

**Water Soluble Phase Oxygenates in Gasoline
From New Jersey Service Stations
An Update**

William H. Kramer
Handex Environmental
Morganville, NJ

Presented at the

US EPA 13th Annual UST / LUST Conference
March 19-21, 2001
Albuquerque, New Mexico

Introduction

This is an update to a paper presented at the API/NGWA Petroleum Hydrocarbons Conference in Anaheim California in November 2000.

Oxygenates have been detected in groundwater samples from New Jersey for the last 20 years. One of the first documented cases of a municipal well impacted with Methyl tertiary butyl ether (MTBE) occurred in New Jersey in 1980 (McKinnon and Dyksen, 1984). Analysis of groundwater for MTBE and TBA at gasoline underground storage tank release sites has been required in New Jersey since 1988 (NJDEP, 1988). New Jersey developed drinking water criteria of 70 ug/l for MTBE in 1994 and promulgated a maximum contaminant level (MCL) for MTBE in drinking water of 70 ug/l in 1996. In 1993, the NJ DEP developed drinking water criteria for tertiary butyl alcohol (TBA) of 500 ug/l. This level was revised to 100 ug/l in 1997. A drinking water MCL has not been adopted for TBA in New Jersey.

The impact of MTBE on groundwater became more visible nationwide with the advent of reformulated and oxygenated fuel programs in the early 1990s. The degradation pathway for MTBE includes TBA as a breakdown product (Church and others 1997). TBA can also be used as a gasoline octane booster or it may appear as an impurity in other oxygenates (API, 2000, Landmeyer and others 1997, and Church and others 1999). A memo from USEPA (2000a) to State UST program managers recommends that they "should carefully consider assessing for other oxygenates (that include, but are not limited to, TAME, DIPE, ETBE, ethanol and methanol)". The USEPA memo states that "TBA is both a degradation product of MTBE and a fuel additive in its own right." The presence of TBA in groundwater could be construed to be an indicator of MTBE biodegradation. In New Jersey, field experience has shown widespread occurrence of TBA with MTBE in groundwater at concentrations that are equal to or in some cases exceed MTBE concentrations. If the presence and widespread occurrence of TBA in groundwater is to be explained primarily as a degradation product of MTBE, then conflict appears to exist with literature reports (e.g. Salinitro, 2000) that natural MTBE biodegradation is a relatively slow process compared to BTEX biodegradation. This paper presents the results of 12 mixing experiments conducted to determine if TBA is present in gasoline as an original constituent and what concentrations can be expected, relative to BTEX and MTBE, in the water phase. Another objective of the mixing experiments was to determine if there were any other oxygenates in use that may contribute to the water-soluble phase.

Oxygenate Field Data from New Jersey Gasoline Retail Sites.

Oxygenate behavior in groundwater at gasoline retail sites in New Jersey can be characterized as rapid rises and falls in concentrations resulting in "slug" behavior. TBA occurs in conjunction with MTBE at many sites in concentrations close to or exceeding MTBE concentrations. It is not unusual to detect only TBA in a well without BTEX or MTBE.

In one case, TBA concentrations have ranged from 40,000 to 280,000 ug/l while MTBE is below 300 ug/l and benzene is below 1,500 ug/l. In another case, TBA increased to 90,000 ug/l as MTBE concentrations decreased from 40,000 to 5,000 ug/l. The highest TBA concentration observed by the author at a UST release site in New Jersey in the 1990s was 650,000 ug/l at a source area monitoring well near a gasoline tankfield. MTBE peaked at 160,000 ug/l in this same well at about the same time as the TBA peak. This behavior has raised suspicions that the TBA may be in the gasoline as opposed to a degradation product of MTBE.

The highest concentrations of MTBE observed in source area wells in New Jersey by the authors in the 1990s are approximately 1,000,000 ug/l. This is a limited number of sites however and may be a result of entrapment of residual phase liquid in the groundwater sample. The most frequently detected ranges of MTBE in the 1990s is from 5,000 to 300,000 ug/l. This range of concentrations can be detected without free phase gasoline being present in the monitoring well. TBA concentrations tend to fall in the same range as MTBE concentrations.

Previous Studies

In a study by Kramer and Hayes (1987) three grades of gasoline were collected from a service station in central New Jersey. The samples were mixed via agitation in the lab at a 1:1 water to fuel ratio for 24 hours. Results are summarized in **Table 1**. Both MTBE and TBA were detected in all three grades of gasoline with the TBA concentration ranging from 45% to 96% of the MTBE concentrations. Enrichment of aromatics and oxygenates is evident with the higher-octane (93.5) gasoline. The lead scavengers 1,2-dichlorethane and 1,2-dibromoethane were detected in the regular leaded gasoline.

American Petroleum Institute (1991) conducted mixing experiments with various concentrations of MTBE and methanol in gasoline. The API study noted that equilibrium was reached within one hour. This is probably a result of the shake flask batch contacting equilibrium procedure used in the API study, compared to periodic gentle stirring used in the current study. A summary of the API study using 85% PS-6 gasoline and 15% MTBE is shown in **Table 2**.

In 1999, USEPA analyzed groundwater samples from monitoring wells at UST release sites in seven eastern States and the District of Columbia for MTBE, TBA and other geochemical parameters (Kolhatkar and others, 2000). Samples were analyzed at USEPA's Robert S. Kerr Environmental Research Center in Ada, OK. A scatter plot of the data shows a nearly one to one ratio of MTBE to TBA in groundwater samples. TBA concentrations exceeded MTBE concentrations in many cases with approximately 24 of the samples having TBA concentrations in a range of 20,000 to 100,000 ug/l.

Linder (2000) describes the detection of up to 18,000 ug/l TBA in source area wells in Santa Monica, CA and in the area of South Lake Tahoe, CA.

Procedure

Twelve samples of gasoline (87 to 93 octane) were collected at seven different central New Jersey gasoline service stations between February 2000 and February 2001. All service stations were those of major oil companies and two regional oil companies. The UST systems were under the ownership of those companies however the stations were not necessarily operated by the UST system owner. The origin of the gasoline (i.e. terminal or refinery) sampled at these stations is not known. At one of the stations (#005), gasoline samples were collected on May 29, 1998, February 17, 2000 and April 2, 2000 to compare changes in fuel composition over time. Samples were collected at three of the same stations in February 2001 to compare results from samples collected at the stations in February 2000.

Tests were conducted in a 2000-ml separatory funnel at a water to fuel ratio of 4:1. First, 800 ml of tap water was dispensed into the separatory funnel, followed by 200 ml of the gasoline sample. The gasoline and water was stirred gently for approximately 1 minute. Mixing duration was 16 hours with 3 gentle, one minute duration, stirring events. The agitation of the mixture was kept to a minimum to more closely simulate mixing with groundwater under field conditions. The tests were carried out at air temperatures ranging from 45 to 58° F. The air temperature during mixing of the sample from station # 006 was approximately 78°F.

The following non-oxygenate hydrocarbon compounds were searched for in the water-soluble phase: benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene and isopropylbenzene. Naphthalene and Isopropylbenzene (cumene) were selected because they are regulated as chemicals of concern for gasoline in adjacent Pennsylvania. The oxygenates searched for in the water phase were methyl tertiary butyl ether (MTBE), tertiary butyl alcohol (TBA), ethanol, methanol, di-isopropyl ether (DIPE), tertiary amyl methyl ether (TAME), ethyl tertiary butyl ether (ETBE) and tertiary butyl formate (TBF). Analysis was conducted by a NJDEP certified laboratory (Accutest Laboratories, Dayton, NJ NJDEP Certification # 12129) using EPA Method 8260B (GC/MS). Ethanol and methanol were analyzed using EPA Method 8015 (GC/FID). Glassware was cleaned with Alconox between tests. Equipment blanks were run early in the mixing experiments to insure that there was no carry-over from the previous test. Samples for analysis were

drawn off the bottom of the separatory funnel into 2-40 ml VO vials, refrigerated or placed on ice and transported to the laboratory within 24 hours of collection.

Analytical Methods

US EPA Method 8260B was utilized to identify and quantify Methyl Tertiary Butyl Ether (MTBE), Tertiary Butyl Ether (TBA), Di-isopropyl ether (DIPE), Tertiary amyl methyl ether (TAME), Ethyl tertiary butyl ether (ETBE) and Tertiary Butyl Formate (TBF). An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at ambient temperature. The volatiles are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatiles are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the volatiles onto a gas chromatographic (GC) column. With the exception of TBA, the compound detection limit for the purge and trap procedure ranges from 0.5 to 5.0 ppb, depending on the method and detector sensitivity. TBA has poor purge efficiency, which results in a higher reportable limit of 10 to 25 ppb. The column separates the volatile compounds, which are then identified by a mass spectrometer. The mass spectrometer fragments separated compounds with an electron beam to create ions of different mass. The ions are sorted by their mass and abundance to create a spectrum of the compound. Different compound classes have different mass spectra, which enables an analyst to qualitatively identify the compound. The spectra of TBA and MTBE each have unique ions that simplify their identification. The base peak (100% relative abundance) of TBA is m/e 59, while the base peak of MTBE is m/e 73. Combining the chromatographic retention time differences of these two compounds with their different mass spectra facilitates their identification. The GC/MS instrumentation performs computerized searches for target compounds that first locates the assigned chromatographic retention time window for the compound. The program then searches all chromatographic peaks in the window for key ions in the target compounds mass spectra. The spectra of all identified compounds, which meet the qualitative identification criteria, are reviewed to insure that errors in qualitative identification do not occur.

Methanol and Ethanol were analyzed by a direct injection technique, commonly referred to as SW846 8015. This is a gas chromatography procedure that utilizes a Flame Ionization Detector (FID) and sample introduction by direct injection 1-3ul of the aqueous sample. The instrument is also calibrated with aqueous standards. A column specific to alcohol type compounds is used to separate the compounds for identification by the FID. Since a smaller amount of sample is analyzed, the detection limit ranges from 500 to 1000 ppb.

Results

The results of the 12 mixing experiments are shown in **Table 3 and 4** and are summarized below:

- All 5 of the gasoline samples collected from service stations in February 2000 showed TBA occurring in the water-soluble phase at approximately 83% of the concentration of MTBE. MTBE concentrations averaged 1,638,000 ug/l while TBA averaged 1,356,000 ug/l (after 16 hours).
- TBA concentrations in the water phase in samples collected in April, May, July and August 2000 and January and February 2001 showed significantly lower TBA concentrations, ranging from ND (< 500,000 ug/l) to 180,000 ug/l.
- At station # 005, 87 octane gasoline samples were collected on three different dates (5/29/98, 2/17/00 and 4/2/00) to compare differences in water soluble phase composition. Results are shown in **Table 3**. The most notable difference was the lack of significant TBA (ND<2500 and ND <500,000 ug/l) in the May 1998 and April 2000 samples respectively. The February 2000 sample from station # 005 however had significantly higher TBA concentrations, similar to the other gasoline samples collected in February 2000 (TBA =1,270,000 ug/l).
- Ethanol was detected in 2 of 11 samples at 17,300 ug/l. and 24,500 ug/l.

- TAME was detected in 8 of 11 samples . One sample (station #001) appeared to be enriched in TAME with a concentration of 153,000 ug/l. The average TAME concentration in the remaining 7 samples was 8,100 ug/l.
- Methanol was detected in all 12 of the samples ranging from 21,500 to 356,000 ug/l after 16 hrs.
- DIPE, ETBE and TBF were not detected in any of the samples (detection limit ranging from 2,500 to 5,000 ug/l)
- Total BTEX concentrations in the water-soluble phase were about 0.75% of total oxygenate concentrations after 16 hours of mixing.
- Isopropylbenzene (cumene) and naphthalene were not detected in any of the mixing experiments (detection limit = 2000 to 5,000 ug/l)

Supplemental Analysis

To investigate the occurrence of the significantly higher TBA concentrations in the February 2000 samples, three gasoline samples were collected at three of the same service stations in January and February 2001 and analyzed.

A summary of the 2001 sampling is shown in **Table 4**. The TBA concentrations in the water phase of the January and February 2001 samples were significantly lower than the TBA concentrations in the February 2000 samples. TBA concentrations in the water phase ranged from ND to 181,000 ug/l.

To further investigate the occurrence of TBA in MTBE, a sample of neat (undiluted) MTBE and tank bottom water was obtained in August 2000 from the bottom of an MTBE storage tank at a New Jersey bulk storage facility. The MTBE was added to a separatory funnel at a ratio of 40:1 water to MTBE and stirred periodically over 16 hours. The bottom water was diluted 3:1 tap water: bottom water and dispensed into 40 ml VO vials for analysis. Samples were analyzed for BTEX, MTBE, TBA, TAME methanol and ethanol. The bottom water analysis and analysis of the water soluble phase of neat MTBE also showed relatively low TBA contents. (149,000 and 198,000 ug/l TBA) compared to MTBE concentrations of 1,470,000 and 12,800,800 ug/l). A summary of the neat MTBE analysis is shown in **Figure 5**.

Discussion

The solubility of an oxygenate is related to the pure compound solubility and the mole fraction of the oxygenate in the mixture This relationship is discussed in Squillace and others (1997), API (1991) and API (2000). There is a significant difference in the solubility of MTBE and TBA. MTBE solubility in water is approximately 48,000 mg/l while TBA is totally miscible in water. A relatively small percentage of TBA in MTBE could therefore result in a significant TBA concentration in the water-soluble phase.

Oxygen contents of Oxygenated Fuel (Oxyfuel) and reformulated gasoline (RFG) required in some areas since 1992 and 1995 range from 2.7 % by weight (Oxyfuel) to 2% by weight (RFG). To meet this requirement using MTBE requires approximately 15% by volume MTBE in Oxyfuel and 11% by volume MTBE in an RFG (USEPA 1998). Oxygenate concentrations have increased dramatically on UST sites in New Jersey in the 1990s compared to the 1980s. This increase can be attributed to higher oxygenate content of gasoline and more widespread use of oxygenates as a result of the requirements of the 1990 Clean Air Act Amendments.

After 4 days of mixing, MTBE content of the water phase increased by 153% to 3,530 mg/l. TBA concentrations increased by 133% to 2,970 mg/l. The ratio of TBA to MTBE in the water phase remained

around 84%. Assuming all of the TBA had dissolved at this point results in an estimated TBA content of the original gasoline of approximately 1.6%. It is apparent that TBA and MTBE had not yet reached equilibrium concentrations at 16 hours so the actual TBA content of the gasoline samples was somewhat higher than estimated from the 16 hour mixing duration. Assuming the TBA originated in the MTBE and assuming an MTBE content of 13% in the gasoline, the TBA content of the MTBE would be approximately 11% by volume. This is significantly higher than the levels of 0.5 to 2 % TBA contents reported in MTBE by manufacturers.

The estimated TBA contents of gasoline from the mixing experiments at 16 hours (1.5%) is significantly higher than values reported in analysis of reformulated gasoline samples from New Jersey in 2000 (USEPA, 2000b). The data is summarized in **Table 6**. The elevated TBA levels in the February 2000 samples was not a surprise however since field data from New Jersey UST release sites often shows TBA concentrations equal to or exceeding MTBE concentrations .

The TBA concentrations on the supplemental analysis in January and February 2001 are closer to manufacturers specifications for TBA in MTBE and within the range reported in the USEPA RFG database (USEPA, 2000b) for New Jersey in 2000. The analysis of the MTBE bottom water and water soluble phase did not show the enrichment in MTBE seen in the February 2000 gasoline samples.

New Hampshire Department of Environmental Services (2000) reported TBA in 3 of 145 samples of gasoline collected. TBA concentrations ranged from 0.2 to 0.7 volume percent. MTBE contents of the gasoline in this study ranged from 8 to 12 % by volume.

USEPA (1999) reported 0.04 to 0.05% TBA by volume in 5 out of 10 test and control gasoline samples. The five samples in the EPA study that showed TBA also contained 8 to 11 % MTBE by volume in the gasoline. The five samples that did not show any TBA used ethanol as the primary oxygenate.

The average methanol concentration in the water-soluble phase (n=12) was 84,000 ug/l with a range of 21,500 ug/l to 356,000 ug/l. Some methanol would be expected to be present in MTBE since methanol is a feedstock for MTBE production. Producers report methanol contents of MTBE ranging from 0.2 to 0.5%. The water volume in the tests was 800 ml (0.8 l). This would result in a total dissolved methanol mass of 67.2 mg. Assuming all the methanol in the MTBE dissolved into the water phase (methanol is miscible in water) then the methanol content of the MTBE would have been approximately 0.39% by weight assuming 12 % MTBE by weight. This is consistent with methanol contents reported in MTBE specifications from manufacturers.

Caution should be exercised in using the concentrations observed in the mixing experiments in drawing conclusions about field observations. The mixing ratio of 4:1 needs to be kept in mind along with the method of mixing (gentle stirring) and the duration of the experiment (16 hrs in most cases). In the mixing experiments, using gentle stirring and 16 hours of contact time, the BTEX concentration was 0.75% of the oxygenate concentration. API (1991) showed BTEX concentrations to be 2% of oxygenate concentrations after 1 hr mixing using a shake flask agitation mixing method. The relatively low BTEX concentrations compared to oxygenate concentrations helps explain why, under field conditions, only MTBE or TBA are sometimes detected in source area wells. The API (1991) study did not include TBA in the analysis. If TBA were present in the API study then the BTEX to oxygenate concentrations would be closer to 0.01 (1%). Theoretical concentration limits and those observed in the mixing experiments are rarely if ever encountered in the field. This has been pointed out in several papers including Squillace and others (1997) and API (2000). A number of variables will affect the actual concentration seen under field conditions including characteristics of the source, dilution by infiltration, distance the groundwater sample is from the source area, screen length and resulting dilution of the sample, mole fraction of oxygenate in the gasoline, the degree of mixing that takes place at the water table, and the time since the release occurred.

Bauman (1997) indicated that there is very limited use of DIPE and ETBE in the U.S. It was reported that fuel grade MTBE may contain TAME and TBA with the TBA content of the MTBE at approximately 1%. Ethanol was reported to be used mainly in the Midwest. These statements are consistent with the results of the mixing experiments with the exception of the TBA concentration of 1% in MTBE. As discussed above,

TBA contents of MTBE in five samples (February 2000) in this study were estimated at 11% in MTBE or 1.5% of the total gasoline.

At this time it is difficult to assess the nationwide occurrence of TBA at UST release sites since New Jersey is one of the few states that currently requires routine analysis for TBA. Linder (2000) discusses the detection of TBA (up to 18,000 ug/l) in source area wells in Santa Monica, CA. Kolhatkar (2000) presents results of MTBE and TBA analysis in seven eastern states and the District of Columbia.

To assess whether or not the elevated TBA concentrations from the February 2000 samples could be due to a laboratory error, the QA/QC data was reviewed again by Accutest. All samples were analyzed using EPA Method 8260B (GC/MS). Analytes were purged from the water sample using helium and were separated on a J & W DB624 60 m 0.25 or 0.53 mm ID capillary column with a film thickness of 1.4 microns. A 5 point calibration standard (5 ug/l to 2000 ug/l for TBA and 1 to 400 ug/l for MTBE) was utilized and a check standard was run every 12 hours to verify that the initial calibration continued to be valid. The retention time for TBA was approximately 5.2 minutes and 5.4 minutes for MTBE. To quantify TBA, an internal standard quantification technique was utilized as specified in Method 8260 using the extracted ion current profile. For TBA, the primary characteristic ion used for quantification was 59 AMU which falls within the retention time criteria for TBA. Four secondary characteristic ions of TBA (at similar ratios to the standard) were used to validate the identification of TBA. The primary characteristic ion used for MTBE quantification was 73 AMU within the retention time criteria of MTBE. The review of the QA/QC data indicated that the identification and quantification of TBA in February 2000 was valid.

Some knowledge of the oxygenate production process may explain the presence of TBA in gasoline. Limited information was found on manufacturer specifications for commercial grade MTBE. Generally, commercial MTBE for gasoline is 95 to 98% pure; it may contain 0.6 to 2% TBA, and 0.2 to 1% methanol (personal communication with Lyondell and Huntsman, and ARCO, (1989) MTBE specification). The United States is the largest manufacturer of MTBE followed by Saudi Arabia, Netherlands, Venezuela and Canada. The US imports approximately 25 to 35% of its total MTBE demand (US International Trade Commission (USITC), 1999). Generally, the production of MTBE requires the reaction of isobutylene with methanol. In this process, isobutane is dehydrogenated to generate isobutylene which is then reacted with methanol to form MTBE. This process accounts for about 35% of US MTBE production and 92% of Saudi Arabian MTBE production (USITC, 1999). Approximately 20% of US MTBE production however, uses TBA to generate MTBE (USITC, 1999). This method uses propylene oxide and methanol. Starting with an isobutane feedstock, TBA is generated as a coproduct of propylene oxide production. The TBA is then converted to MTBE either directly or with an isobutylene intermediate. This process is used primarily by two US manufacturers, Huntsman and Lyondell (formerly Arco Chemical).

Summary

TBA is present in gasoline but the TBA content can vary considerably. The elevated TBA detected in five samples in February 2000 explains the occurrence of TBA at some UST sites at concentrations equal to or exceeding MTBE concentrations. TAME and Methanol were detected in nearly all the samples but at significantly lower concentrations than MTBE and TBA. It is difficult to predict the types of oxygenates that will be detected at a site given the variables involved in product origin and distribution. The presence of TBA in gasoline indicates that caution needs to be exercised in drawing any conclusions about potential biological decay of MTBE under field conditions using TBA as an indicator. The time for a water sample to reach equilibrium is dependent on the degree of mixing between the product and water phase. Rapid rises and falls in concentration are characteristic of MTBE and TBA behavior in groundwater. Further study is required of the occurrence of TBA in the water soluble phase of gasoline in different geographical areas to investigate the apparent discrepancy between literature values of TBA in gasoline and the higher TBA contents found in the five February 2000 samples.

References

- American Petroleum Institute (1991) Chemical Fate and Impact of Oxygenates in Groundwater: Solubility of BTEX from Gasoline-Oxygenate Mixtures, Publication No. 4531, Washington, D.C.
- American Petroleum Institute (2000) Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE Publication No. 4699 API, Washington, DC
- Bauman, B. (1997) MTBE and Groundwater Quality: Bioremediation Research, Proceedings USEPA OUST 9th Annual National Conference, Charlotte, NC March 12, 1997
- Church, C., Isabelle, L., Pankow, J., Rose, D., and Tratnyek, P. (1997) Method for Determination of methyl tert-butyl ether (MTBE) and its degradation products in water. Environmental Science & Technology Vol. 31, No. 2 p 3723-3726
- Church, C., Tratnyek, P., Pankow, J., Landmeyer, J., Baehner, A., Thom, M., Schriener, M., (1999) Effects of Environmental Conditions on MTBE Degradation in Model Aquifer Columns, in: Proceedings USGS Toxic Substances Hydrology Program Technical Meeting Charleston, S.C. Mar 7-12
- Kolhatkar, R., Wilson, J. and Dunlap, L. (2000) Evaluating Natural Biodegradation of MTBE at Multiple UST Sites. In : Proceedings of the 200 Petroleum Hydrocarbons and Organic Chemicals in Ground Water Conference, Anaheim, CA, Nov 15-17, 2000 pp 32-49
- Kramer, W. and Hayes, T. (1987) Water Soluble Phase of Gasoline: Results of a Laboratory Mixing Experiment, New Jersey Geological Survey Technical Memorandum 87-5. Trenton, NJ. 13 pp.
- McKinnon R. and Dyksen J (1984) Removing Organics from Groundwater through Aeration Plus GAC, Journal of the American Water Works Association. Pg 42-47
- Landmeyer, J., Pankow, J., and Church, C. (1997) Occurrence of MTBE and tert-butyl alcohol in a gasoline-contaminated aquifer. In: American Chemical Society Division of Environmental Chemistry pre-prints of papers, 213th, San Francisco, CA Vol. 37 No. 1 p 413-415
- Linder, S. (2000) Tertiary Butyl Alcohol (TBA): MTBE may not be the only gasoline oxygenate you should be worrying about. LUSTLINE, Bulletin 34, New England Interstate Water Pollution Control Commission, Lowell, MA. P. 18
- New Hampshire Department of Environmental Services, (2000) Study of Reformulated Gasoline (RFG) Distributed Outside of New Hampshire's Four County Nonattainment Area, NHDES, Concord, NH
- New Jersey Department of Environmental Protection (1988) Scope of Work for Investigation and Corrective Actions at Underground Storage Tank Release Sites, Bureau of Underground Storage Tanks, Trenton, NJ
- Salanitro J. (2000) In-Situ Control of MTBE Plumes with Inoculated Biobarriers, In: Proceedings API/EPA MTBE Biodegradation Workshop, February 1-3 2000, Cincinnati, Ohio pp 73-83.
- Squillace, P., Pankow, J., Korte, N., and Zogorski, J. (1997) Review of the Environmental Behavior and fate of Methyl tert-butyl Ether, Environmental Toxicology and Chemistry, Vol. 16, No. 9 p 1836-1844.
- U.S. International Trade Commission (1999) Methyl Tertiary Butyl Ether (MTBE): Conditions Affecting the Domestic Industry, Publication 3231 September 1999 USITC, Washington D.C. 165 pp.
- US EPA (1998) MTBE Fact Sheet # 1 – Overview Office of Solid Waste and Emergency Response, Washington, D.C. EPA 510-F-97-014, 5 pp.

US EPA (1999) Phase II RFG – Report on Performance Testing, Office of Air and Radiation, EPA420-R-99-025, 22 pp.

US EPA (2000a), Monitoring and Reporting of MTBE and Other Oxygenates at UST Release Sites, memo from Director Office of Underground Storage Tanks to Regional UST Program Mangers and State UST Program Managers January 18, 2000 4 pp.

US EPA (2000b), Database from the Reformulated Gasoline Compliance Surveys from the State of New Jersey, RFG Survey Association, USEPA Office of Transportation and Air Quality, Washington, D.C.

Biographical Sketch

William H. Kramer is a principal hydrogeologist with Handex Environmental, Inc. and a member of the Corporate Technical Services Group. Mr. Kramer has 20 years experience in the field of subsurface hydrocarbon investigation and remediation. He holds a Masters degree in Geological Sciences from the State University of New York at Binghamton and a Masters degree in Public Health from the University of Medicine and Dentistry of New Jersey, Robert Wood Johnson Medical School in Piscataway, NJ. Previously he worked for the New Jersey Geological Survey and New Jersey Department of Environmental Protection. He is an ASTM certified RBCA trainer and RNA trainer.

William H. Kramer
Handex Environmental, Inc.
500 Campus Drive
PO Box 451
Morganville, NJ 07751
Phone: (732)-536-8667 x 290
Fax: (732)-536-7751
Email: Bkramer@Handexmail.com

Table 1
Summary of Laboratory Gasoline Mixing Experiments
From Kramer and Hayes (1987)
All results in ug/l

Sampling date	Sept. 1986	Sept. 1986	Sept. 1986
Mixing Duration (lab agitator)	24 hr	24 hr	24 hr
Water / Gasoline Ratio	1:1	1:1	1:1
Product Type	Regular Leaded 89 Octane	Regular Unleaded 86 Octane	Super Unleaded 93.5 Octane
Service Station Location	Central New Jersey	Central New Jersey	Central New Jersey
Benzene	30,500	28,100	67,000
Toluene	31,400	31,100	107,400
Xylene	19,950	15,740	17,160
Ethylbenzene	4,040	2,420	7,400
MTBE	43,700	35,100	966,000
TBA	22,300	15,900	933,000
DIPE	ND	ND	ND
1,2 dichloroethane	1,330	ND	ND
1,2 dibromoethane (EDB)	576	ND	ND

Table 2
Summary of API (1991)
Mixing Experiment
All results in ug/l

	85% PS-6 gasoline and 15% MTBE	Volume % in the original PS-6 gasoline
Water / Gasoline Ratio	10:1	
Benzene	57,200	1.69
Toluene	28,700	3.99
Xylene	18,000	8.14
Ethylbenzene	3,500	1.69
MTBE	5,140,000	0

BTEX to Oxygenate ratio is 0.02

or

BTEX concentration is 2% of Oxygenate concentration

Table 3
Summary of Laboratory Gasoline Mixing Experiments
All samples collected from central New Jersey Gasoline retail outlets
All results in ug/l

Service Station No.	001	002	003	004	005	005	005	006
Product Sampling date	2/11/00	2/15/00	2/10/2000	2/9/2000	5/29/98	2/17/00	4/2/00	7/31/00
Mixing Duration	16 hr	16 hr	16 hr	16 hr	48 hr	16 hr	48 hr	20 hr
Water / Gasoline Ratio	4:1	4:1	4:1	4:1	4:1	4:1	4:1	4:1
Gasoline Type	89 Octane	89 Octane	89 Octane	89 Octane	87 Octane	87 Octane	87 Octane	87 Octane
Benzene	4,640	6,560	7,460	9,690	24,200	8,020	6,960	4,280
Toluene	7,700	7,420	11,600	18,100	35,000	12,200	4,490	6,760
Xylene	2,370	2,050	3,450	4,900	12,400	2,990	ND (<10,000)	ND (<10,000)
Ethylbenzene	473	ND	649	1,130	2,350	609	ND (<10,000)	ND
Naphthalene	ND <2000	ND	ND	ND	ND(<350)	ND	NA	NA
Cumene	ND <2000	ND <2000	ND	ND	NA	ND	NA	NA
MTBE	1,330,000	1,990,000	1,480,000	2,000,000	3,240,000	1,390,000	2,080,000	1,210,000
TBA	1,120,000	1,430,000	1,270,000	1,690,000	ND (<2,500)	1,270,000	ND (<500,000)	ND (<500,000)
Methanol	48,000	26,000	50,800	26,000	51,300	27,200	71,300	44,900
TAME	153,000	2,940	1,490	5,170	1,960	ND	NA	9,790
Ethanol	ND (<500)	ND (< 500)	17,300	ND (<500)	ND (<500)	ND	NA	ND (<500)
TBF	ND	ND	ND	ND	ND (<2,500)	ND	NA	NA
DIPE	ND	ND	ND	ND	ND (<2,500)	ND	NA	ND
ETBE	ND	ND	ND	ND	ND (<2,500)	ND	NA	ND
TBA as a % of MTBE in water phase	84%	72%	86%	84%	< 0.1	91 %	< 24	< 41
TBA as a weight % of gasoline (1)	0.6%	0.8%	0.7%	0.9%	< 0.002%	0.7%	<0.3%	<0.3%

(1) Assumes all TBA dissolved into the water phase at 16 hours

ND = < 5,000 ug/l unless otherwise noted

NA = Not Analyzed

Table 4
2001 Supplemental Analysis
All samples collected from central New Jersey Gasoline retail outlets
All results in ug/l

Service Station No.	007	004	002	003
Product Sampling date	8/23/00	1/28/01	2/3/01	2/10/01
Mixing Duration	16 hr	16 hr	16	16 hr
Water / Gasoline Ratio	4:1	4:1	4:1	4:1
Gasoline Type	87 Octane	87 Octane	89 Octane	93 Octane
Benzene	5,790	10,700	11,700	12,100
Toluene	6,180	16,600	23,400	23,800
Xylene	2,400	4,310	ND (<50,000)	ND (<50,000)
Ethylbenzene	405	900	ND (<10,000)	ND (<10,000)
MTBE	2,221,000	2,430,000	2,730,000	2,460,000
TBA	130,000	181,000	ND (<250,000)	ND (<250,000)
Methanol	356,000	270,000	25,800	21,500
Ethanol	ND	24,500	ND (<500)	ND (<500)
TAME	2,440	33,100	ND (<50,000)	ND (<50,000)
ETBE	ND	ND	ND (<50,000)	ND (<50,000)
TBA / MTBE Ratio	5.8%	7.4%	< 9%	< 10%
TBA as a % of gasoline(1)	0.07%	0.1 %	< 0.14%	<0.14%

(1) Assumes all TBA dissolved into the water phase at 16 hours

Table 5
Water Soluble Phase of Neat MTBE
And Bottom Water Analysis
all results in ug/l
Sample Collected August 2000 from New Jersey Bulk Storage Facility

	Neat MTBE 40:1 16 hr mixing duration	Bottom water 3:1
MTBE	12,800,000	1,470,000
TBA	198,000	149,000
TAME	3,230	ND (<100,000)
Methanol	60,400	3,090,000
Ethanol	ND (<500)	ND (<250,000)
Benzene	ND (<10,000)	ND < 1,000
Toluene	ND (<10,000)	431
Xylene	ND (<10,000)	536
VO + 15	ND	ND
TBA: MTBE ratio	0.015 (1.5%)	0.1 (10%)

Table 6
Summary Statistics on Analysis of
Reformulated Gasoline Samples from New Jersey
Sampling period 2/17/2000 to 7/17/2000
n = 771 samples
All values are in weight %

Oxygenate	Range (above detection limit) Wgt %	Mean Wgt %	Std. Deviation	% of samples above detection limit (out of 771 samples)
MTBE	0.05 – 14.7	10.8	2.1	99.6%
TBA	0.005 – 0.1	0.015 (0.036)	0.02	42%
TAME	0.01 – 6.73	0.66 (1.38)	1.36	48%
Methanol	0.01 – 0.18	0.02	0.021	49%
Ethanol	0.04 – 10.4	0.13	1.11	1.8%

NOTE: (0.036) = mean weight % if Non-Detect values are Excluded
Source: USEPA (2000b)