ system was calculated taking into account additional costs as outlined by Keller and coworkers [25] and was depreciated over a 10-yr period at a rate of 4 percent. Operating costs were based on \$0.08/kWh for energy and \$1.58/kg for peroxide.

The treatment costs were tabulated in Table II-5 for each water tested assuming various flows, and influent and effluent MTBE concentrations. These treatment costs were in the range of from 0.2 to 2.8 \$/1000L treated for each study water with the exception of Site C due to its very low treatment efficiency. For the more efficient waters (i.e. lower EE/Os at Sites A, D and E), annualized capital costs were generally 70 percent of total unit costs for a 38 L/min system but only 20 percent for a 3,800 L/min system. Due to economy-of-scale with respect to capital costs, larger flow systems have lower unit treatment costs. For example, unit costs for treating lower EE/O waters (e.g., Sites A, D and E) at both pH 7 and 9 were significantly lower for higher flow systems (Table II-5).

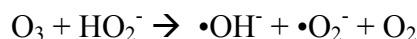
3.4 Ozone/Peroxide AOP

EE/O values were determined for the O₃/H₂O₂ process in a similar manner to the UV/H₂O₂ process except that the energy costs relate primarily to ozone rather than UV generation. Based on a generation efficiency of 150 g O₃/kWhr [30], the EE/O for the O₃/H₂O₂ process was determined by:

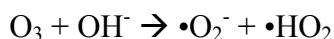
$$\text{EE/O} = \frac{\text{O}_3(\text{mg/L})}{150(\text{g/kWh}) \cdot \log(C_i / C_e)} = \frac{\text{Energy(kWh/1000L)}}{\log(C_i / C_e)}$$

EE/O values were determined for each study groundwater at both pH 7 and 9 with ozone dosages of 36, 71, and 141 mg/L. Peroxide was always applied at the stoichiometric dosage of 0.35 mg H₂O₂ per mg O₃.

In the O₃/H₂O₂ process, ozone decomposes to •OH radicals in an autodecomposition cycle involving various radical species including the •OH radical [31]. This ozone decomposition can be catalyzed by either the hydroperoxide ion (HO₂⁻; the conjugate base of H₂O₂) via:



or by the hydroxide ion (OH⁻) via:



[31]. At typical pH levels for groundwater treatment processes (e.g., pH<9), the peroxide-catalyzed reaction (Eq. 8) dominates [31]. The O₃/H₂O₂ process has an advantage over the UV/H₂O₂ process in that the UV absorbance of a water itself does not prevent energy input into the system. However, the generation of •OH in the O₃/H₂O₂ process is strongly affected by promoters and inhibitors, as well as by pH and alkalinity [32]. Additionally, stripping of volatile organic chemicals (VOCs) can occur upon ozone injection. This affect was experimentally determined to be negligible for MTBE in these experiments.

Calculated EE/O values for each water and condition are plotted in Figure 6 with the exception of Site C samples. Only negligible removal of MTBE was observed for the Site C experiments due presumably to very high radical scavenging, and hence, EE/Os were very high or incalculable. EE/Os were generally higher at higher pH (7 vs. 9) by a factor of from 2 to 5 (Table II-6 and Figure II-15). A primary reason for this lower efficiency at higher pH is that higher pH lead to greater scavenging of generated •OH radicals by CO₃²⁻ (vs. HCO₃⁻) and HO₂⁻ (vs. H₂O₂) as was discussed for the UV/H₂O₂ process above.

Table II-6. Treatment costs for MTBE removal in O₃/H₂O₂ process.

Site	pH	EE/O (kWh/1000 L/order)	Flow (Lpm)	C _{inf} (ug/L)	C _{eff} (ug/L)	Unit Cost (\$/1000 L)
A	7	1.5	38	100	20	0.8
A	7	1.5	38	1,000	5	1.1
A	9	6.4	38	100	20	1.2
A	9	6.4	38	1,000	5	2.4
A	7	1.5	3800	100	20	0.3
A	7	1.5	3800	1,000	5	0.5
A	9	6.4	3800	100	20	0.6
A	9	6.4	3800	1,000	5	1.8
B	7	1.5	38	100	20	0.8
B	7	1.5	38	1,000	5	1.1
B	9	6.6	38	100	20	1.2
B	9	6.6	38	1,000	5	2.5
B	7	1.5	3800	100	20	0.3
B	7	1.5	3800	1,000	5	0.5
B	9	6.6	3800	100	20	0.7
B	9	6.6	3800	1,000	5	1.9
C	No calculations due to lack of MTBE removal in process.					
D	7	2.1	38	100	20	0.9
D	7	2.1	38	1,000	5	1.3
D	9	8.2	38	100	20	1.4
D	9	8.2	38	1,000	5	2.9
D	7	2.1	3800	100	20	0.3
D	7	2.1	3800	1,000	5	0.7
D	9	8.2	3800	100	20	0.8
D	9	8.2	3800	1,000	5	2.3
E	7	1.3	38	100	20	0.8
E	7	1.3	38	1,000	5	1.1
E	9	3.6	38	100	20	1.0
E	9	3.6	38	1,000	5	1.7
E	7	1.3	3800	100	20	0.3
E	7	1.3	3800	1,000	5	0.5
E	9	3.6	3800	100	20	0.4
E	9	3.6	3800	1,000	5	1.1

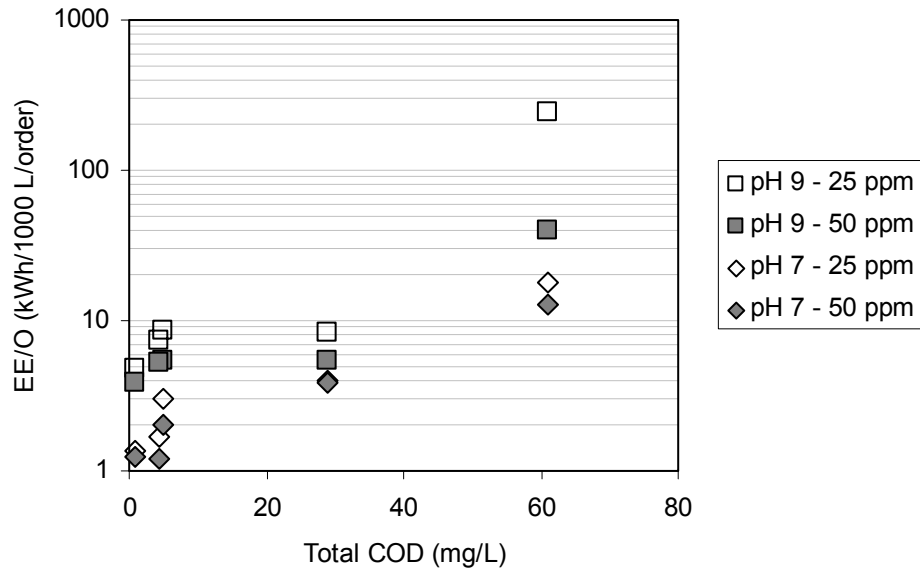


Figure II-15. Effect of COD and pH on EE/O for MTBE removal in O₃/H₂O₂ process.

Oxidant dosage had a significant effect on process efficiency. Specifically, higher EE/O values (lower efficiency) were observed at greater peroxide concentrations by an average of 40 percent (Figure II-15). This may be caused in part by increased scavenging by the oxidant itself at higher dosages. It is possible that a more optimum peroxide dosage or pH could exist for a given system (e.g., pH 8 and/or lower dosages), but examination of further matrix conditions were beyond the scope of the current study.

No correlations ($\alpha=0.05$) of EE/O versus COD or alkalinity were observed (with Site C excluded in which MTBE removal was not accurately determinable). Overall, the most efficient MTBE removals (lowest EE/O) were observed at pH 7 (vs. 9) and at the stoichiometric peroxide dosage (i.e., 12.5 mg/L).

As with other alternatives, treatment costs for the O₃/H₂O₂ process were calculated based on estimated capital and operating costs. Capital costs for an O₃/H₂O₂ process were calculated using equipment cost estimates from industry for 38 and 3,800 L/min systems [33].

Calculations for the O₃/H₂O₂ process showed that unit treatment costs (capital plus O&M) ranged from 0.4 to 2.9 \$/1000 L for the study waters (excluding Site C in which little or no MTBE removal was observed) (Table II-6). Capital costs were a greater percentage of unit costs in low flow systems due to economies of scale, specifically 6-52 percent at high flow versus 24-85 percent at low flow. (Capital costs were lowest for processes requiring less MTBE removal operating at a lower pH of 7.) Economy-of-scale also provided greater unit costs (capital plus O&M) (\$/1000 L) for the low flow (38 L/min) systems compared with the high flow (3800 L/min) systems by a factor of from 1.2 to 3.3 times (Table II-6). Finally, unit costs at pH 9 were 1.2 to 3.6 times greater than at pH 7 for reasons discussed for the UV/H₂O₂ process above.

II-4.0 Summary

This study has shown that air stripping, carbon adsorption and advanced oxidation can each be effective at removing MTBE from a variety of groundwaters. Water quality and/or process conditions were shown to significantly affect removals and unit treatment costs. Air stripping provided the lowest unit treatment costs for high treatment flowrates (i.e., 3800 L/min) for each site water. In cases where a high removal efficiency was required,

however, relatively tall packed towers were often required. While the results show that at high flowrates air stripping may be the least costly treatment option for MTBE, the best process selection for a given location requires consideration of additional factors. For example, air stripping towers are subject to fouling by iron floc, carbonate scaling, and biofouling. Air stripping becomes less efficient at low temperatures, whereas some other processes (e.g., GAC sorption) may become more effective. Air stripping of VOCs may require additional offgas treatment.

Activated carbon adsorption provided the highest treatment costs for all conditions with the exception of the high-COD Site C water in which advanced oxidation was relatively ineffective. GAC sorption is also subject to fouling by iron, carbonate or biological growth as well as to competitive sorption with other compounds (i.e., BTEX). Activated carbon adsorption, however, may have other advantages such as each of use.

For low treatment flowrates (e.g., 38 L/min), the lowest unit costs option varied. The O₃/H₂O₂ AOP had the lowest unit costs for four of five waters, but was ineffective at MTBE removal for the high-COD Site C water. At low flowrate, the UV/H₂O₂ process provided the second lowest costs compared with the other treatment options. A number of key factors were involved in process efficiency including the presence of radical scavengers, pH, and the background UV absorbance (in the UV/H₂O₂ process).

The results of this study show that the selection of the best process for treatment of MTBE is site specific and must include consideration of a variety of factors. This study has shown the effect of key process parameters and serves as a guide in the process selection procedure.

II-5.0 References for Chapter II.

- [1] US EPA Health risk perspectives on fuel oxygenates. US Environmental Protection Agency, Report No. EPA/600/R-94/217, 1994.
- [2] Eweis J, Ergas S, Chang, D, Schroeder E. Bioremediation principles. Boston, MA: McGraw-Hill, Inc., 1998.
- [3] Squillace P, Pankow J, Kortés N, Zogorski J. Environmental behavior and fate of methyl tert-butyl ether. US Geological Survey, National Water Quality Assessment Program, USGS Fact Sheet FS-203-96 (Revised 2/98), 1998.
- [4] Delzer G, Zogorski J, Lopes T, Bosshart R.. Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991-95. US Geological Survey Water-Resources, Report No. 96-4145, 1996.
- [5] Mackay D, Shiu W, Ma K. Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals—volatile organic chemicals, vol. III. Chelsea, MI: Lewis, 1993.
- [6] McKinnon R, Dyksen JE. Removing organics from groundwater through aeration plus GAC. J Am Water Works Assoc 1984; May: 42-47.
- [7] Speth T, Miltner R. Technical note: adsorption capacity of GAC for synthetic organics. J Am Water Works Assoc 1990;82:72-75.
- [8] Squillace P, Pankow J, Kortés N, Zogorski JS. Review of the environmental behavior and fate of methyl tert-butyl ether. Environ Tox Chem 1997;16:1836-1844.
- [9] Kang J, Hoffman MR. Kinetics and mechanism of the sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation in the presence of ozone. Environ Sci Technol 1998;32(20):3194-3199.

-
- [10] Liang S, Palencia LS, Yates RS, Davis MK, Bruno J, Wolfe RL. Oxidation of MTBE by ozone and peroxone processes. *J Am Water Works Assoc* 1999;91(6):104-114.
- [11] Melin G, editor. Treatment technologies for removal of methyl tertiary butyl ether (MTBE) from drinking water. National Water Research Institute, Center for Groundwater Restoration and Protection, Report No. NWRI-99-06., 2000.
- [12] Cater SR, Stefan MI, Bolton JR, Safarzadeh-Amiri A. UV/H₂O₂ treatment of methyl tert-butyl ether in contaminated waters. *Environ Sci Technol* 2000;34(4):659-662.
- [13] Calgon Carbon Corp. Fitratorb 600. GAC of Trace Removal Applications. Product Bulletin, 1999.
- [14] Onda K, Takeuchi H, Okumoto Y. Mass transfer coefficients between gas and liquid phases in packed columns. *J Chem Eng Japan* 1968;1(1):56-62.
- [15] Lamarche P, Droste R. Air-stripping mass transfer correlations for volatile organics. *J Am Water Works Assoc* 1989; 81(1):78-89.
- [16] Staudinger J, Knocke WR, Randall CW. Evaluating the Onda mass transfer correlation for the design of packed-column air stripping. *J Am Water Works Assoc* 1990;82(1):73-79.
- [17] Djebbar Y, Narbaitz RM. Improved Onda correlations for mass transfer in packed towers. *Water Sci Technol* 1998; 38(6):295-302.
- [18] Hand D, Crittenden JC, Gehin J, Lykins Jr B. Design and evaluation of an air-stripping tower for removing VOCs from groundwater. *J Am Water Works Assoc* 1986; 78(9):87.
- [19] Crittenden J, Ferrigan J, Hand D. Design of rapid small-scale adsorption tests for a constant diffusivity. *J Wat Poll Control Fed* 1986;58(4):312-319.
- [20] Letterman R. Water quality and treatment. New York: McGraw-Hill, Inc., 1999.
- [21] Kekobad, J. Removal of MTBE from water using granular activated carbon, UMR M.S. Thesis 2002.
- [22] Perry , Green D. Perry's Chemical Engineers Handbook. 7th Ed. McGraw-Hill, Inc., 1997.

-
- [23] Chemical engineering. Economic Indicators Section, June 16, 1980.
- [24] Chemical Engineering. Economic Indicators Section, 109 (5), 2002.
- [25] Keller AA, Sandall OC, Rinker RG, Mitani MM, Bierwagen B, Snodgrass MJ. An evaluation of physicochemical treatment technologies for water contaminated with MTBE. *Ground Water Monit Rem* 2000;Fall:114 – 126.
- [26] Pontius F. *Water quality and treatment*, 4th Ed., New York: McGraw-Hill, 1990.
- [27] Speth T, Miltner R. Technical note: adsorption capacity of GAC for synthetic organics. Isotherms of 15 compounds in organic-free water are presented. *J Am Water Works Assoc* 1998;90(4):171 – 174.
- [28] Calgon Carbon Corporation. Personal communication, 2002.
- [29] Calgon Carbon Oxidation Technologies. *AOT handbook*. Markham, Ontario, Canada: Calgon Carbon Corporation, 1996.
- [30] Eckenfelder WW. *Industrial water pollution control*, 3rd ed., Boston, MA: McGraw-Hill, 2000
- [31] Staehelin J, Hoigne J. Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. 1982;16:676-681.
- [32] Staehelin J, Hoigne J. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. 1985;19:1206-1213.
- [33] Applied Process Technology, Inc. Personal communication, 2002.

Chapter III.

Treatment of Alternative Oxygenate Ethers and Alcohols

Chapter Summary

Methyl *tert*-butyl ether (MTBE) is a gasoline oxygenate that has become a significant threat to groundwater supplies across the United States. Due to its physiochemical properties it has proven difficult and costly to remove from contaminated sites. This study was conducted to determine whether an alternative oxygenate (AO)—diisopropyl ether (DIPE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), *tert*-butyl alcohol (TBA), and ethanol (EtOH)—presents a more efficient and less costly option from a remediation standpoint. Four common treatment processes—air stripping, carbon adsorption, UV/H₂O₂ and O₃/H₂O₂ - advanced oxidation processes (AOPs)—were examined at pilot scale to develop design parameters from which technical and economic comparison were made for each alternative oxygenate versus MTBE. The experimental results showed that the ether AOs—DIPE, TAME, and ETBE—were each more efficiently and more economically treated than MTBE. The alternative alcohol oxygenates—TBA and EtOH—were less efficiently and less economically treated by the processes studied. The paper details the effects of primary process parameters and properties of individual oxygenates on process efficiency.

III-1. Background

The Clean Air Act Amendments of 1990 established a mandate for the use of oxygenates in gasoline (EPA 1994a). Two general classes of oxygen-containing compounds have been used to fill this need: ethers and alcohols. From these two groups, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), ethanol (EtOH), and *tert*-butyl alcohol (TBA) have been used in varying degrees in nearly 30% of the Nation's gasoline with MTBE being the dominant choice (American Petroleum Institute 2000).

Despite the advantage to air quality from using MTBE in gasoline, its impact on groundwater supplies has become an issue of public concern (Delzer et al. 1996, Squillace et al. 1998, State of Maine 1998, National Research Council 1999, State of New York 2000, State of California 2002). The impact of MTBE is not only due to its widespread use, but its persistence once released into the environment due to its physicochemical characteristics—high water solubility, low Henry's law constant, low sorptivity, and relative biorecalcitrance under common conditions (Mackay et al. 1993; Squillace et al. 1998).

Pilot-scale treatment results for MTBE show that at higher flowrates (i.e., 3800 L/min) air stripping is more economical than carbon adsorption or advanced oxidation (i.e., H_2O_2 , $\text{O}_3/\text{H}_2\text{O}_2$) (Sutherland et al. 2003). At lower flow rates (i.e., 38 L/min), each the four treatment alternatives have more similar unit costs which are strongly dependent on water quality parameters. Sutherland et al. (2003) and others (McKinnon and Dyksen 1984; Wagler and Malley 1994; Liang et al. 1999; Keller et al. 2000) have shown that the treatment of MTBE in groundwater is relatively inefficient due to its physicochemical properties.

A few studies have examined the use of alternative oxygenates (AOs) although none have compared the AOs in side-by-side comparison at pilot- or full-scale (Karpel vel Leitner et al. 1994, Mezyk et al. 2001). This interest in alternative oxygenates arises from the concern of the EPA, local governments, and the petroleum industry in finding an environmentally friendly gasoline oxygenate.

There remains the important question as to whether AOs offer more efficient and less costly groundwater remediation (compared to MTBE) via treatment technologies commonly used for groundwater (packed-tower air stripping, carbon adsorption (GAC), $\text{UV}/\text{H}_2\text{O}_2$, and $\text{O}_3/\text{H}_2\text{O}_2$) (Cater 2000b, Melin 2000). To address this question, this study was conducted to compare the treatment of selected AOs at pilot scale, to develop design parameters, to determine the effects of process variables, and to develop an economic comparison based on unit treatment costs.

III-2. Experimental

2.1 Materials

MTBE, ETBE, TBA, TAME, EtOH, and DIPE were reagent grade and used as received from Sigma-Alrich (St. Louis, MO). All other chemicals were at least reagent grade. Calgon F-400 and F-600 granular activated carbons (GAC) were obtained directly from Calgon Corporation.

2.2 Analytical methods

The AO compounds were analyzed using gas chromatography/mass spectrometry (GC/MS) with an Agilent 6890 GC with a 5970 MSD. Samples were concentrated and injected using a Tekmar Dohrmann 3100 purge-and-trap system. The method used a J&W Scientific DB-624 capillary column (25m×0.25) with a temperature ramp of: 40°C for 2 minutes, a ramp of 10°C per minute to 180°C, and then 180°C for 1 minute. A typical chromatogram and mass spectra for each compound are presented in Figure III-1.

Wet chemical methods were used to measure nitrate, nitrite, ferrous iron, and total iron using Hach Methods 8171, 8507, 8146 and 8112, respectively. Chemical oxygen demand (COD) was measured using Hach Method 8000 with low-range digestion vials. Titration methods were used for total hardness (Hach Method 8213), calcium hardness (Hach Method 8204), and alkalinity (Hach Method 8203). pH was measured with a Corning 400-Series meter and combination electrode.

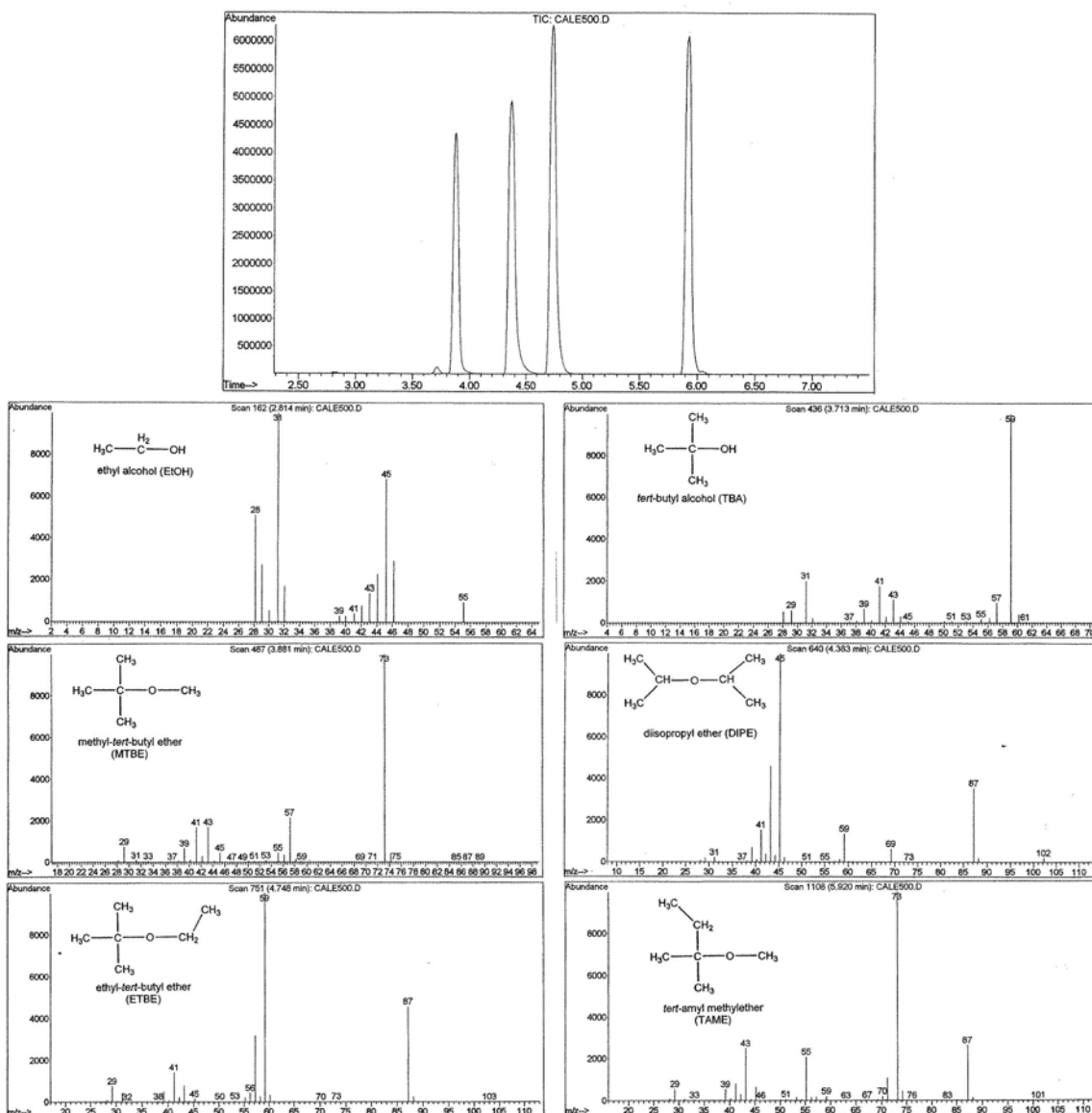


Figure III-1. Representative chromatogram and mass spectra from GC/MS with chemical structures for alternative oxygenates (AO).

2.3 Methods

Pilot Plant – To conduct this research, each unit process (i.e., air stripping, activated carbon rapid small scale column test (RSSCT), UV/H₂O₂ and O₃/H₂O₂ systems) was housed in a 2.2×5 m trailer (internal dimensions), collectively designated as the MWTPP. The MWTPP also contained a data acquisition computer, analytical laboratory capability, and heating/cooling capability.

Packed Tower – The packed tower used for air stripping was 0.3-m diameter and contained 2.9-m of 0.025-m polypropylene Tri-Pack packing (Jaeger Products, Inc.; Houston, TX). The packed tower was operated in counter-current mode with water feed rates to the top of the tower of 0.00025 m³/s, and air flow rates of up to 0.033 m³/s fed from the bottom. Liquid redistributors were placed 33- and 66-percent up the packing height. The column was insulated with reflective foil and operated at a constant temperature of 20±1°C.

Rapid Small Scale Column Test (RSSCT) – RSSCT methodology was used to develop breakthrough curves for each study compound based on Crittenden et al. (1986). The carbon was prepared for the RSSCT by grinding and sieving. The 80×140 mesh (110×180 μm) was used in the RSSCT. The feed reservoir had a floating cover (polyethylene sheet) to retard volatilization. The columns were fed at 7 mL/min (4.4 m/hr) via piston pumps and a pulse dampener, and consisted of 30 cm×1.1-cm glass columns (Ace Glass) in series connected with 0.32-cm SS or Teflon™ tubing. Samples were periodically removed from the feed and from the effluent from each column in series. Breakthrough curves were plotted as bed volumes (BV) versus concentration with appropriate correction for the sample volumes removed from the preceding columns. The water temperature was held constant at 21.5(±2)°C in the RSSCT experiments.

UV/Peroxide – The UV/H₂O₂ system used for this research utilized a 1-kW medium-pressure, mercury vapor lamp (Hanovia UR, C002716-001) and an ARC Power/Control System (Aquionics). An 8.7-L, 316L passivated stainless steel UV-reactor was used with the dimensions of 0.050-m long by 0.015-m ID. AOs, sodium hydroxide and hydrogen peroxide were fed into the groundwater feed using separate peristaltic pumps (Masterflex L/S).

Ozone/Peroxide – The O_3/H_2O_2 system used for this research was operated in the continuous, plug-flow mode at a treatment rate of 3.8 L/min. Oxygen and ozone were generated with an pressure-swing oxygen generator (AirSep AS-12) and a corona discharge ozone generator (Ozonix Model CF-0B OZAT). Ozone injection was accomplished with a Venturi injector (Mazzei Model 484) and mass flow controller (Tylan DFC-2900). A UV-ozone monitor (PCI HC-12) was to measure feed and offgas ozone concentrations. AOs, sodium hydroxide and hydrogen peroxide were fed with separate peristaltic pumps (Masterflex L/S). A centrifugal degas system with thermal-catalytic ozone destruction (GDT DS-100-WM) was used to remove and treat excess entrained gas.

III-3. Experimental Results

3.1 Groundwater

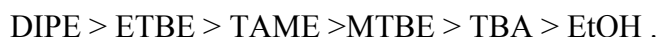
The water used for these experiments was a local tap water obtained from groundwater sources. Nitrate, nitrite, ferrous iron, total iron, and chemical oxygen demand were measured prior to any chemical spike and were not detected in the groundwater studied. Total hardness, calcium hardness, and alkalinity were measured to be 266, 262, and 225 mg/L as $CaCO_3$, respectively. The natural pH of the water was measured to be 7.0.

3.2 Packed Tower

From the observed removal of each AO in the packed tower experiments, mass transfer coefficients (K_{La}) were determined for EtOH, TBA, MTBE, ETBE, TAME, and DIPE stripped from a mixture in the packed tower at the predetermined optimum air:liquid ratio of 150:1. This ratio was based on extensive stripping testing of MTBE from five different groundwaters at air:liquid ratios of 75:1, 100:1 and 150:1 (Sutherland et al., 2003). All experiments were conducted in duplicate.

Neither EtOH or TBA stripped readily from solution ($K_{La} = 0.00002$ and 0.00007 , respectively) due to their very low Henry's constant and high miscibility in water (Tables III-1 and III-2). MTBE, ETBE, TAME, and DIPE all stripped fairly readily with K_{La} values from 0.00223 sec^{-1} for MTBE to 0.00507 sec^{-1} for DIPE.

K_{La} values were generally, though not strictly, ranked in the order of their increasing Henry's constant (H) (Table III-2), specifically K_{La} is ordered:



No correlation ($\alpha=0.05$) was observed between K_{La} and Henry's constant ($p=0.087$, $r = 0.74$) (although the correlation is significant at $\alpha=0.1$). It should be noted that reported Henry's constants vary considerable especially for MTBE (Table III-1). When correlating K_{La} values with the lower end of the range reported Henry's constants in the literature for 20°C (Table III-1), a correlation ($\alpha=0.05$) was observed between K_{La} and H ($p=0.034$, $r=0.85$).

Table III-1. Selected properties for alternative oxygenates in study.

Oxygenate	CAS [†]	Formula	Molecular Weight	Pure Phase Solubility (mg/L) [†]	log K_{oc} [†]	log K_{ow} [‡]	Henry's Law Constant [†] (dimensionless)	Specific Gravity [†]
EtOH	64-17-5	C ₂ H ₅ OH	46.1	miscible	0.20 - 1.21	-0.16 -- -0.31	0.00021 - 0.00026	0.789
TBA	75-65-0	(CH ₃) ₃ CO(CH ₃)	74.1	miscible	1.57	0.35	0.00048 - 0.00059	0.786
MTBE	1634-04-4	C ₅ H ₁₂ O	88.1	43,000 - 54,300	1.0 - 1.1	1.2	0.023 - 0.12	0.741
ETBE	637-92-3	(CH ₃) ₃ COCH ₂ CH ₃	102.2	26,000	1.0 - 2.2	1.74	0.11	0.752
TAME	994-05-8	(C ₂ H ₅)(CH ₃) ₂ COCH ₃	102.2	20,000	1.3 - 2.2	---	0.052	0.764
DIPE	108-20-3	(CH ₃) ₂ CHOCH(CH ₃) ₂	102.2	2,039 - 9,000	1.46 - 1.82	---	0.195 - 0.41	0.724

[†]Source: "<http://www.epa.gov/swerust1/oxygenat/oxytable.htm>" (Table A-1, page A-3,

"MTBE Site Characterization: API Technical Bulletin (DRAFT Final), American Petroleum Institute)

[‡] National Science and Technology Council (1997) Interagency assessment of oxygenated fuels. Washington, D.C.

Table III-2. Experimentally determined $K_L a$ values, Henry's constants, tower height and diameter, and unit costs for alternative oxygenates (AO) in study.

Cmpd	$K_L a$	Flow (L/min)	C_{inf} (ppb)	C_{eff} (ppb)	Tower Height (m)	Height (vs. MTBE)	Unit Cost (\$/1000L)	Unit Cost (vs. MTBE)
EtOH	0.00002	---	---	---	NC	NC	NC	NC
TBA	0.00007	---	---	---	NC	NC	NC	NC
MTBE	0.00223	38	100	20	2.5	1.0	1.47	1.00
		38	1000	5	9.2	1.0	1.69	1.00
		3800	100	20	2.5	1.0	0.10	1.00
		3800	1000	5	9.2	1.0	0.18	1.00
ETBE	0.00473	38	100	20	1.2	0.48	1.42	0.97
		38	1000	5	4.1	0.44	1.52	0.90
		3800	100	20	1.2	0.48	0.09	0.86
		3800	1000	5	4.1	0.44	0.12	0.68
TAME	0.00424	38	100	20	1.4	0.56	1.43	0.97
		38	1000	5	4.9	0.53	1.54	0.91
		3800	100	20	1.4	0.56	0.09	0.88
		3800	1000	5	4.9	0.53	0.13	0.73
DIPE	0.00507	38	100	20	1.1	0.44	1.42	0.97
		38	1000	5	3.7	0.40	1.51	0.89
		3800	100	20	1.1	0.44	0.09	0.85
		3800	1000	5	3.7	0.40	0.12	0.65

NC = Not calculated due to ineffective stripping

The packed tower height required for a given removal was estimated using a method detail elsewhere (Cornwell, 1990) as the product of the height of a transfer unit (HTU) and the number of required transfer units (NTU) where:

$$\text{Tower Height} = \text{HTU} \cdot \text{NTU}$$

and

$$\text{HTU} = \frac{L}{K_L a}$$

where L is the liquid loading rate ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{sec}^{-1}$). The NTU was estimated analytically via:

$$\text{NTU} = \frac{R}{R-1} \ln \left(\frac{(c_i/c_e)(R-1)+1}{R} \right)$$

where c_i and c_e are the initial and final contaminant concentrations, respectively, G is the gas loading rate ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{sec}^{-1}$), H is Henry's constant, and R is the dimensionless stripping factor (or $H \cdot G \cdot L^{-1}$).

These $K_L a$ values were used to estimate absolute unit treatment costs as well as treatment costs relative to MTBE. To estimate costs, the diameter of the required column was determined as the product of the desired liquid flowrate and the inverse of the assumed liquid loading rate. A cost ratio (cost per meter of tower height) was determined using the method of Peters and Timmerhaus (*Perry's Chemical Engineers' Handbook*, 1997). The cost of the tower and ancillary equipment was determined by the product of the cost ratio and tower height, and was adjusted to 2001 dollars using Marshall and Swift's Equipment Cost Index (*Chemical Engineering* 1980 and 2002). Capital costs estimation included equipment and factors such as piping, site work, electrical systems, and engineering costs as presented by Keller et al. (2000). Capital costs were depreciated at a rate of 4 percent over a 10-year period.

For purposes of comparison, tower heights and overall (capital plus O&M) unit treatment costs were estimated for each AO and MTBE assuming a "low required removal" (100 to 20 ppb) and a "high required removal" (1000 to 5 ppb) (Table III-2). Due to their extremely low $K_L a$ values, neither column height nor treatment costs were calculated for EtOH or TBA as stripping does not appear to be a viable option for these AOs.

For the alternative AO ethers—ETBE, TAME, and DIPE—the required column heights were 44–60 percent less than for MTBE, and unit treatment costs were 3–29 percent less due to their greater K_La values. The reason the differences in column height were much greater than differences in unit treatment costs, is that annualized capital costs only accounted for 8 and 31 percent of total annual costs for the lower flow (38 L/min) and higher flow (3800 L/min) systems, respectively.

For each AO, tower height scales with required removal and packing surface scales with flow (Table III-2). For example, greater removal requirements for each AO resulted in taller columns and greater treatment costs. The results show that the tower heights were from 3.3–3.7 times higher for the greater removal scenario (99.5%) versus the lesser removal scenario (80%) (Table III-2). Unit treatment costs were 1.1–1.7 times greater for the greater versus lesser removal scenarios (Table III-2). Larger flow rates, however, result in significant economy-of-scale resulting in unit treatment costs (\$/1000 L treated) for high flows (3800 L/min) being only 6–11 percent of those at low flows (38 L/min). Because a constant liquid surface loading rate was used, flowrate correlates linearly with surface area and non-linearly (power of 2) with column diameter.

Overall, it may be concluded that the AOs with lower Henry's constants (EtOH and TBA) are much less effectively treated than MTBE by air stripping. However, those with greater Henry's constants (ETBE, TAME, and DIPE) are much more easily stripped than MTBE resulting in much smaller columns and lower unit treatment costs.

3.3. *RSSCT*

Breakthrough curves from the RSSCT for the mix of oxygenates for both Calgon F-400 and F-600 GACs are presented in Figure III-2. The results showed that for both carbons, the less soluble the oxygenate, the greater the preferential selectivity on the carbons (Figure III-2 and Table III-1). Specifically, the relative selectivity on the carbon was:

$$\text{EtOH} < \text{TBA} < \text{MTBE} < \text{ETBE} < \text{TAME} < \text{DIPE}$$

or the reverse order of water solubility. The order of breakthrough of AOs was also ranked in order of increasing organic carbon sorption coefficient (K_{OC}) listed in Table III-1 with the exception of TBA which has a higher K_{OC} than MTBE. It should be noted, however, that the

octanol-water partition coefficient for TBA is lower than for MTBE indicating that MTBE is the more hydrophobic compound of the two (EPA, 1994b)

These results indicate that the more soluble AOs (EtOH and TBA) may be more difficult to treat with GAC sorption than MTBE, while the less soluble oxygenates (ETBE, TAME and DIPE) may be more favorable. Ongoing studies are determining the specific sorption capacity of various GACs for these AOs, and the effects of competition with BTEX compounds (i.e., benzene, toluene, ethylbenzene, and xylenes) on that sorption capacity. This information will allow determination and comparison of treatment costs for AOs versus MTBE using the GAC sorption process.

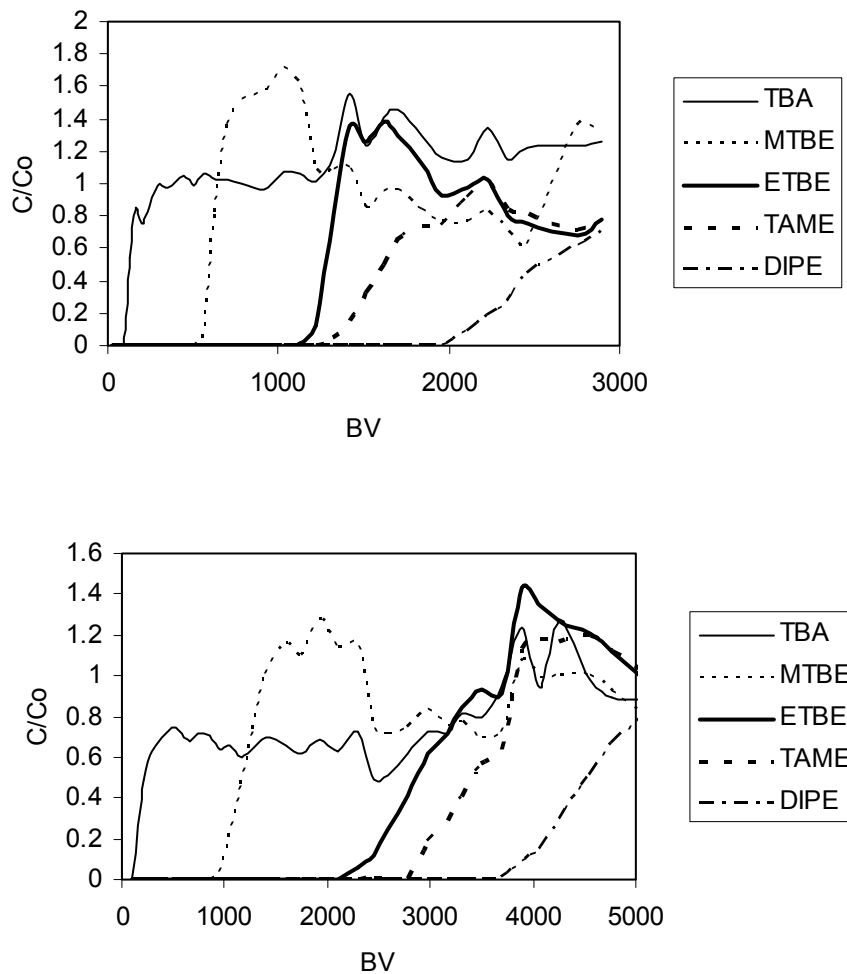


Figure III-2. RSSCT breakthrough curves for Calgon F-400 carbon (top) and Calgon F-600 (bottom). EtOH broke through columns immediately.

3.4. UV/Peroxide

For design of advanced oxidation processes (AOPs), an EE/O value ($\text{kWh}\cdot\text{order}^{-1}\cdot 1000\text{L}^{-1}$) was experimentally determined and subsequently used to estimate power requirements and treatment cost. An EE/O is the amount of energy required to reduce the concentration of a contaminant by one order of magnitude per 1000 L (Calgon 1996). Because the hydroxyl radical ($\bullet\text{OH}$) is the primary oxidant in most UV/ H_2O_2 and $\text{O}_3/\text{H}_2\text{O}_2$ AOPs, the EE/O is strongly affected by the relative rates of reaction of $\bullet\text{OH}$ with the target species (e.g., a fuel oxygenate) versus any other species in solution that will scavenge or react with $\bullet\text{OH}$ (e.g., background organics, COD, bromide, alkalinity, etc.). The fraction ($f_{\text{OH},i}$) of $\bullet\text{OH}$ reacting with a target species i can be estimated by:

$$f_{\text{OH},i} = \frac{k_{\text{OH},i} \cdot [i] \cdot [\bullet\text{OH}]}{\sum_{j=1}^{\text{all cmpd}} k_{\text{OH},j} \cdot [j] \cdot [\bullet\text{OH}]} = \frac{k_{\text{OH},i} \cdot [i]}{\sum_{j=1}^{\text{all cmpd}} k_{\text{OH},j} \cdot [j]}$$

Factors such as pH potentially play an important role in process efficiency for oxidation of fuel oxygenates, for example, because of the effect on $\bullet\text{OH}$ generation efficiency as well as speciation of scavengers in the systems (e.g., $\text{HCO}_3^-/\text{CO}_3^{2-}$, $\text{H}_2\text{O}_2/\text{HO}_2^-$, carboxyl groups, hydroxyl groups, amine groups, etc.).

In these experiments, EE/O was determined for each AO at both pH 7 and 9. The EE/O was calculated using least-squares linear regression to determine the slope of the line for UV dose ($\text{kWhr}/1000 \text{ L}$) versus the log removal of MTBE ($\log(c_i/c_e)$) (Calgon, 1996):

$$\log\left(\frac{c_i}{c_e}\right) = (\text{EE/O})^{-1} \cdot \text{UV dose} (\text{kWhr}/1000 \text{ L})$$

where $(\text{EE/O})^{-1}$ is the slope. UV dosage was adjusted by varying the flowrate to the pilot reactor. All experiments were conducted in duplicate.

The results showed that EE/O varied with AO type as well as pH (Table III-3). For all AOs, much lower process efficiency (i.e., greater EE/O) was observed at higher pH (9 vs. 7). The primary reason for this is increased $\bullet\text{OH}$ scavenging by carbonate alkalinity and peroxide at higher pH. As the pH increases, HCO_3^- is converted to CO_3^{2-} ($\text{pK}_a = 10.3$) (Stumm and Morgan, 1996) and H_2O_2 is converted to its conjugate base, HO_2^- ($\text{pK}_a = 11.7$)

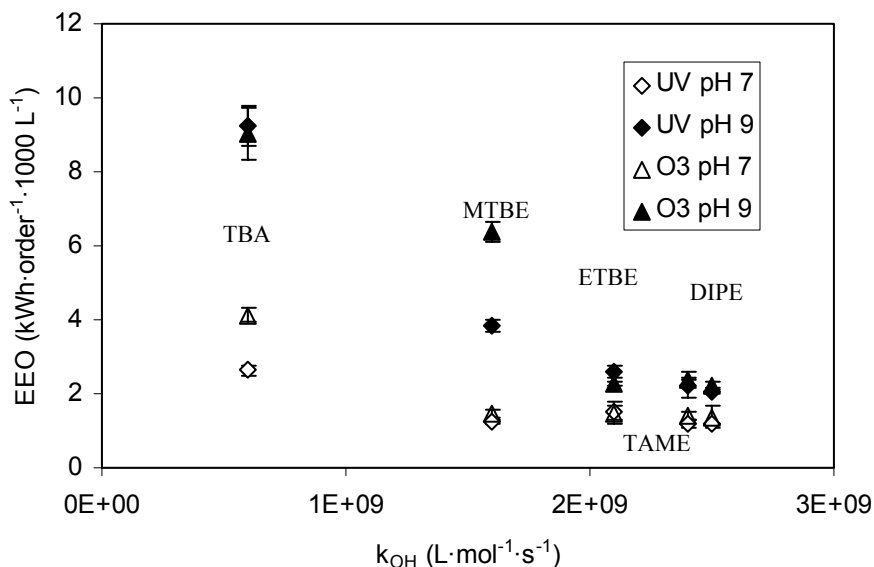
(Hunt et al. 1972). Because the more basic species are much more reactive than their acidic counterparts ($k_{\text{bicarbonate}} = 8.5(10^6) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Buxton et al. 1988), $k_{\text{carbonate}} = 3.8(10^8) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Buxton et al. 1988), $k_{\text{H}_2\text{O}_2} = 3.8(10^7) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Merenyi et al. 1980)), and $k_{\text{HO}_2^-} = 6.8(10^9) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Merenyi et al. 1980)), higher pH leads to increased scavenging and a decreased fraction of $\bullet\text{OH}$ reacting with the target AO.

Table III-3. Unit treatment costs for the UV/H₂O₂ process as at 25 mg/L H₂O₂ as function of pH, flow, and removal.

Cmpd	pH	EE/O	Flow (L/min)	C _{inf} (ppb)	C _{eff} (ppb)	Unit Cost (\$/1000L)	Unit Cost (vs. MTBE)
		(kWh/order/ 1000L)					
TBA	7	2.6	38	100	20	1.26	1.13
	7	2.6	38	1000	5	1.88	1.34
	9	9.2	38	100	20	1.94	1.40
	9	9.2	38	1000	5	4.11	1.80
	7	2.6	3800	100	20	0.36	1.65
	7	2.6	3800	1000	5	0.98	1.92
	9	9.2	3800	100	20	1.04	2.13
	9	9.2	3800	1000	5	3.22	2.31
MTBE	7	1.2	38	100	20	1.11	1.00
	7	1.2	38	1000	5	1.41	1.00
	9	3.8	38	100	20	1.38	1.00
	9	3.8	38	1000	5	2.29	1.00
	7	1.2	3800	100	20	0.22	1.00
	7	1.2	3800	1000	5	0.51	1.00
	9	3.8	3800	100	20	0.49	1.00
	9	3.8	3800	1000	5	1.39	1.00
ETBE	7	1.5	38	100	20	1.14	1.03
	7	1.5	38	1000	5	1.50	1.07
	9	2.6	38	100	20	1.25	0.91
	9	2.6	38	1000	5	1.86	0.81
	7	1.5	3800	100	20	0.25	1.13
	7	1.5	3800	1000	5	0.61	1.19
	9	2.6	3800	100	20	0.36	0.73
	9	2.6	3800	1000	5	0.97	0.69
TAME	7	1.2	38	100	20	1.11	1.00
	7	1.2	38	1000	5	1.39	0.99
	9	2.2	38	100	20	1.22	0.88
	9	2.2	38	1000	5	1.74	0.76
	7	1.2	3800	100	20	0.22	0.98
	7	1.2	3800	1000	5	0.49	0.97
	9	2.2	3800	100	20	0.32	0.66
	9	2.2	3800	1000	5	0.85	0.61
DIPE	7	1.2	38	100	20	1.11	1.00
	7	1.2	38	1000	5	1.39	0.99
	9	2.1	38	100	20	1.20	0.87
	9	2.1	38	1000	5	1.69	0.74
	7	1.2	3800	100	20	0.22	0.98
	7	1.2	3800	1000	5	0.49	0.97
	9	2.1	3800	100	20	0.31	0.63
	9	2.1	3800	1000	5	0.80	0.57

•OH rate constants are presented versus corresponding EE/O values in Figure III-3. The specific •OH rate constants are $k_{TBA} = 6.0(10^8) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Buxton et al. 1988), $k_{MTBE} = 1.6(10^9) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Eibenberger, J. 1980), $k_{ETBE} = 1.8\text{-}2.7(10^9) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Mezyk et al. 2001 and Karpel Vel Leitner 1994, respectively), $k_{TAME} = 2.4(10^9) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Mezyk et al. 2001), and $k_{DIPE} = 2.5(10^9) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Mezyk et al. 2001). Not all hydroxyl radical rate constants were available from a single reference and comparison of rate constants determined at different experimental conditions may be a concern. Current experiments are being conducted to determine •OH rate constants for a wide range of oxygenates.

Figure III-3. Plot of EE/O versus •OH rate constants (with 95% error bars for replicate experiments).



EE/Os were significantly greater ($\alpha=0.05$) at pH 9 than at pH 7 (Figure III-3) due to greater scavenging by CO_3^{2-} and HO_2^- as discussed above. Statistical analysis also showed that a significant correlation ($\alpha=0.05$) was observed between k_i and EE/O at pH 7 ($p=0.041$, $r=0.89$) and at pH 9 ($p=0.006$, $r=0.97$) as would be expected based on the equation presented above. That is, the higher the rate constant, the more efficiently the target oxygenate can compete for $\bullet\text{OH}$, and the more efficient the process. As is apparent from Figure III-3, EE/O for the ethers are all within a narrow range at pH 7 from 1.2 to 1.5 $\text{kWh}\cdot\text{order}^{-1}\cdot 1000 \text{ L}$. These EE/O values compare with “typical EE/Os for contaminant destruction” for benzene and toluene of 0.5–1.3 $\text{kWh}\cdot\text{order}^{-1}\cdot 1000 \text{ L}$, for 1,4-dioxane of 0.5–1.6, and for trichloroethylene of 0.5 to 1.1 (Calgon 1996).

An EE/O was not determined for EtOH (since this is an unlikely treatment scenario). However, the EE/O for EtOH would be expected to be similar to MTBE or ETBE due to a similar $\bullet\text{OH}$ rate constant ($k_{\text{EtOH}} = 1.9(10^9) \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (Buxton et al. 1988)).

Unit treatment costs were calculated for the AOs based on operating plus capital costs. Operating costs included power (based on EE/O at \$0.08/kWh)) and chemicals (based on \$1.58/kg for peroxide). Capital costs were estimated using the equation (Calgon 1996):

$$\text{Equipment cost (\$)} = (0.9875 \cdot \text{UV power (kW)} + 55) \cdot 1000$$

The total capital costs also took into account additional costs using the algorithm of Keller et al. (2000). Costs were depreciated over a 10-year period at a rate of four percent.

Unit treatment costs were determined for the AOs at pH 7 and 9, and for a large removal (99.5%, or 1000 to 5 $\mu\text{g/L}$) or a small removal (80%, or 100 to 20 $\mu\text{g/L}$) requirement. The results show that at pH 7, the unit treatment costs for all AOs were fairly similar for each ether AO but significantly higher for TBA (Table III-3). At pH 9, unit treatment costs for each AO ether ranged from 47–89 percent of MTBE costs, but were much greater (27– 73 percent) for TBA compared with MTBE.

Depending on the compound, unit treatment costs were from 5–22 percent greater at pH 9 as compared with 7 for otherwise identical conditions. This was due primarily to greater EE/Os at pH 9. A significant economy-of-scale was achieved with low flow systems (38 L/min) having unit treatment costs from 74–310 percent greater than for high flow systems

(3800 L/min). An in-depth determination of the effects of treatment parameters on unit costs for MTBE treatment is presented elsewhere (Sutherland et al. 2003). These results suggest that with the UV/H₂O₂ process ether AOs may have similar treatment costs at neutral pH but may have lower treatment costs at higher pH (>7).

3.5. Ozone/Peroxide

The EE/O design parameter was determined for each AO with the O₃/H₂O₂ process in a manner similar to that used with the UV/H₂O₂ process. The primary difference is that the power requirement is for ozone rather than UV generation. A generation efficiency of 150 g O₃·kWhr⁻¹ was assumed in these calculations (Eckenfelder, 2000). Thus, for a given applied ozone dosage (with the associated power requirement) and log removal of an AO, an EE/O was calculated. The EE/O for this process can be influenced by water characteristics, peroxide concentration, pH, alkalinity and other factors. The effects of highly varied water characteristics and peroxide dosage was investigated for MTBE and is reported elsewhere (Sutherland et al., 2003). In these experiments, the optimum peroxide dosage was utilized, specifically the stoichiometric ratio of 0.35 mg peroxide per mg ozone absorbed.

The results show that EE/O varied with both AO and also with pH (Table III-4). As with the UV/H₂O₂ process, higher pH resulted in lower process efficiency and greater EE/O (Table III-4). This effect is expected due to enhanced scavenging at higher pH by CO₃²⁻ and HO₂⁻ relative to their acidic counterparts as discussed above.

At both pH levels, all ether AOs were more efficiently removed than MTBE, while TBA was less efficiently removed (Figure III-3 and Table III-4). The EE/O values correlated ($\alpha=0.05$) with •OH rate constants at both pH 7 ($p=0.034$, $r=0.91$) and pH 9 ($p=0.007$, $r=0.97$) due to more efficient oxidation of target species (i.e., the AO) by •OH with compounds having higher •OH reaction rates (Figure III-3).

Table III-4. Unit treatment costs for the O₃/H₂O₂ process as at 12.5 mg/L H₂O₂ and stoichiometric ozone as function of pH, flow, and removal.

Cmpd	pH	EE/O (kWh/order/ 1000L)	Flow (L/min)	C _{inf} (ppb)	C _{eff} (ppb)	Unit Cost (\$/1000L)	Unit Cost (vs. MTBE)
TBA	7	4.1	38	100	20	1.35	1.25
	7	4.1	38	1000	5	2.32	1.63
	9	9.1	38	100	20	1.86	1.17
	9	9.1	38	1000	5	3.99	1.29
	7	4.1	3800	100	20	0.46	2.46
	7	4.1	3800	1000	5	1.43	2.68
	9	9.1	3800	100	20	0.96	1.40
	9	9.1	3800	1000	5	3.09	1.41
MTBE	7	1.5	38	100	20	1.08	1.00
	7	1.5	38	1000	5	1.43	1.00
	9	6.4	38	100	20	1.58	1.00
	9	6.4	38	1000	5	3.08	1.00
	7	1.5	3800	100	20	0.19	1.00
	7	1.5	3800	1000	5	0.53	1.00
	9	6.4	3800	100	20	0.69	1.00
	9	6.4	3800	1000	5	2.19	1.00
ETBE	7	1.4	38	100	20	1.08	1.00
	7	1.4	38	1000	5	1.42	0.99
	9	2.3	38	100	20	1.16	0.74
	9	2.3	38	1000	5	1.70	0.55
	7	1.4	3800	100	20	0.18	0.99
	7	1.4	3800	1000	5	0.52	0.98
	9	2.3	3800	100	20	0.27	0.39
	9	2.3	3800	1000	5	0.81	0.37
TAME	7	1.4	38	100	20	1.07	0.99
	7	1.4	38	1000	5	1.40	0.98
	9	2.4	38	100	20	1.17	0.74
	9	2.4	38	1000	5	1.74	0.56
	7	1.4	3800	100	20	0.18	0.96
	7	1.4	3800	1000	5	0.51	0.95
	9	2.4	3800	100	20	0.28	0.41
	9	2.4	3800	1000	5	0.84	0.39
DIPE	7	1.4	38	100	20	1.07	0.99
	7	1.4	38	1000	5	1.39	0.98
	9	2.2	38	100	20	1.16	0.73
	9	2.2	38	1000	5	1.68	0.55
	7	1.4	3800	100	20	0.18	0.94
	7	1.4	3800	1000	5	0.50	0.93
	9	2.2	3800	100	20	0.26	0.38
	9	2.2	3800	1000	5	0.79	0.36

Capital costs for treating groundwater with the O₃/H₂O₂ include additional process equipment for ozone generation, contacting, monitoring and offgas destruction not required in the UV/H₂O₂ process. Overall, the increased efficiency of treating ether AOs versus MTBE resulted directly in lower unit treatment costs for the ether AOs. Specifically, unit treatment costs for treating ETBE, DIPE and TAME were from 1–42 percent lower than MTBE at pH 7 and 28–64 percent lower at pH 9 (Table III-4). Due to high EE/O for TBA, its unit treatment costs were greater than for MTBE (Table III-4).

The effect of pH on process efficiency and costs was significant with EE/Os at pH 9 averaging 174 percent greater and unit treatment costs averaging 100 percent greater than at pH 7 (Table III-4). The effect of removal requirement was also significant with costs for high removal (99.5%) averaging 130 percent greater than for low removal (Table III-4). Finally, the effect of economy-of-scale was clearly observed with low flow systems averaging 220 percent higher unit treatment costs (\$/1000 L) than high flow systems (Table III-4).

III-4. Summary

At high flow rates (i.e., 3800 L/min), air stripping was a more economical means of treating MTBE and the ether AOs compared with advanced oxidation. (GAC costs were not determined for each AO individually.) At low flow rates (i.e., 38 L/min), air stripping and advanced oxidation were more comparable to air stripping with respect to unit treatment costs.

With respect to GAC adsorption, all alternative ethers (ETBE, TAME, and DIPE) were preferentially adsorbed while both alcohols (EtOH and TBA) broke through prior to MTBE. It should be noted, however, direct competition between AOs and MTBE would not occur unless they were concurrently in the same groundwater. The primary competition effects (leading to diminished capacity) are with other synthetic organic chemicals (e.g., benzene, toluene, etc.) or natural organic matter (e.g., humic substances).

Air stripping was ineffective at stripping either alcohol, EtOH or TBA. MTBE had marginally higher treatment costs than the alternative ethers (e.g., ETBE, TAME and DIPE). Estimated tower heights for MTBE were on the order of twice as high compared with the

ether AOs for identical removal requirements. It should be noted that other considerations such as fouling of packing (by carbonate scaling, iron floc, or biological growth), system height, and aesthetics are issues that must be considered in addition to costs for the packed tower.

The O₃/H₂O₂ and UV/H₂O₂ AOPs generally had comparable treatment costs for treatment of the AOs. MTBE had the highest unit treatment costs of any of the ether AOs at pH above neutral. It should be noted that a significant disadvantage of advanced oxidative treatment of MTBE and the ether AOs is the formation of oxidation byproducts many of which are biorecalcitrant (e.g., TBA, *t*-butyl formate, etc.). Depending on the treatment objective, removal of these byproducts could require significantly greater oxidant dosages and related costs as compared with treating the parent compound alone.

This study has shown that alternative ethers are generally more amenable than MTBE to treatment by air stripping, carbon adsorption, and advanced oxidation. TBA may be more difficult to treat with air stripping and potentially more costly by AOPs. EtOH is also difficult to treat with these common processes, though offers a significant advantage of being readily biodegradable.

III-5. References for Chapter III.

- [1] American Petroleum Institute (2000). "Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE." Pub. Number 4699. Washington, D.C.
- [2] Buxton, G. V., Greenstock, C. L., Helman, W. P., and Ross, A. B. (1988). *J. Phys. Chem. Ref. Data*, 17, 513-886.
- [3] Calgon Carbon Oxidation Technologies (1996). *AOT Handbook*, Calgon Carbon Corporation, Markham, Ontario, Canada.
- [4] Cater, S. R., Stefan, M. I., Bolton, J. R., and Safarzadeh-Amiri, A. (2000a). "UV/H₂O₂ Treatment of Methyl tert-Butyl Ether in Contaminated Waters." *Environ. Sci. Technol.*, 34 (4), 659-662.
- [5] Cater, S. R., Dussert, B. W., and Megonnell, N. (2000b). "Reducing the Threat of MTBE-Contaminated Groundwater." *Pollution Engineering*, May, 36-39.

- [6] *Chemical Engineering* (1980). Economic Indicators Section, June 16.
- [7] *Chemical Engineering* (2002). Economic Indicators Section, 109 (5).
- [8] Cornwell, D. (1990). Air Stripping and Aeration. in *Water Quality and Treatment*, 4th Ed., McGraw-Hill, New York.
- [9] Crittenden, J.C., Ferrigan, J. K., and Hand, D. W. (1986). "Design of rapid small-scale adsorption tests for a constant diffusivity." *J. Water Pollution Control Federation*. 58 (4), 312-319.
- [10] Delzer, G. C., Zogorski, J. S., Lopes, T. J., and Bosshart, R. L. (1996). "Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States 199-95." Report 96-4145. U.S. Geological Survey Water-Resources, Rapid City, SD.
- [11] Environmental Protection Agency (1994a). "Health risk perspectives on fuel oxygenates." Report EPA 600/R-94/217. Washington, D.C.
- [12] Environmental Protection Agency (1994b) "Chemical Summary for MTBE," Document EPA 749-F-94-017a. Washington, D.C.
- [13] Eibenberger, J. (1980). "Pulse radiolytic investigations concerning the formation and the oxidation of organic radicals in aqueous solutions." Ph.D. Thesis, Vienna Univ., Vienna, Austria, 95.
- [14] Hunt, J., Greenstock, C., Bronskill, M. (1972) *Int. J. Radiat. Phys. Chem.*, 4, 87.
- [15] Kang, J., and Hoffman, M. R. (1998). "Kinetics and mechanism of the sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation in the presence of ozone." *Environmental Science and Technology*, 32(20), 3194-3199.
- [16] Karpel Vel Leitner, N., Papailhon, A. L., Croue, J. P., Peyrot, J., and Dore, M. (1994). "Oxidation of methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE) by ozone and combined ozone/hydrogen peroxide." *Ozone Sci. Eng.*, 16, 41-54.
- [17] Keller, A. A., Sandall, O. C., Rinker, R. G., Mitani, M. M., Bierwagen, B., and Snodgrass, M. J. (2000). "An Evaluation of Physicochemical Treatment Technologies

- for Water Contaminated with MTBE.” *Groundwater Monitoring and Remediation* Fall, 114 – 126.
- [18] Liang, S., Palencia, L. S., Yates, R. S., Davis, M. K., Bruno, J., and Wolfe, R. L. (1999). “Oxidation of MTBE by Ozone and Peroxone Processes.” *J. Am. Water Works Assoc.*, 91(6), 104-114.
- [19] Mackay, D., Shiu, W. Y., and Ma, K.C. (1993). *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals—Volatile Organic Chemicals*, Vol. 3. Lewis, Chelsea, MI, USA.
- [20] McKinnon, R. J. and Dyksen, J. E. (1984). “Removing Organics from Groundwater Through Aeration Plus GAC.” *J. Am. Water Works Assoc.*, May 42-47.
- [21] Melin, G., editor (2000). “Treatment Technologies for Removal of Methyl Tertiary Buyl Ether (MTBE) from Drinking Water.” Report NWRI-99-06. Center for Groundwater Restoration and Protection, National Water Research Institute.
- [22] Merenyi, G., and Lind, J.S. (1980). “Role of a peroxide intermediate in the chemiluminescence of luminol. A mechanistic study.” *J. Am. Chem. Soc.*, 102,5830-5.
- [23] Mezyk, S. P., Cooper, W. J., Bartels, D. M., O'Shea, K. E., Wu, T. (2001). “Radiation Chemistry of Alternative Fuel Oxygenates: Substituted Ethers.” *Journal of Physical Chemistry A*, 105(14), 3521-3526.
- [24] National Research Council (1999). *Ozone-Forming Potential of Reformulated Gasoline*. National Academy Press, Washington, D.C.
- [25] *Perry's Chemical Engineers' Handbook* (1997). 7th ed. New York: McGraw-Hill, Inc.
- [26] Squillace, P. J., Pankow, J. F., Kortes, N. E., and Zogorski, J. S. (1998). “Environmental Behavior and Fate of Methyl tert-Butyl Ether.” U.S. Geological Survey Fact Sheet, FS-203-96 (Revised 2/98).
- [27] State of California (2002). “Drinking Water Monitoring for MTBE.” <http://www.dhs.ca.gov/ps/ddwem/chemicals/mtbe/mtbeindex.htm> (site accessed Jan. 4, 2003). Department of Health Services, Sacramento, CA.

- [28] State of Maine (1998). "The Presence of MTBE and Other Gasoline Compounds in Maine's Drinking Water: A Preliminary Report." Maine MTBE Drinking Water Study, Augusta, ME.
- [29] State of New York (2000). "Final Report: Survey of Active New York State Gasoline Remediation Sites with Potential MTBE Contamination." Bureau of Spill Prevention and Response, Albany, NY.
- [30] Stumm W. and Morgan J. (1996). *Aquatic Chemistry*, 3rd Ed., Wiley Interscience, New York.
- [31] Sutherland J., Adams C., Kekobad J. (2003) "Treatment of MTBE by Air Stripping, Carbon Adsorption, and Advanced Oxidation: Technical and Economic Comparison for Five Groundwaters" In peer-review at *Water Research*.
- [32] Wagler, J.L. and Malley, Jr., J.P. (1994). "The Removal of Methyl Tertiary-Butyl Ether from a Model Ground Water Using UV/Peroxide Oxidation." *J. NEWWA* September: 236-260.

CHAPTER IV.

ANCILLARY STUDIES – ONGOING WORK

The results and conclusions presented in Chapters II, III, and IV addressed the specific objectives of this project as laid out in the original research proposals to MDNR and MPSTIF. Additional work on this topic is also being conducted which will be shared with the sponsors. While outside the original scope of work as defined by the proposal, this additional work will help better understand the application and limitations of the advanced oxidation processes for treating MTBE. This additional work is being funded internally by UMR. No additional costs will be incurred by either MDNR or MPSTIF.

As part of his doctoral dissertation, Justin Sutherland will conduct additional MTBE studies particularly as it pertains to oxidation byproducts of MTBE. A considerable amount of work has been conducted on the formation of advanced oxidation byproducts of MTBE itself. A key issue with AOP treatment of MTBE is the formation of certain biorecalcitrant byproducts (e.g., TBA and *tert*-butyl formate (TBF)). While in some instances regulators or consultants may not need to be concerned with the formation of TBA or TBF. However, in cases with their formation is at issue, the question arises: “How much additional oxidant, energy, and cost will be required to oxidize MTBE, TBA, and TBF to easily degradable, labile byproducts?” Current studies in our labs are addressing this question and will be reported to both MDNR and MPSTIF.

