ENVIRONMENTAL OCCURRENCE AND FATE OF ETHANOL AND MTBE GASOLINE OXYGENATES IN SURFACE WATER AND SHALLOW GROUNDWATER IN NEBRASKA

by

Yi Zhang

A DISSERTATION

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Agronomy

Under the Supervision of Professor Roy F. Spalding

Lincoln, Nebraska

May, 2003

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

DISSERTATION TITLE

Environmental Occurrence and Fate of Ethanol and MTBE Gasoline Oxygenates in Surface Water and Shallow Groundwater in Nebraska

BY

Yi Zhang

SUPERVISORY COMMITTEE:

	Approved	Date
Signature	Roy F. Spalding	4-9-03
Typed Name	Dr. R.F. Spalding	
Signature	S.D. Comfort	4-9-03
Typed Name	Dr. S.D. Comfort	
Signature	Derek M. McCallister	4/9/03
Typed Name	Dr. D.L. McCallister	
Signature	Dale Snow	4-9-03
Typed Name	Dr. D.D. Snow	
Signature	V. Zlotnik	4-9-2003
Typed Name	Dr. V.A. Zlotnik	
Signature	V.	
Typed Name		

University of Nebraska | GRADUATE COLLEGE

ENVIRONMENTAL OCCURRENCE AND FATE OF ETHANOL AND MTBE GASOLINE OXYGENATES IN SURFACE WATER AND SHALLOW GROUNDWATER IN NEBRASKA

Yi Zhang, Ph.D.

University of Nebraska, 2003

Advisor: Roy F. Spalding

Contaminations of fuel oxygenates pose a threat to the environment and human health. Oxygenates are more mobile in groundwater than other fuel components. It has put an increased emphasis on early detection and response to fuel leaks and spills. An innovative method using solid phase microextraction and gas chromatography / mass spectrometry (SPME-GC/MS) was developed to detect ethanol and TBA in low microgram per liter concentrations and MTBE, ETBE, TAME at nanogram per liter concentrations in water. SPME is sensitive for oxygenate analysis in water but its usage for alcohols may be affected in samples containing free product due to fuel matrix interfering effects on SPME fiber. Samples containing oxygenates should be stored at 4°C and analyzed within 3 mo. HCl or $HgCl_2$ properly preserves ethanol, TBA MTBE, ETBE, and TAME in water samples.

Fuel oxygenate pollution results from point and nonpoint sources. Shallow groundwater from 10 sites along Instate-80 (I-80) in Nebraska was analyzed using SPME-GC/MS for oxygenates and young groundwater ages were profiled by the CFC dating technique. Oxygenate concentrations in groundwater along I-80 were compared to 3 sites in agricultural areas with limited atmospheric deposition of oxygenates and those

in surface water in urban areas (Lincoln, NE). Nonpoint sources of oxygenates from vehicle emissions does not appear to affect the quality of shallow groundwater and urban surface waters even in high traffic areas in Nebraska. In groundwater from leaking underground storage tank sites in Nebraska, MTBE, ETBE, TAME, and TBA were detected at various concentrations but ethanol was below 10 mg/L. The decreasing trend of occurrence frequencies of 4 oxygenates was: MTBE >> TAME > TBA > ETBE.

A pulse of 220 mg L^{-1} ethanol and 15.8 mg L^{-1} bromide was injected into a shallow aquifer and monitored for 2.5 mo to estimate the persistence and transport of ethanol. Breakthrough curves were fit to the advection-dispersion model. First-order degradation constants ranged from 0.23 to 0.57 d^{-1} and its half-life values ranged from 1.29 to 3.24 d. Ethanol was not retarded (retardation factor, 0.99 ~ 1.01). How ethanol impacts behavior of BTEX plumes in groundwater needs further study.

ACKNOWLEDGMENTS

Funding for this research, provided through the Nebraska Ethanol Board, the Nebraska Corn Board and National Water Research Institute, is gratefully acknowledged. The assistance from Nebraska Department of Environmental Quality and Nebraska Department of Roads in LUST sampling is also appreciated.

Many people have helped me to complete this research and my Ph.D. studies along the way. I would like to express my deepest gratitude to my advisor Dr. Roy Spalding for his help and advise throughout my Ph.D. program at UNL. My many thanks also go to the rest of my supervisory committee, Dr. Dennis L. McCallister, Dr. Daniel D. Snow, Dr. Steven D. Comfort, and Dr. Vitaly A. Zlotnik, who have spent many hours in the classroom, in the laboratory, and in the discussion on my research. Dr. Joseph Skopp is greatly thanked for technical assistance in curvefitting and programming of ethanol in-situ experiment. The valuable instruction and assistance of all these advisors in my research are greatly appreciated.

I would also like to thank Dr. Thomas Ruher, Dr. Terry Smith, Dr. Kenneth Solomon, and Dr. Kurt Lo for their encouragement during my studies at UNL.

Many thanks to Mr. Jeff Toavs, Dr. Imtiyaz. Khan and Mr. Mark Burbach for field support and to Mr. David Cassada, Mr. Steve Monson and Mrs. Anita Sisco for lab assistance. I am indebted to the staff at the UNL Water Sciences Laboratory for all their help, patience and understanding during the completion of this work. In the laboratory, Dr. Daniel Snow was a valuable resource for everything from obtaining supplies to developing methodologies and interpreting results. The encouragement, knowledge and friendship of my fellow graduate students at UNL are also gratefully acknowledged.

Finally, I would especially like to give my deepest thank to my wife, Qun, for her ceaseless love, unyielding support and patience during my studies and work over the years. Qun has truly provided me inspiration and motivation to seek personal and professional goals, as well as the love and support to achieve them. A large part of my success is attributable to her. I will never forget these things. I owe a lot to my parents, my parents in law and other close family members for their constant encouragement and support in my life.

Table of Contents

List of Tables

List of Figures

INTRODUCTION

Methyl tert-butyl ether (MTBE), ethanol, tert-butyl alcohol (TBA), ethyl tert-butyl ether (ETBE), and tert-amyl ethyl ether (TAME) have been widely used since the 1970s in the US as oxygenates to help fuel burn more efficiently and to reduce vehicle exhaust pollution (Blue Ribbon Panel, 1999). MTBE and ethanol are the most commonly used oxygenates (White et al., 2002). More than 40% of the US population lives in areas where MTBE has been used (Bohm, 1999).

Oxygenate-related releases from point and nonpoint sources contaminate ground and surface waters. Increased use since 1980 combined with MTBE's high solubility, low soil sorptivity, and persistence have contributed to emerging environmental disaster. The USGS identified MTBE as the second most common contaminant in urban aquifers in the United States (Zogorski et al., 1997). In response, USEPA announced actions to significantly reduce or eliminate MTBE use and promote the use of safe alternatives like ethanol (Lazaroff, 2000).

Taste and odor concerns were pivotal in the USEPA's Office of Water (1997) establishing a drinking water advisory level of 20 to 40 ppb MTBE as a guidance limit for state and local regulators. Many states have established their own guidelines and standards for MTBE. Twenty-three states have established regulatory guidelines or standards for MTBE contamination in soil or groundwater or drinking water; MTBE levels that trigger cleanup efforts range from 10 ppb in New York to 240 ppb in Michigan (Blue Ribbon Panel, 1999; Nascarella et al., 2002).

Gasohol, gasoline with 10% ethanol (v/v), is consumed increasingly in the US and most notably in Minnesota, Nebraska, and Iowa (USEPA Office of Research and

Development, 1997). Ethanol production is booming in corn growing areas of the Midwest. Nebraska was the first state to market ethanol-blended gasoline (1930) and in 1978 was the first state to use gasohol in the US (Gomez et al., 1998). Ethanol has been widely utilized in Nebraska as a fuel oxygenate for about a decade (Blue Ribbon Panel, 1999).

Fuel ethers, mainly MTBE, are well documented in groundwater at LUST sites (Moran et al., 1999). However, ethanol is typically not analyzed in groundwater because it is not a regulated pollutant (Rice and Cannon, 1999), and the national surveys of the occurrence of ethanol in groundwater or surface water have not been completed (Blue Ribbon Panel, 1999). The lack of interest in ethanol may be partially due to its low toxicity and low persistence, and also because of the lack of a sensitive and reliable method to determine aqueous ethanol in parts per billion levels.

This dissertation is composed of five chapters that are published or submitted to journals for review. Chapters one through three describe laboratory tasks including: the analytical method development, method limitations, and appropriate sample preservation procedures. Chapter four documents the environmental occurrence of oxygenates in Nebraska's waters and chapter five monitors the fate and transport of ethanol in shallow groundwater.

Task one developed an analytical method for the measurement of ethanol and the other oxygenates at trace concentrations in aqueous samples. Analytical methods used for oxygenates include purge and trap with gas chromatograph (GC) or GC / mass spectrometry (MS), automated heated head space with GC or GC/MS, solid phase micro-extraction with GC/MS (SPME-GC/MS), and direct injection analysis. The SPME-

GC/MS method was developed to detect ethanol and TBA in low microgram per liter concentrations and MTBE, ETBE, TAME in nanogram per liter concentrations in water (Cassada et al., 2000). It offers advantages such as direct immersion, solventless extraction, high selectivity, and low MDLs for oxygenate analytes.

Task two investigated the applicability of the SPME method in analyzing oxygenates in aqueous samples containing varying concentrations of fuel components. In routine monitoring of fuel oxygenates at leaking underground storage tank (LUST) sites, groundwater may contain free product in addition to fuel oxygenates. SPME is quite sensitive for trace level oxygenates in aqueous samples; however, criticisms occur about use of the SPME in fuel contaminated sites due to high residual fuel contents interfering fiber extraction (White et al., 2002).

Task three established appropriate holding times and preservation techniques for analysis of oxygenates by the SPME method. Because MTBE hydrolyzes to TBA during analysis of acidified samples by the heated head space method (White et al., 2002), pH, preservative, and temperature effects were investigated during sample holding and SPME analysis.

Task four described the frequency of oxygenate occurrences in groundwater and surface water in Nebraska. Significant MTBE contamination has been reported from leaks, spills, and unburned fuel from recreational watercraft and boating (Bohm, 1999). Fuel oxygenate contamination was investigated in several lakes in Lincoln areas, some of which are commonly used by jet skiing enthusiasts. Rivers, creeks, and drainage ditches in urban settings receive fuel oxygenates from nonpoint and point sources scattered over the interfaces of environmental media. Qualitative and quantitative investigation on

oxygenates in these surface water bodies was completed to document the contamination levels of oxygenates from various sources (e.g., leaks, spills, runoff, and atmospheric precipitation) in surface waters in the Lincoln urban areas. LUSTs containing fuel are a major source of MTBE pollution in groundwater. In California, MTBE was found in 75% of 9000 LUST sites (Happel et al., 1999). In Kansas, where neither reformulated gasoline (RFG) nor oxygenated fuel use was required, MTBE has been found at 88% of 818 LUSTs (Hatten and Blackburn, 1999). Fuel oxygenates were investigated at eight LUST sites in Nebraska to document oxygenate contamination from the point source releases in groundwater. Task four also investigated the impact of atmospheric deposition as a source of fuel oxygenates from traffic emissions to shallow groundwater and surface water in Nebraska. Sources of oxygenates in groundwater and surface waters can include nonpoint sources such as vehicle emissions and the MTBE concentration in shallow groundwater can exceed 20 $\mu g\ L^{-1}$ beneath high vehicular traffic areas (Zogorski et al., 1997). The investigation occurred at several rural shallow groundwater sites, roadside areas along I-80, and at urban surface waters sampling sites. CFCs dates were determined to assess the relationships between young groundwater ages and contaminant profiles (Portniaguine and Solomon, 1998).

Task five monitored the fate and transport of ethanol in groundwater. Ethanol is infinitely soluble in water and does not adsorb on soil particles. Soil microorganisms preferentially degrade ethanol. In laboratory microcosms using mixtures of groundwater and soil, ethanol rapidly degrades both aerobically (100 $mg\ L^{-1}$ in 7 days, Corseuil et al., 1998) and anaerobically (100 $mg\ L^{-1}$ in 3-25 days depending on conditions, Corseuil et al., 1998; 96 $mg\ L^{-1}$ within 30 days, Suflita and Mormile, 1993; 100 $mg\ L^{-1}$ within 14 d,

Yeh and Novak, 1994). The behavior of ethanol was monitored in a sand and gravel aquifer.

This dissertation describes the development of an SPME-GC/MS method to analyze fuel oxygenates at trace levels in water in Chapter 1. Chapter 2 reports the effects of fuel components on the analysis by SPME in samples containing various amounts of fuel. Chapter 3 details the appropriate preservation methods and holding times for aqueous samples analyzed by the SPME method. Chapter 4 describes the occurrence of fuel oxygenates to waters potentially impacted by atmospheric deposition and spills in Nebraska. Chapter 5 relates to the fate and transport of ethanol in shallow groundwater aquifer.

REFERENCES

Blue Ribbon Panel. 1999. Achieving clean air and clean water. The report of the Blue Ribbon Panel on oxygenates in gasoline (EPA420-R-99-021, September 15, 1999).

Bohm. M. 1999. Methyl tertiary butyl ether (MTBE) is one of the few chemicals that can satisfy the oxygen requirement for cleaner burning fuels under the Clean Air Act and is used to increase octane in standard gasoline. November 12, 1999, Natural Resources Policy Studies Division, NGA Center for Best Practices.

Cassada, D.A., Y. Zhang, D.D. Snow, and R.F. Spalding. 2000. Trace analysis of ethanol, MTBE, and related oxygenate compounds in water using solid phase microextraction and gas chromatography / mass spectrometry. Analytical Chemistry, 72(19): 4654-4658.

Corseuil, H.X., R.C.F. Dos-Santos, and P.J.J. Alvarez. 1998. The influence of the gasoline oxygenate ethanol on aerobic and anaerobic BTX biodegradation. Wat. Res. 32:2065-2072.

Gomez, J., T. Brasil, and N. Chan. 1998. An Overview of the Use of Oxygenates in Gasoline (prepared by the California Environmental Protection Agency and California Air Resources Board, September 1998).

Happel, A.M., B. Dooher, and E.H. Beckenbach. 1999. MTBE impacts to California groundwater, UCRL-MI-133696, Environmental Protection Department, Environmental Restoration Division, Lawrence Livermore National Laboratory, University of California, Livermore, California.

Hatten, G., and G. Blackburn. 1999. Findings of Kansas MTBE Investigation, ASTSWMO MTBE Workshop Newsletter, 2(1).

Lazaroff. C. 2000. Clinton administration takes action to phase out MTBE. Environment News Service, March 20, 2000. available at the web http://ens-news.com/ens/mar2000/2000-03-20-08.asp.

Moran, M.J., J.S. Zogorski, and P.J. Squillace. 1999. MTBE in groundwater of the United States - occurrence, potential sources, and long-range transport. Report approved by the USGS for publication in Proceedings of the 1999 Water Resources Conference, American Water Works Association.

Nascarella, M.A., P. Kostecki, E. Calabrese, and D. Click. 2002. AEHS's 2001 survey of states' soil and groundwater cleanup standards. Contaminated Soil, Sediments, and Water, January/February Issue, 2002.

Portniaguine, O., and D.K. Solomon. 1998. Parameter estimation using groundwater age and head data, Cap Cod, MA. Water Resources Research, 34:637-645.

Rice, D., and G. Cannon. 1999. Executive Summary (Volume 1). Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenates (December 1999, UCRL-AR-135949 Vol.1).

Suflita, J.M., and M.M. Mormile. 1993. Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface. Environmental Science and Technology, 27:976-978.

USEPA Office of Research and Development. 1997. Research strategy for oxygenates in water workshop review draft. (September 5, 1997).

USEPA, Office of Water. 1997. Drinking Water Advisory: Consumer acceptability advice and health effects analysis on methyl tertiary-butyl ether (MTBE). December 1997.

White, H., B. Lesnik and J. Wilson. 2002. Analytical methods for oxygenates. LUSTLINE Bulletin 42, US EPA/OUST, October 2002.

Yeh, C.K., and J.T. Novak. 1994. Anaerobic biodegradation of gasoline oxygenates in soils. Water Environment Research, 66:744-752.

Zogorski, J.S., A. Morduchowitz, A.L. Baehr, B.J. Bauman, D.L. Conrad, R.T. Drew, N.E. Korte, W.W. Lapham, J.F. Pankow, and E.R. Washington. 1997. Fuel oxygenates and water quality: Current understanding of sources, occurrence in natural waters, environmental behavior, fate, and significance. *In* Interagency Assessment of Oxygenated Fuels, Chapter.2, p.2-1--2-80, Washington, D.C., Office of Science and Technology Policy, Executive Office of the President, Washington, D.C.

Chapter 1

Trace Analysis of Ethanol, MTBE, and Related Oxygenate Compounds in Water Using Solid Phase Microextraction and Gas Chromatography / Mass Spectrometry

ABSTRACT

Solid-phase microextraction (SPME) and gas chromatography/mass spectrometry have been combined for trace-level determination of very polar compounds in water, including the widely used gasoline oxygenates ethanol and methyl *tert*-butyl ether (MTBE). A relatively simple extraction method using a divinylbenzene/Carboxen/poly-(dimethylsiloxane) SPME fiber was optimized for the routine analysis of ethanol and MTBE in groundwater and reagent water. A sodium chloride concentration of 25% (w/w) combined with an extraction time of 25 min provided the greatest sensitivity while maintaining analytical efficiency. Replicate analyses in fortified reagent and groundwater spiked with microgram per liter concentrations of ethanol and MTBE indicate quantitative and reproducible recovery of these and related oxygenate compounds. Method detection limits were 15 $\mu g\ L^{-1}$ for ethanol, 1.8 $\mu g\ L^{-1}$ for *tert*-butyl alcohol, 0.038 $\mu g\ L^{-1}$ for *tert*-amyl methyl ether, 0.025 $\mu g\ L^{-1}$ for ethyl-*tert*-butyl ether, and 0.008 $\mu g\ L^{-1}$ for MTBE.