

IMPACTS OF RECREATIONAL WATERCRAFT USE ON CONCENTRATIONS OF  
METHYL TERTIARY BUTYL ETHER (MTBE) IN SURFACE WATERS IN TEXAS

THESIS

A Thesis Submitted to the Graduate Council in Candidacy for the Degree of  
Master of Applied Geography

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## **Abstract**

To determine whether motorized watercraft are a major factor in MTBE surface water contamination through recreation, surface water samples were collected in a multi-purpose reservoir (Lake Austin) during periods of high and low recreational watercraft use. A non-parametric, one-tailed, Mann-Whitney U two-sample analysis was used to determine if there was a significant difference between the summer and winter sampling. Concentrations of MTBE above the Texas taste and odor criteria of 15 ppb were not found in Lake Austin. Although a significant difference was found between the summer and winter concentrations (1.48 ppb) of MTBE ( $p < 0.0001$ ), MTBE contamination due to motorized recreational boating did not pose a health threat in Texas.

## **Chapter I**

### **Introduction**

As populations increase around the globe, the resulting industrialization of nations increasingly stresses the environment and its inhabitants. One of the stresses to the environment and to humans is pollution. Pollution comes in many forms and is caused by many factors such as soil contamination by leaching containers, water pollution from runoff of non-point source pollution in cities, and air pollution by industry and transportation. One of the most significant contributors to pollutants on Earth today is air pollution caused by the internal combustion engine used mainly in automobiles. In the last hundred years, vehicle numbers in the United States alone have increased from 8000 in 1900, to 50 million in 1950, to an estimated 220 million in the year 2000 (U.S. Department of Transportation 1999). With a current population of 270 million people in the U.S. (U.S. Census Bureau 1999) the number of automobiles is not likely to decrease. The convenience of automobile ownership has become an entrenched part of the culture and lifestyle of industrialized nations; with this convenience comes the high price of pollution.

As the use of automobiles, and consequently air pollution, increases, problems continue to arise related to air pollution such as environmental and health risks and even global warming. As a result, new processes and products are constantly being introduced to decrease the amount of air pollution produced and its impacts. One of the products designed for pollution reduction is methyl tertiary butyl ether (MTBE). MTBE is a product that, added to fuel, decreases the amount of air pollution produced by an automobile.

Although MTBE has been proven to reduce some pollutants caused by automobiles (most notably carbon monoxide and hydrocarbons), it has also been proven to leach easily through soils and contaminate water supplies. As MTBE use in the U.S. has increased dramatically since its introduction in 1979, water contamination, causing a different type of pollution than the one MTBE was produced to reduce, has become the overriding issue. As a result the search has begun for an alternative additive. Decreased use of MTBE is currently being recommended across the U.S. (U.S. Environmental Protection Agency 2000). The issue with MTBE is a controversial one of benefits versus risks. The benefits of the use of MTBE include that it is considered more economical and practical relative to other oxygenates. The risks relate to the health, aesthetic, and ecological hazards of its use. Currently, alternatives are considered more costly and equally as harmful to the environment, therefore, MTBE is the most common oxygenate used to date. Although most of the controversy takes place in the U.S. where MTBE use is substantially greater than in any other portion of the globe, MTBE use is not limited to the U.S. In Europe, as air pollution increases in many cities, emissions regulations are tightening and increased use of additives such as MTBE is being considered (Environment Agency 1999a). Use of MTBE and the associated controversies has become a global issue.

In the U.S., many states are required to use oxygenates in fuel in order to reduce smog or carbon monoxide emissions and most have opted for the use of MTBE rather than other, more expensive additives such as ethanol. Currently, 17 states and the District of Columbia use oxygenated gasoline either because of a Congressional mandate or



because they have voluntarily chosen to use it to help achieve their clean air goals (U.S. Environmental Protection Agency 1997). MTBE is used in 87% of these areas with ethanol being the second most commonly used additive (U.S. Environmental Protection Agency 2000). Texas is second only to California in numbers of automobiles and is therefore one of the most highly consumptive states in terms of MTBE. The cities of Houston, Dallas, and El Paso are all required to use oxygenated fuel, although El Paso uses mostly ethanol, and mainly during winter months.

As the use of MTBE has increased in order to reduce of air pollution, water pollution from the additive has also increased in public water supplies, resulting in some drinking water becoming unfit for human consumption. Most of the problems related to the use of MTBE are human health concerns due to contamination of the groundwater that in turn affects drinking water. In many states, this contamination has led to a phase-out of MTBE. In Texas, the legislature has introduced a bill to ban the substance, but like many states, strategies to phase in other oxygenates have not been developed.

MTBE is a volatile compound that readily evaporates when exposed to air. However, in groundwater, evaporation is much more difficult because MTBE may remain for long periods with no potential for escape through volatilization or degradation. For this reason, concerns for high levels of MTBE in water have focused more on groundwater than on surface water. Currently, there are many studies involving MTBE in groundwater and the problems associated with contamination of drinking water supplies (Moran et al. 2000; Pankow et al 1997; Luzzadder-Beach 1997) . However, few studies have looked at contamination from MTBE in surface waters. Although surface waters

can be contaminated by leaking storage tanks, spills, runoff, and air deposition during rainfall, one of the major contributors of MTBE to surface waters is thought to be recreational watercraft.

A search of the literature has revealed that geographers have not produced research specifically focusing on MTBE contamination of surface water due to recreational boating. Geographers (e.g., Kaltenborn 1998) have contributed related research such as how sense of place affects recreational choices. Geographers have studied groundwater contamination plumes in terms of behavior of pollutants and their distribution (Luzzadder-Beach 1997). Broader issues such as historical information on water contamination supporting legal cases have been studied by geographers as have the political and economic ramifications of water contamination. Spatial studies explaining population movements and political choices are peripheral works that contribute vital information to understanding the presence of, and reasons behind, pollution and the implications of policies made toward its remediation. With all of these studies mentioned, findings are far-reaching not only into the realm of geography but also into other areas of study. MTBE contamination related to recreational activities is yet another example of research that not only applies to the geographer but also to many other fields of study.

This study was designed to begin to look at the spatial and temporal aspects of motorized boating as related to MTBE contamination and explores the possibility that motorized watercraft (boats and personal watercrafts) are a major factor in MTBE surface water contamination through recreation. The study will attempt to quantify the level of

contamination in one reservoir in the City of Austin: Lake Austin. In order to provide data on other lakes throughout the state, results from random sampling in reservoirs across Texas will also be noted.

## **Chapter II**

### **Literature Review**

#### *Water*

Water covers over 70% of the Earth's surface and is one of the most important resources we have. It is an integral part of our daily lives and is essential to all life on the planet. The natural processes of most living creatures involve water in some form. Water keeps the planet green, is used to grow our foods, is used to process our products, and is essential to transportation. Surface water provides the aesthetic beauty and recreational opportunities in the forms of beaches, lakes, and rivers while both surface and groundwater provide the water we drink. Water and its many forms are all a part of the hydrologic cycle that begins with evaporation and is returned to earth in the form of rain, hail, sleet, snow, and fog. Precipitation replenishes the surface and groundwaters to begin the cycle once again.

#### *Groundwater and Surface Water*

Over 97% of the water on Earth is in the oceans. The remaining 3% is freshwater including both surface and groundwater. Groundwater, which is the water below the surface and in the soil, is slightly less than 1% of all water. Surface water includes the ice caps and glaciers (almost 2% of all water), and the rivers and lakes (approximately .01% of all water) (Texas Natural Resource Conservation Commission 2000b). About half of the human population drink groundwater and half drink surface water (U.S. Environmental Protection Agency 1998). Because we rely on both surface and

groundwater for drinking, it is vitally important that both sources are healthful and free of harmful impurities that may be harmful to human and nonhuman populations.

### *Pollution*

Although pollution is generally discussed in the form of “air” or “water” or “soils”, each of these types of pollution exist with the potential for creating one of the other types of pollution. Processes on earth are inter-related, each affecting the other. Pollution in air can create pollution in water. Impurities in soil can leach into groundwater that may affect surface water. Polluted surface water may recharge groundwater supplies, causing them to be polluted. Polluted water, along with the impurities, may also evaporate to cause other forms of air pollution through chemical reactions.

Ground and surface water can be discussed in the same way, i.e., polluting one will in many cases cause the other to become polluted. Groundwater and surface water are hydraulically connected; they constantly interact and replenish each other (U.S. Geological Survey 2000). Different pollutants act differently in groundwater and in surface water. Some groundwater pollutants can persist for many years while others dissipate rapidly. In groundwater, some pollutants will be naturally filtered by the rock formations that compose an aquifer. However, other pollutants may be dissolved in the water and persist for many years depending on the nature of the substance. In surface water and groundwater, the flushing rates for impurities vary with the pollutant and the hydrologic and climatic conditions. The amount of rainfall, the mining of the ground and

surface water, and the discharges to the water, affect the rate of recharge and ultimately the rate of pollutant removal (U.S. Geological Survey 2000).

There are many causes for water pollution. Contamination to both ground and surface water is increasing with increasing populations around the world. Bacteria from sewage that is not properly treated can get into drinking water and is a health risk to many populations, especially in rural communities and in countries lacking the infrastructure for treatment facilities. Pesticides and herbicides contain harmful, cancer causing components and create algae blooms due to input of excess nitrogen and phosphorus. Industrial plant discharges to surface water can include toxic metals and elevated water temperature that can be harmful to aquatic life. Runoff from cities and roads contains hydrocarbons from unburned fuels. Direct spills from storage tanks or leaking from inefficient engines can contaminate both air and water. Although we have gotten better at minimizing some of the most significant contaminations from point sources such as industry, growing populations continue to produce non-point source pollution introducing diffuse pollutants to our air, soils and water.

One of the contaminants creating concerns for water providers and consumers today is MTBE. Designed to reduce air pollution caused by automobiles, MTBE has been found to be a possible cancer-causing agent through ingestion from water and a threat to drinking water supplies due to the ability of extremely minute amounts to render large amounts of water undrinkable because of a noxious taste and odor (Texas Natural Resource Conservation Commission 2000a).

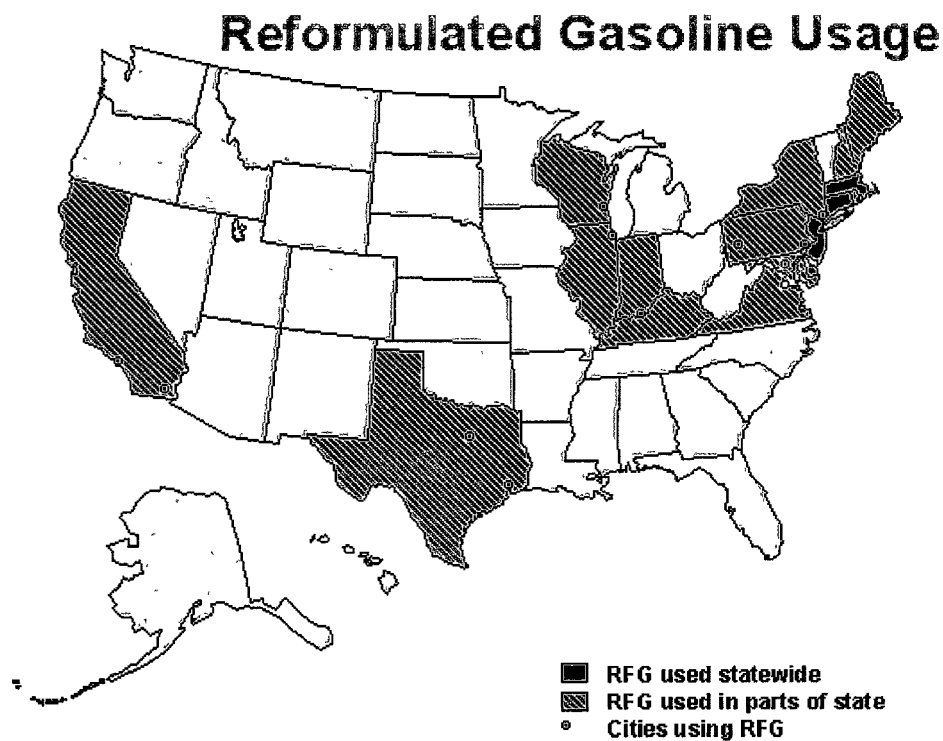
### *History of MTBE Use*

The Clean Air Act of 1990 established the use of oxygenates as gasoline additives to increase engine performance in automobiles and to reduce automobile air pollution. The passing of the act marked the beginning of the Oxygenated Fuel (Oxyfuel) and Reformulated Gas (RFG) programs launched by the Environmental Protection Agency (EPA) to reduce carbon monoxide and hydrocarbon emissions due mainly to automobiles. The Oxyfuel and RFG Programs were initiated in 1992 and 1998 respectively. MTBE use of 15% by volume for Oxyfuel and 11% by volume for RFG are sufficient to bring oxygen levels up to meet requirements in each program (Reuter et al. 1998; Franklin et al. 2000). The Oxyfuel Program requires 2.7% oxygen by weight and is mandated in many cities during winter for carbon monoxide reduction. Increased oxygen promotes more complete burning of fuel, producing carbon dioxide instead of carbon monoxide. The RFG Program requires 2.0% oxygen by weight and is required in some heavily polluted cities year-round to reduce smog and ozone (U.S. Environmental Protection Agency 2000). By lowering the Reid Vapor Pressure (RVP) (a measure of how easily a compound volatilizes), RFG reduces volatile organic compounds and toxic air emissions such as benzene, a known carcinogen.

MTBE is the most commonly used oxygenate for both the Oxyfuel and RFG Programs. Although initially used at very low levels in 1979 when it replaced lead as an octane booster (U.S. Environmental Protection Agency 2000), the use of MTBE has increased substantially in terms of both actual percentage found in gasoline and in the areas of the United States requiring it as an additive. Currently the Clean Air Act requires

areas of the country with the worst ozone-smog problems to use RFG. Cities required to use RFG are those that have exceeded the National Ambient Air Quality Standards for carbon monoxide and ozone (Figure 1). MTBE and ethanol are the two primary additives that are currently being used to meet the RFG mandate. During 1999, MTBE was used in over 80% of RFG and ethanol was used in 15% of RFG with RFG accounting for 30% of gasoline nationwide (U.S. Environmental Protection Agency 1997).

MTBE is the most widely used oxygenate for a number of reasons. MTBE is inexpensive to produce, has a high octane rating, is highly soluble (therefore readily mixes with other components in gasoline), dilutes undesirable compounds such as



**Figure 1.** Map of RFG cities and states (U. S. Environmental Protection Agency 2000)



sulphur and benzene, and refiners prefer MTBE because it can be blended at the refinery and shipped via pipeline (Texas Natural Resource Conservation Commission 2000a).

Other oxygenates are used but are not as preferred including: ethanol, ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), di-isopropyl ether (DIPE), and tertiary butyl alcohol (TBA). Of the five alternate types of oxygenates, MTBE is the most preferred (approximately 90%) with ethanol capturing about 7% of the oxygenate market (Franklin et al. 2000). Some of the alternatives are more expensive due to transport or production costs, and TAME and ETBE are thought to be similar to MTBE in terms of physical characteristics that pose threats to groundwater supplies (Franklin et al. 2000).

#### *Properties of MTBE*

MTBE is a chemical compound that is manufactured using the chemical reaction between methanol and isobutylene. MTBE is a synthetic chemical with the molecular structure  $\text{CH}_3\text{OC}(\text{CH}_3)_3$  and has a terpentine-like odor. MTBE is produced in massive quantities in the U.S. at about 200,000 barrels per day (U.S. Environmental Protection Agency 2000) and is produced almost exclusively for automobiles. MTBE is a volatile, flammable, and colorless liquid that has a relatively high vapor pressure and is water soluble to a significant degree (U.S. Environmental Protection Agency 1993). The properties of the additive are listed in Table 1.

**Table 1.** Properties of MTBE (Environment Agency 1999b)

Molecular Structure	CH <sub>3</sub> OC(CH <sub>3</sub> ) <sub>3</sub>
Molecular Weight	88.14 g/mole
Density	0.741 g/ml at 20deg C
Vapor pressure	313 Torr at 30 deg C
Freezing Point	-108.6 deg C
Boiling Point	55.2 deg C
Solubility in Water	4.8% at 20 deg C
Oxygen Content	18.2%
Energy Content	93.5 MTBU/gallon
Henry's Law Constant at 25 deg	C 0.022

The relatively high vapor pressure of MTBE allows it to volatilize readily from gasoline to air (Gullick et al. 2000). The solubility of MTBE is high, indicating why groundwater contamination easily occurs. The low Henry's Law Constant of MTBE indicates that it is much more likely to be in the aqueous state versus the gaseous state. However, Henry's Law constant alone cannot be used to predict the volatility of MTBE from natural water because volatilization also depends on environmental variables such as surface-water turbulence, and to some extent wind velocity (Squillace et al. 1997).

#### *Health and Aesthetic Effects of MTBE in Water*

Studies in rats indicate MTBE is carcinogenic but causal mechanisms are not understood (Franklin et al. 2000) . The National Science and Technology Council (1997) stated that there is sufficient evidence to classify MTBE as an animal carcinogen and to

regard it as having a human hazard potential. However, the report points out that risks associated with use of gasoline with MTBE are equal to or less than that of conventional gasoline. Because MTBE reduces benzene, a constituent of gasoline and a known human carcinogen, gasoline containing the additive is thought to be less harmful to human health.

MTBE is unique in that it will render water unpalatable at levels much lower than health effects levels. This is a positive characteristic of MTBE because it becomes too noxious to drink and the public will avoid water containing it thereby reducing the probability of consumption without detection. The EPA has not developed health standards for MTBE but has stated in a drinking water advisory document that there is little likelihood of adverse health effects at concentrations of 20-40 parts per billion (ppb) or below (U.S. Environmental Protection Agency 1997). Texas' taste and odor screening levels are 15 ppb while health effects levels have been set at 240 ppb (Texas Natural Resource Conservation Commission 2000a). However, like the EPA, Texas has not set a numeric standard to which concentrations of MTBE sampled must be compared in order to meet water quality requirements.

The general public has become aware of taste and odor concerns associated with water-supply systems contaminated with MTBE. While the possible health side effects are not well studied yet, there is considerable concern in communities where contamination has occurred. Recently, public concerns over MTBE were raised when the television program *60 Minutes* aired a segment on MTBE contamination throughout the country. In September of 1999, as a result of the concerns of the public and of water

purveyors, an independent Blue Ribbon Panel appointed by EPA Administrator Carol Browner recommended a significant reduction in the use of MTBE as an additive in gasoline (U.S. Environmental Protection Agency 1999A). The panel also requested Congress take action to lift the oxygenate mandate in the Clean Air Act (Browner 1999).

Most of the concerns surrounding MTBE contamination have been the result of major spills or leaking tanks that have affected groundwater. In surface water, few studies have focused on community concerns for recreational activities causing contamination. In broad terms, Kaltenborn (1998) found that environmental impacts associated with recreation due to motorized activity were less of a concern for people with a strong attachment to the place of recreation due to their perceived dependence on a motorized need for experiencing the outdoors themselves. It is probable that if the health and environmental risks are perceived to be minimal by most people using the resource, some contamination of MTBE to recreational areas is acceptable.

#### *Sources of MTBE Contamination*

A USGS study indicates the detection of MTBE in groundwater to be 21% in areas where MTBE is used (gasoline requiring an MTBE content greater than 5% by volume) compared to 2% where MTBE is not used (gasoline requiring an MTBE content less than 5% by volume) (Moran et al. 2000). In the areas effected, leaking underground storage tanks contribute more contamination than mobile (automobile) or production (industrial) sources. Squillace et al. (1997) note that low range concentrations in wells tested with no point source contributions must be partly from atmospheric sources.

Mobile and production sources contribute to low concentrations (less than 20 ppb) in groundwater generally through air deposition. The EPA fact sheet on emissions (U.S. Environmental Protection Agency 1999b) states that leaking storage tanks are the number one cause of contamination of water.

Pipeline spills containing RFG are a potential source of surface water contamination with very high levels of MTBE. During March, 2000 near Lake Tawakoni in north central Texas, Explorer Pipeline Company spilled approximately 500,000 gallons of gasoline with an approximate 9% MTBE concentration. A majority of the spill eventually made its way into the lake forcing the closure of two rural water-supply systems, and causing the City of Dallas to shut down its raw-water intake (Texas Natural Resource Conservation Commission 2000a).

Another potential source for surface water contamination is runoff. Precipitation can cause MTBE concentration in water to be as high as 3 ppb (Squillace et al. 1997; Pankow et al. 1997). A U.S. Geological Survey study (U.S. Geological Survey 1997) found that MTBE was the most frequently found volatile organic compound (VOC) in 86 streams tested in New Jersey, New York, and Long Island. The study showed that highly developed portions of the study areas had the highest percentages of MTBE. In another study by the USGS, storm water samples were found to have MTBE as the seventh most frequently found VOC. The cities sampled were not cities required to use RFG fuel (Delzer et al. 1999). Direct spillage from filling tanks or improper disposal can also contaminate water supplies with MTBE.

### *Remediation of MTBE Contamination*

Because of the properties of MTBE (high solubility and low adherence to soils), the problems associated with leaking storage tanks, and the high rate of MTBE detection, concerns regarding the manufacture and use of MTBE have mainly focused on the possibility of groundwater contamination effecting drinking water. As stated earlier, the major cause of MTBE contamination in water is leaking storage tanks (above and below ground). Currently, the EPA has tightened regulations to remove or upgrade leaking storage tanks with spill, overfill, and corrosion protection (U.S. Environmental Protection Agency 2000). Even though the concentrations of MTBE detected are generally below the levels set by the EPA for taste and odor advisories (Browner 1999), contamination at much higher levels, such as the one at Lake Tawakoni, has occurred and required remediation action.

There are technologies available for removal of MTBE from water supplies but they are costly and time consuming. Because MTBE is very soluble in water, treatment is more difficult for removal than for some of the other constituents in gasoline such as benzene (U.S. Environmental Protection Agency 2000). One of the most costly means of treatment is granular activated carbon (GAC). GAC is thought to be one third to one eighth as efficient at removing MTBE in comparison to benzene (Environment Agency 1999b). In the GAC process, passing contaminated water through a bed of activated carbon acts to remove organic compounds. On a household treatment system alone, the carbon bed lasted for only a month, treating water with very low concentrations of MTBE (Squillace et al. 1997).

Another method, air stripping, is a process by which contaminated water is sent through columns filled with packing material while air flows upwards. This process removes MTBE but high air to water volumes are necessary because MTBE does not readily separate from water into the vapor phase in comparison to more highly volatile compounds (U.S. Environmental Protection Agency 2000). Squillace et al. (1997) report that the air stripping process can be improved by heating the influent in order to increase potential for volatilization.

Finally, natural attenuation remains an option if the environmental risks associated with prolonged contamination are acceptable. In some cases, hydrologic conditions exist that favor more rapid removal and natural attenuation may also be the best option due to the low extent and levels of the contaminant. There are other techniques such as oxidation and biotreatment but these treatments have not been proven efficient to date (Squillace et al. 1997).

In soil, MTBE can be removed by a process known as soil vapor extraction (SVE). The SVE process removes MTBE above the saturated zone or water table by extracting the contaminant with a vacuum applied to the subsurface. The vapors are treated using GAC or activated carbon before releasing the remainder to the atmosphere (Environmental Agency 1999B). Another treatment for soil is low temperature thermal desorption (LTTD). In the LTTD process, the soil is heated to enhance volatilization and the vapors are treated in the same manner as with SVE.

### *Surface Water Contamination*

Although surface waters can be contaminated by leaking storage tanks, spills, runoff, and air deposition during rainfall, the major contributor of MTBE to surface waters is thought to be motorized recreational watercraft. Recreational boating activity has been linked to the relative amount (the amount of MTBE compared to other gasoline products) of hydrocarbon and MTBE concentration in reservoirs from several studies (Tahoe Regional Planning Agency 1999; U.S. Geological Survey 1997; McClurg 1998; Reuter et al. 1998; Lee 2000).

In one study in Lake Tahoe, larger concentrations of MTBE were found in areas where boating activity was substantially higher (Boughton and Lico 1998). Reuter and others (1998) found that 86% of the change in MTBE concentration in Donner Lake in California was explained by variation in watercraft use. In a study by the California Department of Water Resources, MTBE was found in 76% of the samples collected with the highest concentrations found near boat launches and during times of the highest boating activity (California Department of Water Resources 1999). An evaluation of management options for water supplies by the University of California-Davis (Kalman and Lund 1998) found that MTBE concentrations were highest in reservoirs allowing recreational boating.

In Texas, an unpublished study by the Lower Colorado River Authority (LCRA) in 1999 found MTBE concentrations during a long holiday weekend ranging from non-detect to 45.8 ppb, often nearing and sometimes exceeding the taste and odor threshold in Texas of 15 ppb (Guajardo, personal communication 2001). Levels of MTBE lowered



significantly approximately 5 weeks after the study when recreational activity decreased significantly. Another unpublished study by the Texas Parks and Wildlife Department (TPWD) in 1999 found MTBE ranging from non-detect to 13.2 ppb during summer recreation (Radloff, personal communication 2000). The Texas Natural Resource Conservation Commission and the USGS conducted a survey of 46 reservoirs in Texas during summer months and found levels ranging from non-detect to 2.98 ppb (Texas Natural Resource Conservation Commission 1999b). Lee (2000) found MTBE concentrations to increase significantly at most sites during recreational months on Lake Lewisville in Texas.

The contamination in surface water is most often caused either by leaks and spills during refueling or from unburned fuel being released during the boating activity (Reuter et al. 1998). The release is partially due to incomplete combustion of fuel in two-cycle engines mainly used in personal watercraft. Two-cycle engines release gasoline and associated additives into the environment at a rate ten times that of four-cycle engines (Tahoe Regional Planning Agency 1997, 1999). Over 30% of MTBE initially contained in fuel tanks of two-cycle watercraft is known to get deposited into the water during operation (Tahoe Regional Planning Agency 1999). In addition to the MTBE, benzene and toluene, also known carcinogens, are also being loaded into lakes during high recreational use.

The purpose of this study was to quantify levels of MTBE during high (summer months when boat counts average >50 per day) and low (winter months when boat counts average <10 boats per day) recreational watercraft use, and with these data, determine if

motorized watercraft (boats and personal watercrafts) are a major factor in MTBE surface water contamination through recreation. A summary of random sampling of reservoirs in the State of Texas is also provided in order to reveal other potential areas of MTBE contamination and to indicate where other sampling of MTBE has occurred in Texas.

## Chapter III

### Study Sites

Lake Austin in Austin Texas was chosen for the intense data collection portion of the study (Figure 2) due to its accessible location, intense use for recreational boating, and the fact it is a drinking water supply for the City of Austin. Lake Austin is a small reservoir that has 100 miles of shoreline and is 20 miles in length. The lake's maximum

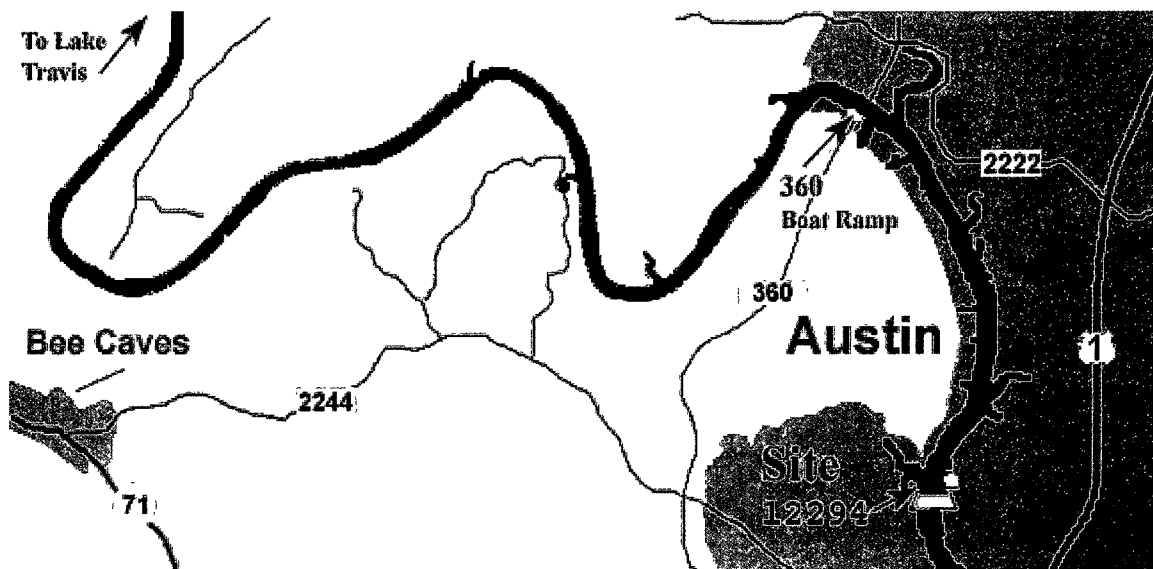


**Figure 2.** Downstream End of Lake Austin, MTBE sampling site 12294. Austin West USGS 7.5 minute topographic map.

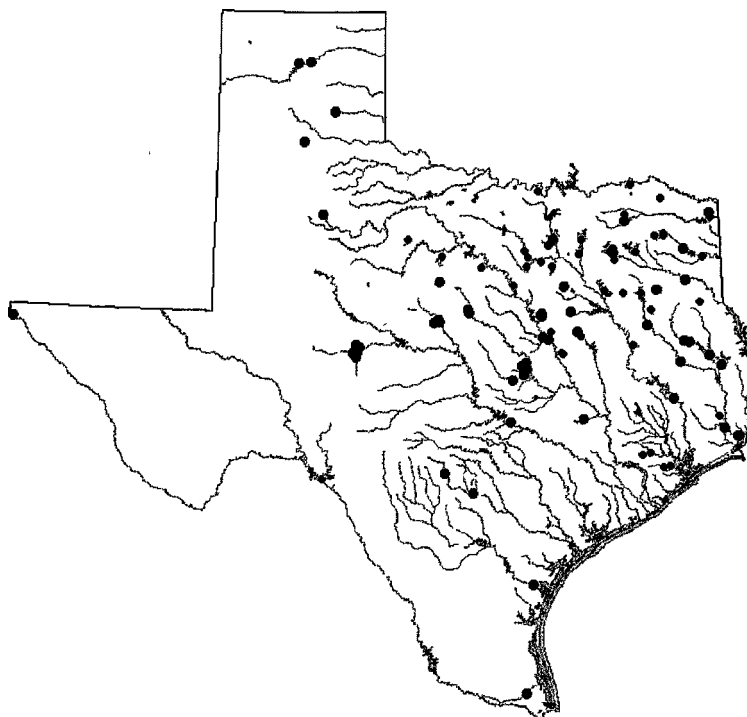
width is 0.3 miles and maximum depth is 30 feet. The lake's capacity is 21,000 acre feet with 1500 acres of surface area. The lake is part of what is known as the Highland Lakes system, which is a series of lakes formed with multiple dams to the Colorado River and supplies water for municipal, agricultural, and industrial use to the City of Austin and surrounding and downstream areas. The reservoir is flanked mostly by private homes, many having private boat docks for recreational use. Public access to the lake is limited to three public boat ramps. There are two marinas that supply gasoline and several restaurants with boat docks for public use. Summers are characterized by sometimes heavy boat traffic, while winters are quiet with occasional fishing use.

One sampling site (12294) was chosen near the drinking water intake at the downstream portion of the reservoir approximately 100 meters from Tom Miller Dam. This site was chosen due to the fact that surface water concerns for MTBE pertain generally to drinking water taste and odor. This site is near one of the public boat ramps on the lake and receives moderate to heavy boat traffic. Boat traffic is not as dense here as it has been observed to be at the larger boat ramp at Highway 360, approximately 20 miles upstream (Figure 3).

The state of Texas has 11,247 named water bodies, 203 of which are major reservoirs (greater than 5000 acre feet) (Texas Natural Resource Conservation Commission 1996). For the statewide portion of the study, approximately 10%, or 21 of the major reservoirs were chosen (Figure 4).



**Figure 3.** Full view of Lake Austin. Created from Texas Outside website map of Lake Austin at <http://www.texasoutside.com/>.



**Figure 4.** MTBE statewide TNRCC sampling sites

## **Chapter IV**

### **Methods and Analysis**

Lake Austin samples were collected on Sundays and Wednesdays during ten weeks of the summer and early fall season (June through October 2000). These weeks represent the times the lake is most heavily impacted by recreational boating according to City of Austin Park Police. Additionally, samples were taken during ten weeks of the colder months (December through February, 2000 and 2001) representing times where virtually no boating activity exists and MTBE contamination by boating activities is at a minimum. Statewide, samples were collected twice, mainly during warmer months, on random days of the week. The day of sampling is random due to the addition of MTBE to the list of water quality parameters already scheduled by TNRCC regional staff for collection. The samples were collected at reservoirs that are public water supplies and at selected stream sites near industrial petroleum facilities or major urban developments.

On Lake Austin, exact boat counts were taken on one Sunday and one Wednesday during the warmer and the cooler months by traveling the entire length of the lake and counting the boats being operated at the time of the count. Boats at docks were not counted unless docked at temporary docks such as restaurants or pumping stations. Field observations were made of the relative (high, medium, or low) amount of boating activity on the statewide sites and noted by TNRCC regional staff.

Samples were collected in 40 ml volatile organics analysis (VOA) bottles pre-preserved with 0.2 ml of concentrated hydrochloric acid (HCL). Samples were collected

under the surface of the water (~0.3m) with a gloved hand. The VOA bottles were then checked to insure that no air bubbles were present. Samples were put on ice, returned to the TNRCC lab, and kept refrigerated prior to shipping.

Trips blanks were included for each sample day and were handled and preserved exactly the same as the field samples. The blanks contained deionized water pre-filled in a laboratory setting. The blanks were then taken to the sampling location but never opened in order to prove MTBE does not contaminate the vial from the gaseous phase through the septum (seal). The blanks were carried to the sample site from the laboratory and kept in the same cooler as the field samples. One duplicate sample was collected once per month or every 10 samples in order to compare two samples from the same time and site for quality assurance purposes (Texas Natural Resource Conservation Commission 1999a).

Samples were shipped overnight on ice to the LCRA lab in Austin to be analyzed for volatile organic compounds (VOC) by Method 524 with a note that MTBE is the primary constituent of concern. Method 524 is a general purpose method for the identification and quantification of purgable volatile organic compounds in surface water, groundwater, or drinking water (U.S. Environmental Protection Agency 1992). VOCs are extracted from the sample matrix by bubbling an inert gas through the sample. Purged components are trapped in a tube containing a suitable sorbent material. The tube is then heated and backflushed with helium to desorb the trapped components into a capillary gas chromatography (GC) column interfaced with a mass spectrometer (MS).

Compounds eluting from the GC column are identified by comparing their mass spectra and retention times to a computerized data base.

Statistical analysis of samples included a non-parametric, one-tailed, Mann-Whitney U two-sample analysis to determine if there was a difference between the summer sampling (June through October) and the winter sampling (December through February) levels of MTBE at the site. The Mann Whitney test, also known as the Wilcoxon rank-sum test, is appropriate for distributions that may not be normally distributed and is designed to determine if two groups come from the same population or whether they differ only in the location of the median. Specifically, the Mann Whitney U tests if one group tends to have larger values than the other by ranking each value from each group and summing the ranks to provide rank sum statistics.



## Chapter V

### Results

The difference between concentrations of MTBE in the summer, high recreational use samples and the winter, low recreational use, samples in Lake Austin was highly significant at  $p < .0001$  (Table 2). Although concentrations were generally low with a median of 1.48 ppb in the summer months, concentrations were zero for all samples during all sampling events in the winter. Figures 5 and 6 show MTBE concentrations and temperatures respectively in Lake Austin. During peak recreational use, generally when air and water temperatures are comfortable for contact recreation, boating activity increases (Table 3) and MTBE concentrations are higher (Figures 5 and 6).

**Table 2.** Statistical Results of Lake Austin MTBE Comparison between Summer and Winter Data

Summer samples (n)	20
Summer median	1.48
Winter samples (n)	20
Winter Median	0.00
Wilcoxon test statistic (w)	600
Significance (p)	<.0001

**Table 3.** Boat Counts in Lake Austin, Summer and Winter

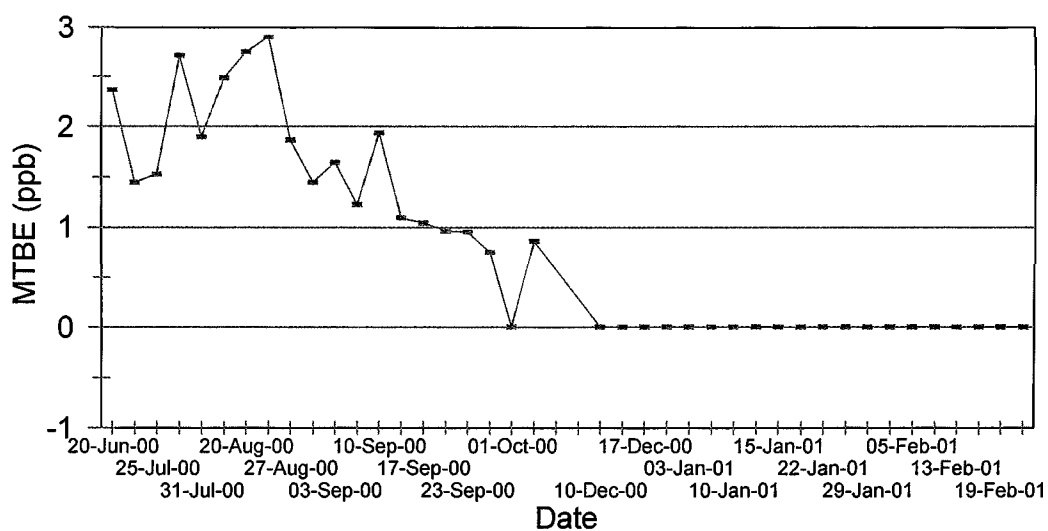
Date/Time	Boats	Personal Watercraft *
September 23, 3 p.m. (Sunday)	127	22
September 27, 6 p.m. (Wednesday)	46	2
February **	2-3	0
March 29, 5 p.m. (Thursday) ***	23	
March 31, 3 p.m. (Saturday) ***	158	

\* Personal watercraft are defined as crafts such as jetskis, waterbikes, or seadoos designed for use by one or two persons.

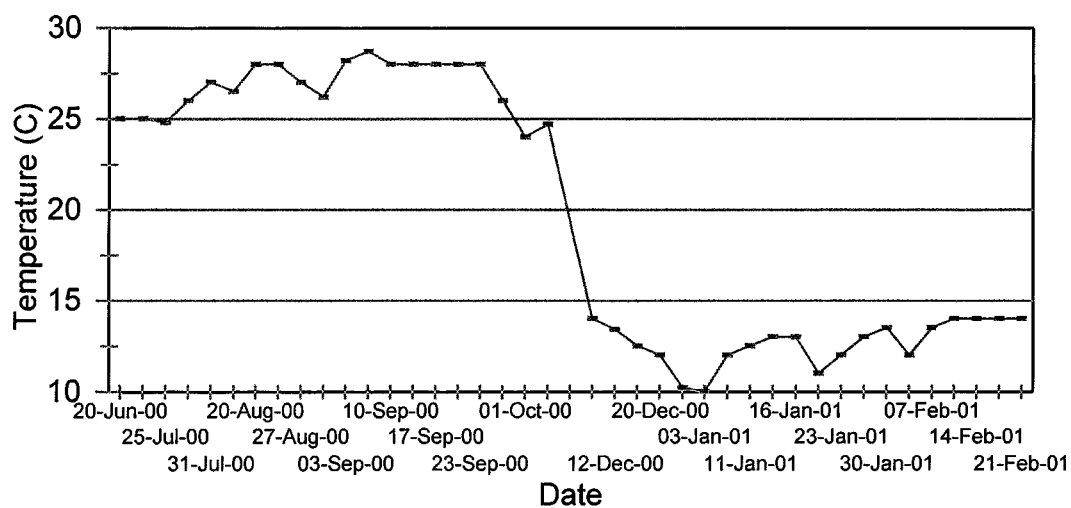
\*\* One of the first warm weekends of the spring. No personal watercraft data available.

\*\*\* Estimated by the City of Austin Park Police through observations from closed boat ramps during the time the lake levels were lowered.

In random sampling of other sites in Texas, MTBE concentrations were generally zero with only three exceedances of the taste and odor criteria of 15 ppb in the Houston Ship Channel which is not a drinking water supply. In reservoirs sampled, MTBE concentrations greater than zero but less than 15ppb were observed in 61 of 420 samples, representing about 15% of the samples (Appendix C). The majority of the 61 samples were from Lake Grapevine and were observed during times of heavy recreational boating activity. Other studies conducted in Texas also found concentrations of MTBE above zero mainly during summer weekends with high boating activity (Appendices C, D, E, F).



**Figure 5.** Lake Austin MTBE concentrations by date.



**Figure 6.** Lake Austin temperatures by date.

## **Chapter VI**

### **Discussion**

MTBE is a volatile compound that readily dissipates in air especially when there is wind and associated turbulence on the water. Due to these characteristics, site selection is important in order to capture MTBE contamination before volatilization. Areas where boats congregate are optimal for finding contamination, however, if the goal is to measure possible effects to drinking water, sites near drinking water intakes are also desirable. Site 12294, Lake Austin was chosen to assess MTBE levels at the intake. Higher concentrations of MTBE were found by LCRA on Lake Austin at the Highway 360 boat launch where boat traffic is considerably higher. The concentrations of MTBE decreased downstream at the water intake site, indicating evaporation had removed some of the contaminant.

It is important to note that Austin is not a “non-attainment” (RFG required in gasoline sold) area and therefore most gas stations do not sell RFG. MTBE is present in gasoline but at lower levels than non-attainment cities where National Ambient Air Quality Standards (NAAQS) are not being met. Quantification of contamination becomes more difficult when low levels of the constituent of choice, in this case MTBE, are present in the source of the vector contaminant, gasoline. Moreover, the LCRA laboratory, where samples were taken, have a Practical Quantification Limit (PQL) of 2.0 ppb for MTBE. The Method Detection Limit is .34 ppb, however, providing 99% confidence in the results above that number (Appendix G).

Although MTBE is a volatile compound, which reduces its impact from surface water to drinking water supplies, this may confound results by evaporation of much of the compound before the sample is taken. Boat traffic will generally be at a peak during the weekend but many samples in the statewide study were taken during the week and possibly late in the week. MTBE levels that may be relatively high on the weekend may dissipate before the sampling event takes place. Extraction of drinking water generally occurs on a continual basis and higher concentrations of MTBE may exist during and just after weekends and holidays but may not be found by surface water monitoring personnel.

In January, the LCRA lowered the level of lake Austin in order to eradicate exotic plant species through dessication and freezing. The lowering of the lake also allowed local property owners to perform maintenance on docks. Because the level changes rendered docks and launches unusable during this period, launching a canoe was impossible. Therefore, the sampling site near the water intake was moved approximately 50m adjacent to the water intake structure. The level of the water was fortuitous because it restricted boating to only a few small fishing vessels able to gain access to the water. The already low winter boating activity was reduced to almost none providing good conditions for comparison of MTBE concentrations during high activity versus low activity.

The results provide data and information to support the hypothesis that contamination of drinking water with MTBE is occurring in water bodies where recreational boating is practiced. In most water bodies studied in Texas, levels of MTBE are not found to be high enough to impose health risks due to ingestion. However, levels

of MTBE that produce a noxious taste and odor are reached during peak recreational activity, mostly during summer weekends. It is important to note that when high levels of MTBE have occurred, they have rapidly decreased in a short period of time.

Lastly, MTBE pollution from two stroke engines will decrease with the introduction of more efficient engines that are mandated to cut hydrocarbon (including MTBE) emissions by 80% starting in 2006 (NA Mercury Marine 2001)."

## **Chapter VII**

### **Conclusion and Recommendations**

To determine whether motorized watercraft are a major factor in MTBE surface water contamination through recreation, surface water samples were collected in a multi-purpose reservoir (Lake Austin) during periods of high and low recreational watercraft use. A non-parametric, one-tailed, Mann-Whitney U two-sample analysis was used to determine if there was a significant difference between the summer and winter sampling. Concentrations of MTBE above the Texas taste and odor criteria of 15 ppb were not found in Lake Austin. Although a significant difference was found between the summer and winter concentrations of MTBE ( $p < 0.0001$ ), MTBE contamination due to motorized recreational boating did not pose a health threat in Texas.

In surface waters, recreational boating activities do not appear to be causing concentrations of MTBE to be high enough to pose health risks, however, little is known about human health risks regarding MTBE ingestion, especially at low levels. At high levels, contamination could pose possible threats to human health. More research into the effects of high and low levels of MTBE ingestion in humans is needed.

Because of the climate in Texas, boating activity is a recreation enjoyed for most of the year. Recommendations regarding the level of recreational boat use include careful planning to avoid excessive use of watercraft that contribute most to MTBE contamination in Texas surface water bodies. If MTBE concentrations increase, restrictions could be placed on all watercraft during days of expected high boating traffic to minimize the amount of MTBE in the lake. Two stroke engines could be phased out or

restricted to minimize direct input of fuel to reservoirs. Two stroke engines will be required to significantly reduce their emissions in 2006 and could eventually be legislated extinct by even more restrictive emission requirements. Pumping stations could be removed from the lake to avoid spillage during refueling. Research to determine a correlation between boat numbers and MTBE concentrations would help lake managers determine boating and fueling restrictions. And finally, if oxygenates continue to be required, states must weigh the health, environmental, and economic impacts of each available option as well as understand the risks versus the benefits of each oxygenate. With the right information, informed choices can be made.



**APPENDIX A**  
**LAKE AUSTIN MTBE DATA**

**Table A1.** Lake Austin MTBE data

<b>Sample ID Number</b>	<b>Sample Date</b>	<b>MTBE(ppb)</b>
0029713	20-Jun-00	2.36
0032035	24-Jul-00	1.44
0032037	25-Jul-00	1.52
0032038	30-Jul-00	2.70
0032039	31-Jul-00	1.89
0032041	01-Aug-00	2.48
0032042	20-Aug-00	2.74
0032043	23-Aug-00	2.89
0032045	27-Aug-00	1.86
0032047	30-Aug-00	1.44
0032048	03-Sep-00	1.64
0032050	06-Sep-00	1.22
0032052	10-Sep-00	1.93
0032053	13-Sep-00	1.09
0032055	17-Sep-00	1.04
0032056	20-Sep-00	0.96
0032057	23-Sep-00	0.95
0032059	27-Sep-00	0.75
0032062	01-Oct-00	0.00
0032060	04-Oct-00	0.86
0032063	10-Dec-00	0.00
0032065	12-Dec-00	0.00
0032066	17-Dec-00	0.00

<b>Sample ID Number</b>	<b>Sample Date</b>	<b>MTBE(ppb)</b>
0032068	20-Dec-00	0.00
0032070	31-Dec-00	0.00
0032071	03-Jan-01	0.00
0032072	10-Jan-01	0.00
0032074	11-Jan-01	0.00
0032075	15-Jan-01	0.00
0032077	16-Jan-01	0.00
0032078	22-Jan-01	0.00
0032080	23-Jan-01	0.00
0032081	29-Jan-01	0.00
0034685	30-Jan-01	0.00
0034686	05-Feb-01	0.00
0034688	07-Feb-01	0.00
0034689	13-Feb-01	0.00
0034692	14-Feb-01	0.00
0034693	19-Feb-01	0.00
0034695	21-Feb-01	0.00

**APPENDIX B**  
**LAKE AUSTIN TEMPERATURE DATA**

**Table B1.** Lake Austin temperature data

<b>Sample ID Number</b>	<b>Sample Date</b>	<b>Temp (C)</b>
0029713	20-Jun-00	25
0032035	24-Jul-00	25
0032037	25-Jul-00	24.8
0032038	30-Jul-00	26
0032039	31-Jul-00	27
0032041	01-Aug-00	26.5
0032042	20-Aug-00	28
0032043	23-Aug-00	28
0032045	27-Aug-00	27
0032047	30-Aug-00	26.2
0032048	03-Sep-00	28.2
0032050	06-Sep-00	28.7
0032052	10-Sep-00	28
0032053	13-Sep-00	28
0032055	17-Sep-00	28
0032056	20-Sep-00	28
0032057	23-Sep-00	28
0032059	27-Sep-00	26
0032062	01-Oct-00	24
0032060	04-Oct-00	24.7
0032063	10-Dec-00	14
0032065	12-Dec-00	13.4

<b>Sample ID Number</b>	<b>Sample Date</b>	<b>Temp (C)</b>
0032066	17-Dec-00	12.5
0032068	20-Dec-00	12
0032070	31-Dec-00	10.2
0032071	03-Jan-01	10
0032072	10-Jan-01	12
0032074	11-Jan-01	12.5
0032075	15-Jan-01	13
0032077	16-Jan-01	13
0032078	22-Jan-01	11
0032080	23-Jan-01	12
0032081	29-Jan-01	13
0034685	30-Jan-01	13.5
0034686	05-Feb-01	12
0034688	07-Feb-01	13.5
0034689	13-Feb-01	14
0034692	14-Feb-01	14
0034693	19-Feb-01	14
0034695	21-Feb-01	14

**APPENDIX C**  
**TEXAS STATEWIDE MTBE DATA**

**Table C1.** Texas statewide MTBE data

Sample ID	Sample Date	Site	MTBE (ppb)
0029052	03/28/00	Neches River at SH87 duplicate	0
0029048	03/28/00	Neches River at SH 87	0
0029049	03/28/00	Neches River at IH 40	0
	03/28/00	Trip Blank	0
	03/28/00	Field Blank	0
0025800	04/04/00	Twin B. North Pool	0
0025804	04/04/00	Twin Bluff (Trip Blank)	0
0025805	04/05/00	Lake Nasworthy at the Dam	0.51
0025806	04/05/00	Lake Nasworthy at S. Cord	0
0025807	04/05/00	Twin Buttes S. Pool @ Dam	0
0025808	04/05/00	O. C. Fischer @ Dam	0
	04/05/00	Trip Blanks	0
0029062	04/10/00	Sam Rayburn Reservoir below Paper Mill Creek	0
0029063	04/10/00	Paper Mill Creek at Angelina River	0
0029064	04/10/00	Angelina River above Paper Mill Creek	0
0029060	04/10/00	Trip Blank	0
0029061	04/10/00	Field Blank	0
0029065	04/10/00	Angelina River at US59	0
0029066	04/10/00	Angelina River at US59 duplicate	0
0029733	04/13/00	Concho River @ Irving St Bridge in San Angelo	0
0029734	04/13/00	Trip Blank	0
0030419	04/13/00	Navarro Mills Reservoir, Mid Lake, Near Dam	0
0030420	04/13/00	Navarro Mills Reservoir, Mid-Lake, Near Dam	0
	04/13/00	Trip Blank	0
0029596	04/13/00	Trip Blank	0
0029597	04/13/00	Field Blank	0
0029584, 585 593, 594, 595	04/13/00	Corpus Christ Inner Harbor - Navig. Bld	0
30073	05/03/00	Pat Mayse Reservoir @ Raw Water Intake	0
0030074		Trip Blank	0
0030278	05/03/00	Lake Aquilla near dam	0
0030279	05/03/00	Duplicate-Lake Aquilla near dam	0
0030285	05/03/00	Lake Aquilla-Aquilla Creek Arm	0
0030284	05/03/00	Lake Aquilla at FM 1947	0
0030280	05/03/00	Trip Blank - using TNRCC Lot # V032700JM	0



Sample ID	Sample Date	Site	MTBE (ppb)
0030292	05/04/00	Lake Mexia near dam	0
0030293	05/04/00	Trip Blanks	0
0030066	05/08/00	Lake O'The Pines NETX - MWD	0
0030067	05/08/00	Lake O'The Pines @NETX MWD - Trip Blank	0
0030299	05/09/00	Trip Blanks	0
0030299	05/09/00	Lake Brazos at LaSalle Avenue	0
0029882	05/10/00	Rio Grande at Courchesne Bridge (Trip)	0
0029883	05/10/00	Rio Grande at Courchesne Bridge	0
0029884	05/10/00	Rio Grande at Courchesne Bridge (Duplicate)	0
0030093	05/11/00	Trip Blank - Lake Tyler @ Langley Island - TB	0
0030094	05/11/00	Lake Tyler @ Langley Island	0
0030300	05/16/00	Old Marlin Lake	0
0030304	05/16/00	New Marlin Lake	0
		Trip Blank	0
0029979	05/17/00	Canadian River at Plemons (Trip Blank)	0
0029980	05/17/00	Canadian River at Plemons	0
0029981	05/17/00	Canadian River at Plemons (Field Duplicate)	0
0029982	05/17/00	Canadian River at Plemons (Field Blank)	0
0030305	05/17/00	Trip Blanks	0
0030303	05/17/00	Lake Somerville near Dam	0
0030307	05/18/00	Lake Waco near dam	0
0030308	05/18/00	Trip Blank	0
0030111	05/18/00	Trip Blank - Lake Bob Sandlin @ Titus County Intake	0
0030112	05/18/00	Lake Bob Sandlin @ Titus County Intake	0
0029507	05/23/00	Waxahachie Reservoir	0
0029509	05/23/00	Trip Blank	0
0030116	05/22/00	Trip Blank	0
0030117	05/22/00	Lake Wright Patman in Elliot Creek Arm	0
0030322	05/24/00	Trip Blank Lot V042400RB	0
0030321	05/24/00	Stillhouse Hollow Reservoir at Headwaters	0
0030319	05/24/00	Stillhouse Hollow Reservoir near dam	0
0030317	05/24/00	Belton Reservoir - Cowhouse Creek Arm	0
0030315	05/24/00	Belton Reservoir - Leon River Arm	0
0030313	05/24/00	Belton Reservoir near dam	0
0030128	05/25/00	Lake Palestine @ Tyler Intake	0
0030127	05/25/00	Trip Blank	0

Sample ID	Sample Date	Site	MTBE (ppb)
00030131	05/26/00	Trip Blank	0
00030132	05/26/00	Lake Fork at Quitman Intake	0
0028763	05/30/00	Medina R. Station 12811-A	0
0028764	05/30/00	Medina R. Station 12811-B	0
0028765	05/30/00	Medina R. Station 12811-D	0
0028766	05/30/00	Medina R. Station 12811-E	0
0025548	05/31/00	Medina Reservoir at Dam	0
	06/13/00	Trip blank	0
	06/13/00	Station A	3.22
	06/13/00	Station B	2.6
	06/13/00	Station C	2.82
	06/13/00	Station D	2.43
	06/13/00	Station E	2
	06/13/00	Duplicate	3.58
0030575	06/12/00	Sam Rayburn Reservoir at SH 147	0
0030576	06/12/00	Sam Rayburn Reservoir at SH147 - duplicate	0
0029093	06/12/00	Neches River at US59	0
0029096	06/12/00	Trip Blank	0
0029097	06/12/00	Neches River at US59 - duplicate	0
0028555	06/14/00	Trip Blank - Arroyo Colorado @ Low Water Bridge	0
0028554	06/14/00	Arroyo Colorado @ Low Water Bridge	0
0028553	06/14/00	Duplicate - Arroyo Colorado @ Low Water Bridge	0
0030579	06/14/00	Star Lake Canal	0
0030580	06/14/00	Star Lake Canal - Duplicate	0
0029860	06/14/00	Lake Brownwood at Dam	0
0029858	06/14/00	Lake Brownwood Hwy 279	0
0029856	06/14/00	Lake Brownwood at Goat Island	0
0029713	06/20/00	Ulrich Plant - Lake Austin	2.36
007971	06/22/00	Trip Blanks	0
007971	06/22/00	Lake Worth	0
007971	06/22/00	Eagle Mountain Lake	0.66
007971	06/22/00	N/A	0.79
007970	06/20/00	Trip Blanks	0
007970	06/20/00	Lake Arlington	0.87
0028778	06/21/00	Amistad Reservoir Buoy 1 (Station A)	0

Sample ID	Sample Date	Site	MTBE (ppb)
0028779	06/21/00	Amistad Reservoir Buoy 1 (Station B)	0
0028780	06/21/00	Amistad Reservoir Buoy 1 (Station C)	0
0028781	06/21/00	Amistad Reservoir Buoy 1 (Station D)	0
0028782	06/21/00	Amistad Reservoir Buoy (Station E)	0
0030149	06/21/00	Lake Tyler @ Langley Island	0
0030150	06/21/00	Trip Blank - Lake Tyler @ Langley Island	0
0030160	06/22/00	Lake Tawakoni @ City of Point Intake	0
0030161	06/22/00	Lake Tawakoni @ City of Emory Intake	0
0030162	06/22/00	Lake Tawakoni @ McBee Raw Water Intake	0
0030163	06/22/00	Lake Tawakoni @ Will's Point Raw Water	0
0030164	06/22/00	Duplicate - Lake Tawakoni @ Will's Point Raw Water	0
	06/22/00	Trip Blank	0
0030602	06/26/00	Neches River at IH-10	0.7
0030592	06/26/00	Neches River at SH87	0
0030603	06/26/00	Trip Blank	0
0029830	06/27/00	Lake Proctor near Dam	0
0029833	06/27/00	Proctor Headwaters	0
0029891	06/27/00	Rio Grande at Courchesne Bridge	0
0029892	06/27/00	Duplicate - Rio Grande at Courchesne Bridge	0
0029893	06/27/00	Field Blanks - Rio Grand at Courchesne Bridge	0
0030465	06/27/00	Trip Blank	0
0030463	06/27/00	Elm Fork @ SH121	0
0030464	06/27/00	Replicate - Elm Fork @ SH121	0
0029810	06/28/00	Lake Cisco at Dam	0
003630	06/29/00	Trip Blank	0
003630	06/29/00	Station A	4.15
003630	06/29/00	Station A Dup	4.43
003630	06/29/00	Station B	4.27
003630	06/29/00	Station C	3.64
003630	06/29/00	Station D	3.62
003630	06/29/00	Station E	2.96
003631	07/03/00	Trip Blank	0
003631	07/03/00	Station A	7.36
003631	07/03/00	Station B	4.49
003631	07/03/00	Station C	4.11
003631	07/03/00	Station D	3.84

Sample ID	Sample Date	Site	MTBE (ppb)
003631	07/03/00	Station E	3.45
007972	07/05/00	Trip Blank	0
007972	07/05/00	Station A	7.65
007972	07/05/00	Station B	5.57
007972	07/05/00	Station C	4.62
007972	07/05/00	Station D	4.45
007972	07/05/00	Station E	3.87
007972	07/05/00	Station A Dup	7.47
0030171	06/29/00	Lake Palestine at City of Tyler Raw Water Intake	0
0030191	06/29/00	Trip Blank - Lake Palestine @ City of Tyler Raw Wa	0
0030187	07/03/00	Cooper Lake @ NT MWSD Intake	0
0030177	07/03/00	Lake Murvaul @ Intake	0
0030176	07/03/00	Lake Cherokee @ Intake	0
0030178	06/30/00	Trip Blank - Lake Chrerokee at Intake	0
003632	07/07/00	Trip Blanks	0
003632	07/07/00	Station A	7.24
003632	07/07/00	Station B	5.31
003632	07/07/00	Station C	4.75
003632	07/07/00	Station D	4.71
003632	07/07/00	Station E	4.27
0030193	07/10/00	Big Creek Lake at City of Cooper Intake	0
0030194	07/10/00	Trip Blank - Big Creek at City of Cooper Intake	0
0030181	07/06/00	Lake Jacksonville, Upper Lake	0
0030182	07/06/00	Trip Blank - Lake Jacksonville, Upper Lake	0
0030200	07/10/00	Pat Mayse Reservoir @ Paris Intake	0
0030199	07/10/00	Trip Blank - Pat Mayse Reservoir at Paris Intake	0
0030198	07/07/00	Neches River @ City of Palestine Intake	0
0030196	07/07/00	Lake Athens	1.06
0030195	07/07/00	Trip Blank - Lake Athens	0
0030609	07/10/00	Trip Blank	0
0030611	07/10/00	Angelina River at US 59	0
0030617	07/10/00	Angelina River above Paper Mill Creek	0.6
0030625	07/11/00	Paper Mill Creek at Angelina River	0
0031488	07/13/00	Sam Rayburn Reservoir at Main Pool	0
0031489	07/13/00	Sam Rayburn at Main Pool - Duplicate	0
0030009	07/17/00	Trip Blank - Lake MacKenzie Near Dam	0

Sample ID	Sample Date	Site	MTBE (ppb)
0030014	07/17/00	Lake MacKenzie Near Dam	0
0030015	07/17/00	Duplicate - Lake MacKenzie Near Dam	0
0030016	07/17/00	Field Blank - Lake MacKenzie Near Dam	0
0031642	07/17/00	Whilcrilen Lake at Dam	0
0030213	07/13/00	Trip Blank	0
0030214	07/13/00	Lake Gladewater	0
0030215	07/13/00	Canton City Lake	0
0030231	07/18/00	Brazos River at River View Park	0
0030232	07/18/00	Field Dup-Brazos River at River View Pk	0
0030233	07/18/00	Field Blank	0
0030234	07/18/00	Trip Blank	0
0031783	07/18/00	Lake Greenbelt Near Dam	0
0031497	07/18/00	Village Creek at US96	0
0031498	07/18/00	Duplicate - Village Creek at US96	0
0031499	07/18/00	Trip Blank	0
0031843	07/18/00	Trip Blank	0
0031844	07/18/00	Edgewood City Lake	0
0031848	07/19/00	Langford Lake @ City of Clarksville Water Intake	0
0031859	07/19/00	Trip Blank - Lake Cypress Springs @ SH115	0
0031860	07/19/00	Lake Cypress Springs @ SH 115	0
0030246	07/20/00	Ft Parker Lake near Dam	0
0030248	07/20/00	Trip Blank	0
0030243	07/20/00	Lake Mexia near Dam	0
003639	07/18/00	Trip Blank	0
003639	07/18/00	Lake Granbury	1.69
003639	07/18/00	Duplicate - Lake Granbury	1.76
003639	07/18/00	Benbrook Lake	2.44
003640	07/19/00	Trip Blank	0
003640	07/19/00	Navarro Mills Lake	0
003640	07/19/00	Joe Pool Lake at Marina	4.09
003640	07/19/00	Joe Pool Lake by Dam	4.5
0032033	07/23/00	Lake Austin near Tom Miller Dam	1.57
0032034	07/23/00	Trip Blank - Lake Austin at Tom Miller Dam	0.98
0032035	07/24/00	Lake Austin @ Tom Miller Dam	1.44
0032036	07/23/00	Lake Austin @ Headwaters	0
0032037	07/25/00	Lake Austin at Tom Miller Dam	1.52

Sample ID	Sample Date	Site	MTBE (ppb)
0031791	07/25/00	Lake Meredith Near Dam	0
0030250	07/25/00	Lake Bazos at LaSalle Avenue	0
0030252		Trip Blank	0
0030254	07/25/00	Lake Waco Near Dam	0
0031666	07/26/00	Lake Graham near Dam	0
0031665	07/26/00	Lake Graham near Dam	0
0030260	07/26/00	Stillhouse Hollow at Headwaters	0
0030257	07/26/00	Stillhouse Hollow Lake near Dam	0
0030258	07/26/00	Trip Blanks	0
0030261	07/27/00	Laek Somerville near Dam	0.83
0030262	07/27/00	Trip Blanks	0
0031667	07/27/00	Lake Stamford near Dam	0
0031668	07/27/00	Lake Stamford near Dam	0
0031669	07/27/00	Hubbard Creek near Dam	0
0032038	07/30/00	NA	2.7
0032039	07/31/00	NA	1.89
0032040	07/31/00	NA	1
0032041	08/01/00	NA	2.48
0030499	08/02/00	Nas. S. Concho Arm	0
0030503	08/02/00	Nasworthy @ Dam	0.6
0030504	08/02/00	Trip Blank	0
0030270	08/03/00	Belton Reservoir near Dam	0
0030269	08/03/00	Belton Reservoir near Dam - Duplicate	0
0030264	08/03/00	Belton Reservoir - Cowhouse Creek Arm	0
0030266	08/03/00	Belton Reservoir - Leon River Arm	0
0030268	08/03/00	Trip Blank	0
0029738	08/03/00	Concho (Irving Street)	0
0029739	08/03/00	Trip Blank	0
0031887	08/02/00	Trip Blank - Lake Wright Patman @ IP	0
0031888	08/02/00	Lake Wright Patman @ IP	0
0031892	08/02/00	Lake Wright Patman in Elliot Creek Arm	0
0032384	08/09/00	Old Marlin Lake Near Dam	0
0032389	08/09/00	New Marlin Lake Near Dam	0
0021983	08/09/00	Trip Blank	0
0028800	08/09/00	Medina River at La Soya - D	0
0028799	08/09/00	Medina River at La Soya - A	0
003641	08/09/00	Trip Blanks	0

Sample ID	Sample Date	Site	MTBE (ppb)
003641	08/09/00	Lake Lewisville	0.71
003641	08/09/00	Lake Grapevine Station A	4.09
003641	08/09/00	Station A - Dup	4.81
003641	08/09/00	Station B	2.78
003641	08/09/00	Station C	1.97
003641	08/09/00	Station D	2.12
003641	08/09/00	Station E	2.18
003650	08/10/00	Trip Blank	0
003650	08/10/00	Lake Ray Hubbard	0
0028812	08/10/00	Leon Ck. @ Ruiz Ranch	0
0028813	08/10/00	Leon Ck. Ruiz Ranch Station D	0
0028814	08/10/00	Leon Ck. @ Ruiz Ranch Station E	0
0031517	08/15/00	Houston County Lake near Dam - Duplicate	0.97
0031516	08/15/00	Houston County Lake near Dam	0.99
0031518	08/15/00	Trip Blank	0
0032406	08/15/00	Lake Aquilla at Aquilla Creeek	0
0032401	08/15/00	Lake Aquilla at FM1947	0
0032395	08/15/00	Lake Aquilla near Dam	0
0032409	08/15/00	VOA Trip Blank	0
0031917	08/16/00	Lake Bob Sandlin at Mt. Pleasant Intake	0
0031916	08/16/00	Trip Blank - Lake Bob Sandlin at Mt Pleasant Intak	0
0031918	08/16/00	Lake Bob Sandlin at Pittsburg Intake	0
0031919	08/15/00	Lake Fork at Quitman Intake	0
0031920	08/15/00	Field Blank	0
0032042	08/20/00	Lake Austin near Tom Miller Dam	2.74
0032043	08/23/00	Lake Austin near Tom Miller Dam	2.89
0032044	08/20/00	Trip Blank - Lake Austin near Tom Miller Dam	0
0031803	08/24/00	Canadian River at Plemons (Trip Blank)	0
0031804	08/24/00	Canadian River at Plemons	0
0031805	08/24/00	Canadian River at Plemons (Duplicate)	0
0031806	08/24/00	Canadian River at Plemons - Field Blank	0
0032104		Corpus Christi Inner Harbor near	0
0032105		Trip Blank	0
0031700	08/29/00	Hubbard Creek near dam	0
0031701	08/29/00	Trip blank - Hubbard Creek near dam	0
0031702	08/29/00	Lake Stamford near dam	0

Sample ID	Sample Date	Site	MTBE (ppb)
0031703	08/29/00	Trip Blank -Lake Stamford	0
0031704	08/29/00	White River Lake at dam	0
0031705	08/29/00	Trip Blank - White River Lake at dam	0
0032045	08/27/00	Lake Austin near Tom Miller Dam	1.86
0032047	08/30/00	N/A	1.44
0032046	08/27/00	Trip Blank - Lake Austin	0.75
0030514	08/30/00	O.C. Fisher	0
0030515	08/30/00	Twin Buttes N. Pool	0
0030517	08/30/00	Twin Buttes S. Pool	0
0030521	08/30/00	Trip Blank	0
0031929	08/28/00	Big Cypress Bayou @ City of Marshall Intake	0.91
0031930	08/28/00	Trip Blank - Big Cypress Bayou @ City of Marshall	0
0031927	08/23/00	Cedar Creek Reservoir @ Cherokee Shores Intake	0
0031928	08/23/00	Trip Blank - Cedar Creek	0
0031931	08/31/00	Lake O'The Pines @ NETX-MWO Raw Water Intake	0
0031932	08/31/00	Trip Blank - Lake O' the Pines	0
0032544	08/29/00	Medina Lake @ dam	0
0032543	08/29/00	Mediana Lake @ dam - Duplicate	0
0032545	08/28/00	Canyon Reservoir @ dam	0
0032546	08/28/00	Canyon Reservoir @ dam - Duplicate	0
0032048	09/03/00	Lake Austin @ Tom Miller Dam	1.64
0032049	09/03/00	Trip Blank Lake Austin	0.7
0032050	09/06/00	Lake Austin @ Tom Miller Dam	1.22
0030527	09/12/00	Trip Blank	0
0030528	09/12/00	S. Concho Arm @ Nasworthy	0
0030529	09/12/00	S. Concho Arm @ Nasworthy - Duplicate	0
0030530	09/12/00	Nasworthy @ Dam	0
0032051	09/10/00	Trip Blank - Lake Austin near Tom Miller Dam	0.52
0032052	09/10/00	Lake Austin near Tom Miller Dam	1.93
0032053	09/13/00	Lake Austin near Tom Miller Dam	1.09
0031087	09/19/00	Buffalo Bayou @ Piney Pt.	0
0031088	09/19/00	White Oak Bayou @ Heights	0.99
0031089	09/19/00	Lake Houston 300m from dam	0
0031090		Trip blank	0
0031008	09/18/00	Trip Blank	0



Sample ID	Sample Date	Site	MTBE (ppb)
0031004	09/19/00	Clear Creek @ FM 2351	0
0031006	09/19/00	Clear Lake 0.3 Km SE of Nasa 1 bridge	7.57
0031007	09/19/00	Clear Lake 0.3 Km SE of Nasa 1 bridge - Field Dup.	7.65
0031000	09/19/00	Clear Creek Tidal @ SH 3	9.43
0031003	09/19/00	Clear Creek @ SH 35	0
0032054	09/17/00	Trip Blank Lake Austin near Tom Miller Dam	0
0032055	09/17/00	Lake Austin near Tom Miller Dam	1.04
0032056	09/20/00	Lake Austin near Tom Miller Dam	0.96
0032123	09/26/00	Guadalupe River @ US 59 in Victoria	0
0032124	09/26/00	Guadalupe River @ US 59 (Trip Blank)	0
0032121	09/25/00	Nueces River @ US 59 East of George West	0
0032122	09/25/00	Nueces River @ US 59 (Trip Blank)	0
0032119	09/25/00	Lake Corpus Christi Mid-lake @ the Dam	0
0032120	09/25/00	Lake Corpus Christi (Trip Blank)	0
0032112	09/25/00	Choke Canyon Reservoir, 1/4 Mile Upstream from dam	0
0032118	09/25/00	Choke Canyon Reservoir (Trip Blank)	0
0032125	09/26/00	Lake Texana @ Hwy 111 Bridge	0
0032126	09/26/00	Lake Texana @ Hwy 111 Bridge (Trip Blank)	0
0031387	09/26/00	Navarro Mills Reservoir	0
0031388	09/26/00	Navarro Mills Reservoir - Trip Blank	0
0032057	09/23/00	Lake Austin near Tom Miller Dam	0.95
0032058	09/23/00	Lake Austin near Tom Miller Dam - Trip Blank	0
0032059	09/27/00	Lake Austin near Tom Miller Dam	0.75
0032413	09/27/00	Aquilla Reservoir near dam	0
0032414	09/27/00	Aquilla Reservoir at Dam - Duplicate	0
0032417	09/27/00	Aquilla Reservoir at Aquilla Creek	0
0032419	09/27/00	Aquilla reservoir at FM 1947	0
0032415	09/27/00	VOA Trip Blank	0
0031091	09/27/00	Lake Houston 300m upstream from dam	0
0031092	09/27/00	White Oak @ Heights	0.84
0031093	09/27/00	Buffalo Bayou @ Piney Point	0
0031094	09/27/00	Blank Water - Lot# V092600RB	0
0031009	09/26/00	Trip Blank	0
0031010	09/27/00	Clear Creek @ FM 2351	0
0031011	09/27/00	Clear Lake 0.3Km SE of NASA I Bridge	1.81

Sample ID	Sample Date	Site	MTBE (ppb)
0031012	09/27/00	Clear Lake 0.3Km SE of NASA Bridge - Field Dup.	1.71
0031013	09/27/00	Clear Creek Tidal @ SH3	2.56
0031014	09/27/00	Clear Creek @ SH35	0
0032421	09/28/00	New Marlin City Lake	0
0032425	09/28/00	Old Marlin Lake	0
0032426	09/28/00	Trip Blank	0
0032583	10/03/00	Amistad Reservoir @ the dam buoy 1 (Trip Blank)	0
0032584	10/03/00	Amistad Reservoir @ the dam (buoy 1) Duplicate	0
0032585	10/03/00	Amistad Reservoir @ dam by buoy 1	0
0032060	10/04/00	Lake Austin near Tom Miller Dam	0.68
0032061	10/01/00	Lake Austin near Tom miller Dam Trip Blank	0
0032062	10/01/00	Lake Austin near Tom Miller Dam	0.86
0030753	10/12/00	Lake Houston 300m from dam	0
0029431	10/12/00	MTBE Blank	0
0032445	10/19/00	Little River at US 77	0
0032446	10/19/00	Little River at US 77 Duplicate	0
0032448	10/19/00	Trip Blank (for VOA/MTBE)	0
0033688	10/24/00	Lake Nasworthy In River Channel in South Concho arm	0
0033689	10/24/00	Trip Blank	0
0033691	10/24/00	Lake Nasworthy near dam	0
0034040	11/27/00	Medina River at Lasoya - Duplicate	0
0034041	11/28/00	Medina River at Lasoya - Trip Blank	0
0034042	11/28/00	Medina R. at Lasoya	0
0033697	11/28/00	Trip Blank	0
0033699	11/28/00	Lake Nasworth - South Concho Arm	0
0033701	11/28/00	Lake Nasworthy Near Dam	0
0033057	11/28/00	MTBE Trip Blank	0
0033056	11/29/00	Clear Creek Tidal @ SH3	2.5
0034177	12/07/00	Lake Proctor at Leon & Sabana	0
0034178	12/07/00	Lake Proctor at Leon & Sabana (Blank)	0
0034179	12/07/00	Lake Proctor Near Dam	0
0034180	12/07/00	Lake Proctor Near Dam (Blank)	0
	12/08/00	MW - 12	0
0032063	12/10/00	Lake Austin near Tom Miller Dam	0

Sample ID	Sample Date	Site	MTBE (ppb)
0032064	12/10/00	Lake Austin near Tom Miller Dam - Trip Blank	0
0032065	12/13/00	Lake Austin near Tom Miller Dam	0
0032066	12/17/00	Lake Austin near Tom Miller Dam	0
0032067	12/17/00	Trip Blank - Lake Austin near Tom Miller Dam	0
0032068	12/20/00	Lake Austin near Tom Miller Dam	0
0032069	01/03/01	Lake Austin near Tom Miller Dam Trip Blank	0
0032070	01/03/01	Lake Austin near Tom Miller Dam	0
0032071	12/31/00	Lake Austin near Tom Miller Dam	0
0033711	01/03/01	Lake Nasworthy in South Concho arm (MTBE) Field	0
0033712	01/03/01	Lake Nasworthy near the dam (MTBE) Field	0
0033713	01/03/01	Trip Blank	0
0032072	01/10/01	Lake Austin near Tom Miller Dam	0
0032073	01/10/01	Lake Austin near Tom Miller Dam - Trip Blank	0
0032074	01/11/01	Lake Austin near Tom Miller Dam	0
0032075	01/15/01	Lake Austin near Tom miller Dam	0
0032076	01/15/01	Lake Austin near Tom Miller Dam - Trip Blank	0
0032077	01/16/01	Lake Austin near Tom Miller Dam	0
033176	01/22/01	Lake Houston 300m upstream from dam	56.29
033178	01/22/01	Blank - MTBE 0033178 Lot#V101600RB	0
033054	01/22/01	Clear Lake @ CM 17	3.96
0032078	01/22/01	Lake Austin near Tom Miller Dam	0
0032079	01/22/01	Lake Austin near Tom Miller Dam - Trip Blank	0
0032080	01/23/01	Lake Austin near Tom Miller Dam	0
0033240	01/24/01	HSC @ Hess dock	19.22
0033238	01/24/01	HSC upstream of Greens Bayou Confluence	26.88
0033239	01/24/01	Trip Blank	0
0032081	01/29/01	Lake Austin near Tom Miller Dam	0
0032082	01/29/01	Lake Austin near Tom Miller Dam - Trip Blank	0
0034685	01/30/01	Lake Austin near Tom Miller Dam	0
0032216	01/30/01	Frio River at 3 Rivers Dam	0
0032215	01/30/01	Nueces River at US 59	0
0032213	01/30/01	Lake Corpus Christi @ Sunrise Beach Park Pier	0
0032214	01/30/01	Choke Canyon Reservoir, 1/4 mile upstream from dam	0
0032217	01/30/01	Trip Blanks - VOA/MTBE (2)	0
0032218	01/30/01	Choke Canyon Reservoir Duplicate	0

Sample ID	Sample Date	Site	MTBE (ppb)
0032220	02/01/01	Lake Texana @ Hwy 111 Bridge	0
0032221	02/01/01	Guadalupe River @ Hwy 59 Bridge	0
0032222	02/01/01	Trip Blanks	0
0033949	02/05/01	Lake Mackenzie near Dam (Trip Blank)	0
0033953	02/05/01	Lake Mackenzie near Dam	0
0033954	02/05/01	Lake Mackenzie near Dam (Duplicate)	0
0033955	02/05/01	Lake Maskenzie near Dam (Field Blank)	0
0034686	02/05/01	Lake Austin near Tom Miller Dam	0
0034687	02/05/01	Lake Austin near Tom Miller Dam Trpi Blank	0
0034688	02/07/01	Lake Austin near Tom Miller Dam	0
0034052	02/07/01	Leon Ck at Ruiz Ranch Trip Blank	0
0034053	02/07/01	Leon Ck at Ruiz Ranch Duplicate	0
0034054	02/07/01	Leon Ck at Ruiz Ranch	0
0031706	02/07/01	Lake Cisco at Dam (Trip Blank)	0
0031707	02/07/01	Lake Cisco at Dam	0
0031708	02/07/01	Lake Cisco at Dam (Field Duplicate)	0
0031712	02/07/01	Whiteriver Lake near Dam	0
0033319	02/08/01	0033319 - Trip Blank MTBE LOT# V101600RB	0
0033318	02/08/01	Clear Lake Tidal @ SH3	2.53
0033966	02/12/01	Lake Meredith near Dam	0
0033967	02/12/01	Trip Blank (station #10036)	0
0033975	02/13/01	Greenbelt Reservoir near dam	0
0033964	02/13/01	Greenbelt Reservoir near dam - Trip Blank	0
0034689	02/13/01	Lake Austin near Tom Miller Dam	0
0034690	02/13/01	Lake Austin near Tom Miller Dam - Trip Blank	0
0034691	02/13/01	Lake Austin near Tom Miller Dam - Duplicate	0
0034692	02/14/01	Lake Austin near Tom Miller Dam	0
0033264	02/20/01	Clear Lake @ CM 17 - Dup	3.53
0033262	02/20/01	Clear Lake @ CM 17	3.64
0033344	02/20/01	MTBE Blank Lot# VO12001RB	0
0033971	02/20/01	Lake Palo Duro near dam	0
0033972	02/20/01	Lake Palo Duro near dam (Trip Blank)	0
0034693	02/19/01	Lake Austin near Tom Miller Dam	0
0034694	02/19/01	Lake Austin near Tom Miller Dam - Trip Blank	0
0034695	02/21/01	Lake Austin near Tom Miller Dam	0
0034122	02/26/01	Medina R. @ FM 1937 @ La Soya	0
0034123	02/26/01	Medina River @ FM 1937 (La Soya) Duplicate	0

Sample ID	Sample Date	Site	MTBE (ppb)
0034122	02/26/01	Medina R @ FM 1937 (La Soya) Trip Blank	0
0033346	02/26/01	Lake Houston - Trip Blank	0
0033347	02/26/01	Lake Houston - Field Blank	0
0033348	02/26/01	Lake Houston Dam (Initial sample by piling)	3.05
0033349	02/26/01	Lake Houston Dam (Duplicate)	5.16
0033350	02/26/01	Lake Houston Dam (Drift)	0.71
0033365	02/26/01	Lake Houston Dam (Drift Duplicate)	0.67
0032961	03/06/01	Star Lake Canal	1.18
0032963	03/06/01	Star Lake Canal - Duplicate	1.19
0032962	03/06/01	Trip Blank	0
0033385	03/09/01	HSC @ Near Ferry landing on Galveston side	0.62
0033386	03/09/01	HSC near Bouy #1	0
0033387	03/09/01	HSC near Bouy 11	0
0033395	03/09/01	HSC @ Bouy 9	1.57
0033394	03/09/01	HSC @ SE of Bouy 7A	11.38
0033392	03/09/01	HSC @ South of Ferry Landing (Bolivan side)	0
0033391	03/09/01	HSC @ N. of Ferry Landing	2.62
0033393	03/09/01	HSC @ North of Ferry Landing (Field Duplicate)	0
0033390	03/09/01	HSC SW of Barge	0
0033388	03/09/01	Blank Lot# V101600RB	0
0033457	03/21/01	Lake Houston - 300m upstream from dam	0
0033455	03/21/01	Trip Blank - MTBE	0
0032978	03/22/01	Nueces River at SH 10	0
0032979	03/22/01	Nueces River at SH 82	0
0032977	03/22/01	Trip Blank	0
0034727	03/19/01	Lake Waxahachie - Trip Blank for MTBE	0
0034728	03/19/01	Lake Waxahachie	0
0034729	03/19/01	Lake Waxahachie - Duplicate MTBE	0

**APPENDIX D**  
**LOWER COLORADO RIVER AUTHORITY MTBE DATA**

**Table D1.** Lower Colorado River Authority MTBE data

Site	MTBE Sept. 4&5	MTBE Sept. 9	MTBE Oct.
Buchanan Upper Lake	ND		ND
Buchanan Mid Lake	ND		ND
Buchanan Lower Lake	ND	ND	ND
Inks Mid Lake	8.59	3.79	ND
LBJ Colorado River Arm	45.8	7.1	ND
LBJ Near Confluence	4.74		2
LBJ Llano River Arm	ND		ND
LBJ Mid Lake	2.35		ND
LBJ Lower Lake	5.7		ND
Marble Falls Mid Lake	7.53	2.7	2.4
Travis Upper Lake	3.54		ND
Travis Near Pedernales	15.1		2.1
Travis Mid Lake	3.34		ND
Travis Near Baldwin Bend	4.23		5.3
Travis Near Lakeway	5.97		2.3
Travis Near Arkansas Bend	3.98		2.4
Travis Near Hudson Bend	6.55		2.4
Travis Lower Lake	16.3	7.39	ND
Travis East Side	3.05		ND
Travis Near Cypress Creek	24.9	4.79	ND
Austin Mid Lake	24.9	11.3	8.8

Note: ND = Non-detect.

**APPENDIX E**  
**TEXAS PARKS AND WILDLIFE MTBE DATA**



**Table E1. Texas Parks and Wildlife MTBE data**

<b>Lake</b>	<b>Date</b>	<b>Site 1</b>	<b>Site 2</b>	<b>Site 3</b>	<b>Average</b>
Lake Austin	08/21/99	5.5/6.1	7.9/7.9	5.9/5.6	6.5
Belton Lake	08/22/99	ND/ND	ND/ND	ND/ND	ND
Lake Brownwood	08/22/99	ND/ND	ND/ND	ND/ND	ND
Lake Conroe	08/15/99	13.2/12.8	6.1/5.5	8.4/9.1	9.2
Grapevine Lake	08/28/99	4.0/4.1	4.2/4.7	3.5/3.5	4
Lewisville Lake	08/21/99	6.6/7.3	9.8/11.3	9.3/9.0	8.9
Possom Kingdom Lake	08/28/99	ND/2.0	2.2/ND	2.6/2.5	*1.6 - 2.2
Lake Sweetwater	08/22/99	ND/ND	ND/ND	ND/ND	ND
Lake Texoma	08/21/99	ND/ND	ND/ND	ND/ND	ND
Wright Patman Lake	08/29/99	ND/ND	ND/ND	ND/ND	ND

Note: All sites were at Marinas or high boat traffic areas. Averages of 3 sites are represented for each water body.

ND= Non-detect

\* 1.6 if ND=0, 2.2 if ND=2.0

**APPENDIX F**  
**TEXAS NATURAL RESOURCE CONSERVATION COMMISSION AND USGS**  
**MTBE DATA**

**Table F1.** Texas Natural Resource Conservation Commission

<b>Lake</b>	<b>MTBE (ppb)</b>
Lake Waco	E - 0.15, 0.92
Lake Granger	E - 0.10, 0.37
Lake Belton	0.53, 0.80
Lake Travis	1.22, 2.29
Lake Medina	1.28
Choke Canyon Reservoir	<0.2
Falcon International Reservoir	<0.2
Lake Mexia	1.22
Lewisville Lake	1.14
Aquilla Lake	E - 0.11
Lake JB Thomas	<0.2
Buffalo Springs Lake	1.14
Lake Limestone	0.43
Richland Chambers	0.33
Somerville Lake	1.41
Lake Houston	2.98
Lake Lavon	2.03
Lake Ray Hubbard	0.75
OC Fisher Lake	< 0.4
EV Spence Reservoir	<0.4
Donna Reservoir	<0.2
Lake Sweetwater	0.35
Fort Phantom Lake	E - 0.11
La Feria Reservoir	E - 0.15
Greenbelt Reservoir	E - 0.15
Lake Meredith	<0.2

<b>Lake</b>	<b>MTBE (ppb)</b>
White River Lake	0.35
Livingston Reservoir	<0.2
Sam Rayburn Reservoir	E - 0.14
Toledo Bend Reservoir	0.27
Lake Murvaul	E - 0.15
Wright Patman Lake	<0.2
Lake Tyler	0.18
OH Ivie Reservoir	0.20, 0.20
Lake Proctor	0.86
Lake Brownwood	0.99
Fayette County Lake	0.72
Lake Texana	E - 0.13
Lake Anahuac	0.26
Lake McKenzie	E - 0.11
Hubbard Creek Reservoir	0.18
Lake Kickapoo	<0.2
Lake Stamford	<0.4
Lake Bridgeport	0.25
Lake Bonham	1.04

**APPENDIX G**  
**LOWER COLORADO RIVER AUTHORITY LABORATORY METHOD 524.2**

## 7.1 ANALYTICAL LIMITS

A Method Detection Limit (MDL) is a minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. MDLs are determined and documented annually or as determined by the method.

Practical Quantitation Limit (PQL), Method Quantitation Limit, Estimated Quantitation Limit (EQL), and Reporting Limit (RL) are used synonymously at ELS and defined as the lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The value is *generally* three to ten times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the PQL analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample PQLs are highly matrix-dependent.

METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY  
CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 4.0

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## MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

### 1.0 SCOPE AND APPLICATION

- 1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in surface water, ground water, and drinking water in any stage of treatment<sup>1,2</sup>. The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Compound	Chemical Abstract Service Registry Number
Acetone*	67-64-1
Acrylonitrile*	107-13-1
Allyl chloride*	107-05-1
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone*	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon disulfide*	75-15-0
Carbon tetrachloride	56-23-5
Chloroacetonitrile*	107-14-2
Chlorobenzene	108-90-7
1-Chlorobutane*	109-69-3
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7



Compound	Chemical Abstract Service Registry Number
trans-1,4-Dichloro-2-butene*	110-57-6
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
1,1-Dichloropropanone*	513-88-2
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Diethyl ether*	60-29-7
Ethylbenzene	100-41-4
Ethyl methacrylate*	97-63-2
Hexachlorobutadiene	87-68-3
Hexachloroethane*	67-72-1
2-Hexanone*	591-78-6
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methacrylonitrile*	126-98-7
Methylacrylate*	96-33-3
Methylene chloride	75-09-2
Methyl iodide*	74-88-4
Methylmethacrylate*	80-62-6
4-Methyl-2-pentanone*	108-10-1
Methyl-t-butyl ether*	1634-04-4
Naphthalene	91-20-3
Nitrobenzene*	98-95-3
2-Nitropropane*	79-46-9
Pentachloroethane*	76-01-7
Propionitrile*	107-12-0
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Tetrahydrofuran*	109-99-9
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5

Compound	Chemical Abstract Service Registry Number
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

\*New Compound in Revision 4.0.

- 1.2 Method detection limits (MDLs)<sup>3</sup> are compound, instrument and especially matrix dependent and vary from approximately 0.02-1.6 µg/L. The applicable concentration range of this method is primarily column and matrix dependent, and is approximately 0.02-200 µg/L when a wide-bore thick-film capillary column is used. Narrow-bore thin-film columns may have a capacity which limits the range to about 0.02-20 µg/L. Volatile water soluble, polar compounds which have relatively low purging efficiencies can be determined using this method. Such compounds may be more susceptible to matrix effects, and the quality of the data may be adversely influenced.
- 1.3 Analytes that are not separated chromatographically, but which have different mass spectra and noninterfering quantitation ions (Table 1), can be identified and measured in the same calibration mixture or water sample as long as their concentrations are somewhat similar (Section 11.6.2). Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times (Section 11.6.3). Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as isomeric pairs. The more water soluble compounds (>2% solubility) and compounds with boiling points above 200°C are purged from the water matrix with lower efficiencies. These analytes may be more susceptible to matrix effects.

## 2.0 SUMMARY OF METHOD

- 2.1 Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to facilitate the separation of the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference

spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

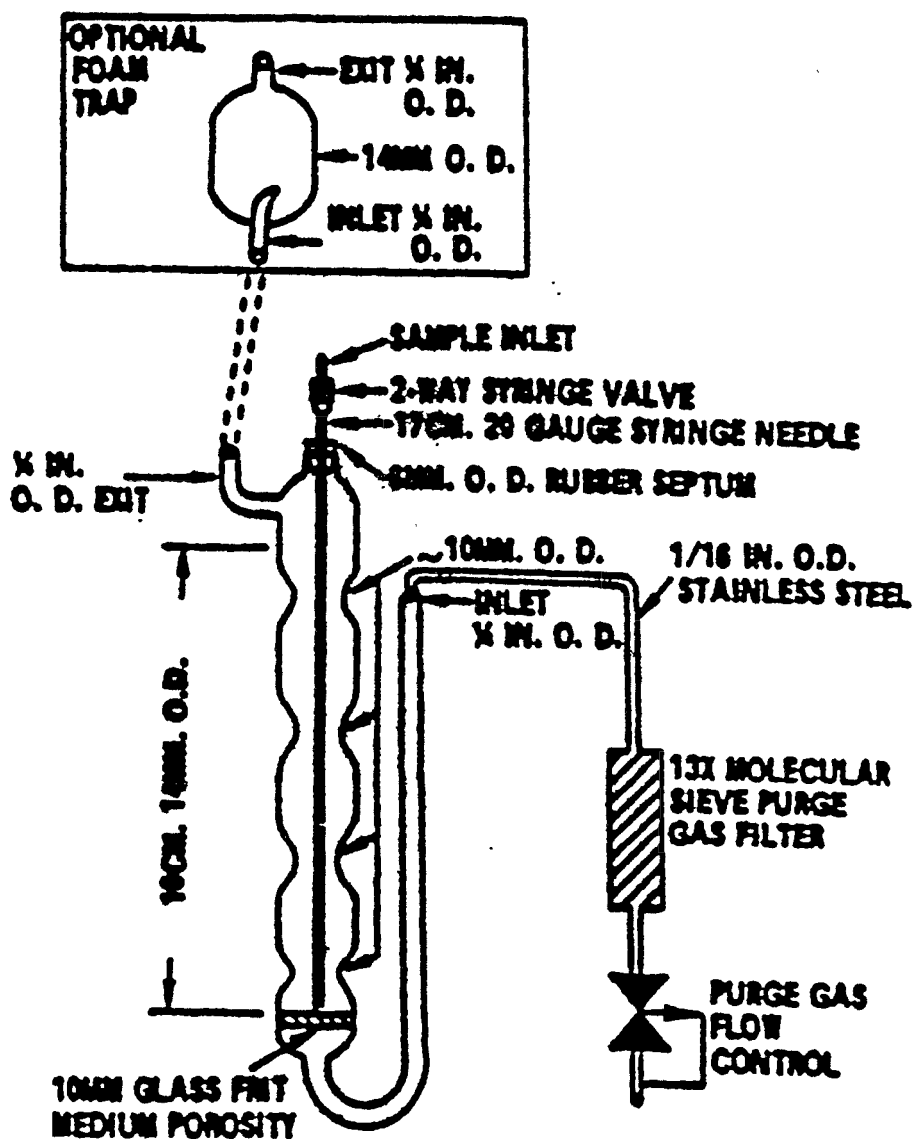


FIGURE 1. PURGING DEVICE

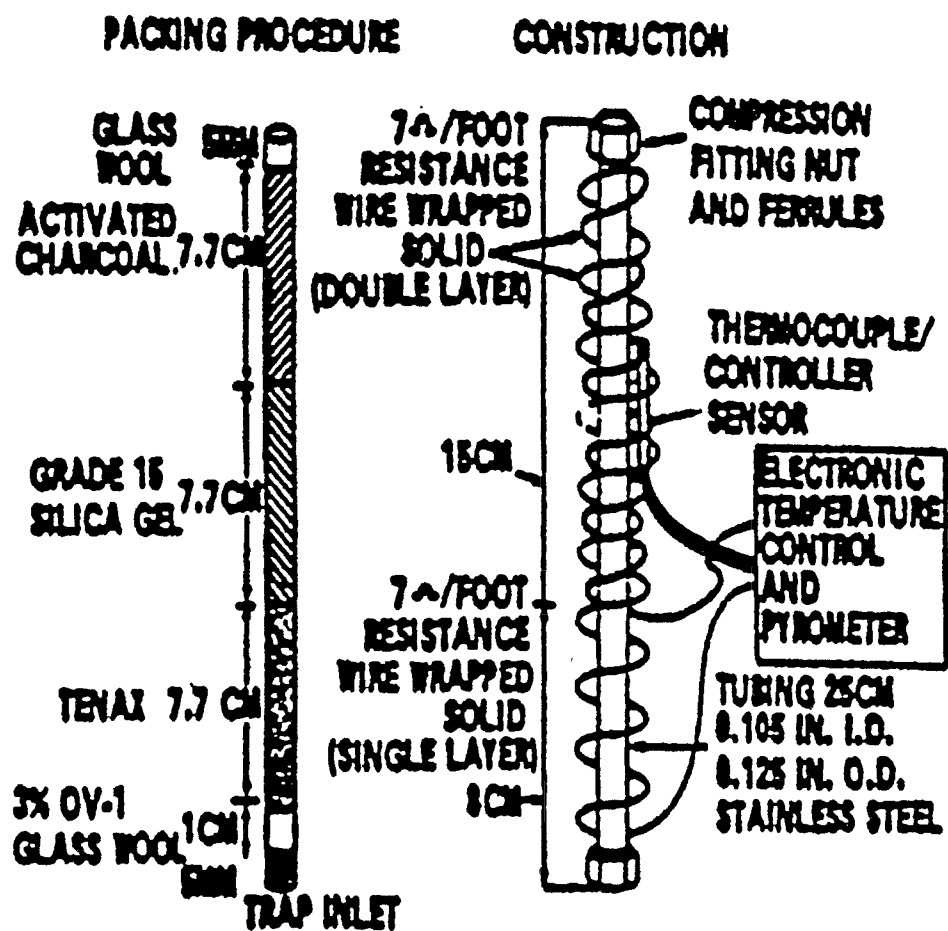


FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

FIGURE 3. NORMALIZED TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF MOST COMPOUNDS. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.

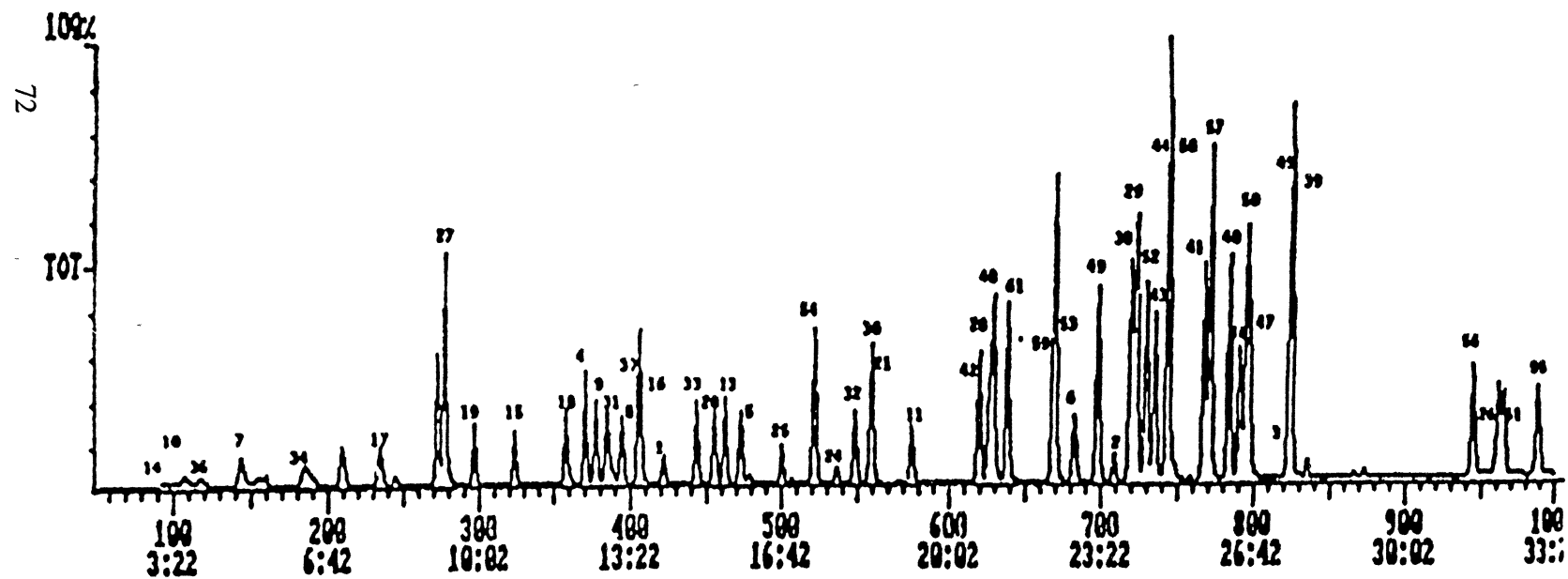
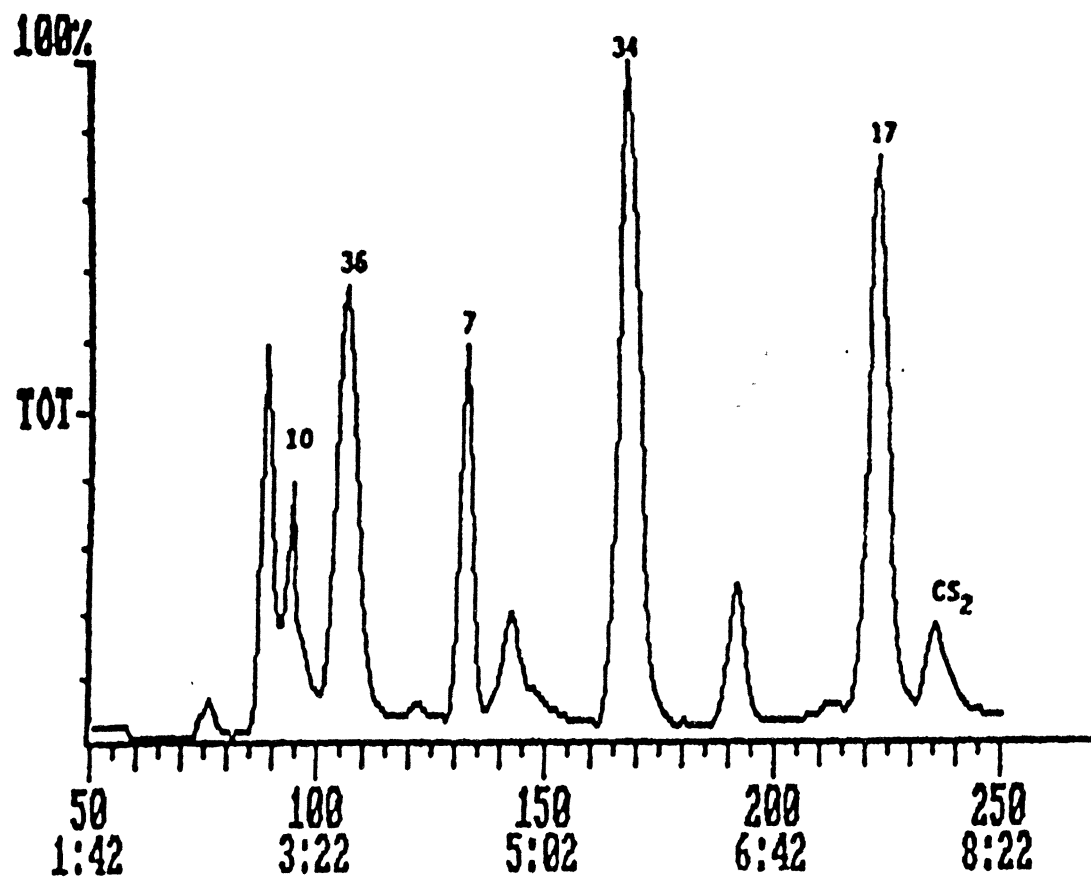


FIGURE 4. AMPLIFIED FIRST EIGHT MINUTES OF A TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF EACH COMPONENT. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.



## Literature Cited

- Boughton, Carol J., and M. S. Lico. 1998. "Volatile organic compounds in Lake Tahoe, Nevada and California, July-September 1997." U.S. Geological Survey (USGS) Fact Sheet. FS-055-98.
- Balling, Robert C. "The geographer's niche in the greenhouse millennium." *Annals of the Association of American Geographers*. (2000) : 90(1) 114-122.
- Browner, Carol M. 1999. Statement on findings by EPA's Blue Ribbon MTBE Panel. Available from: <http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm>; Internet; accessed 11 October 2000.
- California Department of Water Resources. Environmental Assessment Branch. "Assessment of MTBE in state water project reservoirs." April 1999.
- Delzer, Gregory C., J. S. Zogorski, T. J. Lopes, and R. L. Bosshart. 1999. "USGS study tracks storm water." *Water Online*. Available from: <http://www2.wateronline.com/content/news/article.asp>; Internet; accessed 4 September 1999.
- Environment Agency. 1999A. National Groundwater and Contaminated Land Centre. "MTBE – Air Quality vs. Groundwater Quality." Available from: <http://www.environment-agency.gov.uk/gwcl/publications.htm>; Internet; accessed 30 January 2001.
- Environment Agency. 1999B. National Groundwater and Contaminated Land Centre. "The fuel additive MTBE- a groundwater protection issue"? Available from: <http://www.environment-agency.gov.uk/gwcl/publications.htm>; Internet; accessed 30 January 2001.
- Franklin, Pamela., Catherine P. Koshland, Donald Lucas, and Robert F. Sawyer. 2000. "Clearing the air: Using scientific information to regulate reformulated fuels." *Environmental Science and Technology* 34 no. 2 (2000) : 3857-3863.
- Gullick, Richard W. and Mark W. LeChevallier. 2000. "Occurrence of MTBE in drinking water sources". *Journal of the American Water Works Association* 92 no.1 (2000) : 100-113.
- Kalman, Orit and Jay R. Lund. 1998. "MTBE: Evaluation of management options for water supply and ecosystem impacts." Unpublished draft report to the Department



of Civil and Environmental Engineering, University of California, Davis.  
Available from: [http://tsrtp.ucdavis.edu/mtberpt/vol5\\_2.pdf](http://tsrtp.ucdavis.edu/mtberpt/vol5_2.pdf); Internet; accessed 30 January 2001. Environmental Engineering, University of California, Davis. 1998.  
Available at: [http://tsrtp.ucdavis.edu/mtberpt/vol5\\_2.pdf](http://tsrtp.ucdavis.edu/mtberpt/vol5_2.pdf)

Kaltenborn, Bjorn P. "Effects of sense of place on responses to environmental impacts." *Applied Geography*. (1998) : 18(2) 169-189.

Lee, Anne. 2000. "Assessing the spatial and temporal distribution of MTBE and BETX compounds in Lake Lewisville, Texas. February 1999–February 2000". Unpublished MS Thesis. University of North Texas.

Lower Colorado River Authority. 1999. Unpublished results of MTBE concentrations in LCRA lakes.

Luzzadder-Beach, Sheryl. 1997. "Spatial sampling strategies for mapping a volcanic groundwater plume in Sierra Valley, California." *Professional Geographer*. (1997) : 49(2) 179-192.

McClurg, S. 1998. "The challenge of MTBE: Clean air vs. clean water." *Western Water*. Available from: <http://www.water-ed.org/julyaug98.asp>; Internet; accessed 29 November 2000.

Moran, Michael J., John S. Zogorski, and Paul J. Squillace. 2000. "MTBE in groundwater of the United States—Occurrence, potential sources, and long-range transport." *Proceedings of the 1999 Water Resources Conference, American Water Works Association*.

National Science and Technology Council. 1997. "Interagency assessment of potential health risks associated with oxygenated gasoline." Washington D.C. Available from: <http://www.epa.gov/ncea/oxygenates/fulasmnt.htm>; Internet; accessed 13 February 2001.

Pankow, James F., Neil R. Thomson, Richard L. Johnson, Arthur L. Baehr, and John S. Zogorski. 1997. "The urban atmosphere as a non-point source for the transport of MTBE and other volatile organic compounds (VOCs) to shallow groundwater." *Environmental Science and Technology* 31 no. 10 (1997) : 2821-2828.

Reuter, John E., Brant C. Allen, Robert C. Richards, James F. Pankow, Charles R. Goldman, Roger L. Scholl, and J. Scott Seyfried. 1998. "Concentrations, sources, and fate of the gasoline oxygenate MTBE in a multiuse lake." *Environmental Science and Technology* 32 no. 23 (1998) : 3666-3672.

- Squillace, Paul J., James F. Pankow, Nic E. Korte, and John S. Zogorski. 1997. "Environmental behavior and fate of methyl *tert*-butyl ether (MTBE)." *Environmental Toxicology and Chemistry* 16 no. 9 (September 1997) : 1836-1844.
- Tahoe Regional Planning Agency (TRPA). 1997. "Lake Tahoe motorized watercraft environmental assessment." Zephyr Cove, NV. Available from: <http://www.trpa.org/>; Internet; accessed 11 November 2000.
- \_\_\_\_\_. 1999. "Environmental assessment for the prohibition of certain two-stroke powered watercraft." Zephyr Cove, NV.
- Texas Natural Resource Conservation Commission. 1996. "Texas water quality inventory." SFR-50
- \_\_\_\_\_. 1999. Surface water quality monitoring procedures manual. GI-252.
- \_\_\_\_\_. 1999. News release, from the Texas Natural Resource Conservation Commission: TNRCC announces comprehensive lake sampling results. Available from: <http://www.tnrcc.state.tx.us/exec/media/press/10-99lakesample.html>; Internet; accessed 15 February 2001.
- \_\_\_\_\_. 2000. Fact sheet, MTBE in groundwater.
- Texas Parks and Wildlife. 1999. Unpublished results of MTBE sampling in reservoirs.
- U.S. Census Bureau. 1999. Population Estimates Program, Population Division, U.S. Census Bureau. State population estimates and demographics components of population change. Available from: <http://www.census.gov>; Internet; accessed 13 February 2001.
- U.S. Department of Transportation. 1999. Federal Highway Administration. Highway Statistics. Available from: <http://www.fhws.dot.gov>; Internet; accessed 13 February 2001.
- U.S. Environmental Protection Agency. 1992. Office of Research And Development. Method 524.2 measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry. Cincinnati, Ohio 45268.
- \_\_\_\_\_. 1993. Office of Pollution Prevention and Toxics Technical Information Review. Methyl tertiary-butyl ether. (CAS No. 1634-0404)

- \_\_\_\_\_. 1997. Fact sheet. Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary Butyl Ether (MTBE). EPA-822-F-97-009.
- \_\_\_\_\_. 1999A. "Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline." Available from: <http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm>; Internet; accessed 18 January 2000.
- \_\_\_\_\_. 1999B. Emission Facts. EPA420-F-99-040.
- \_\_\_\_\_. 2000. Methyl Tertiary Butyl Ether (MTBE) An overview. Available from: <http://www.epa.gov/mtbe/faq.html>; Internet; accessed 25 October 2000.
- U.S. Geological Survey. 1997. U.S. Department of the Interior. Fact Sheet. "Spatial variability of volatile organic compounds in streams on Long Island, New York, and in New Jersey." FS-194-97.