

Water Soluble Phase Oxygenates in Gasoline From Five New Jersey Service Stations

William H. Kramer and Timothy L. Douthit
Handex Environmental, Inc.
Morganville, NJ

Mixing experiments were conducted using gasoline samples collected at five different central New Jersey gasoline service stations in February 2000 to identify water soluble phase oxygenates along with benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene and isopropylbenzene. Gasoline from one station was sampled twice over a two year period to compare changes in fuel composition. Tests were conducted in a 2000-ml separatory funnel at a water to fuel ratio of 4:1 using 87 and 89 octane gasoline. Mixing duration was 16 hours with 3 gentle stirring events. The oxygenates searched for in the water phase were MTBE, TBA, Ethanol, Methanol, DIPE, TAME, ETBE and TBF. Analysis was conducted by a NJDEP certified lab using EPA Method 8260B (GC/MS). Ethanol and methanol were analyzed using EPA Method 8015 (GC/FID). All of the gasoline samples 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). All samples contained methanol ranging from 26,000 to 51,000 ug/l. One sample showed ethanol at 17,300 ug/l and another sample contained TAME at 153,000 ug/l. DIPE, ETBE and TBF were not detected. Total BTEX concentrations in the water-soluble phase were about 0.75% of total oxygenate concentrations. For one of the mixing experiments, water samples were collected at 16, 48 and 96 hours to evaluate the effect of mixing time on concentration and time to reach equilibrium. BTX, MTBE and TBA concentrations more than doubled between 16 and 96 hours, however the relative concentration of total BTX remained constant at 0.87% of total oxygenate concentration at 16, 48 and 96 hours. The wide occurrence of TBA, at similar concentrations to MTBE, indicates that caution needs to be exercised in drawing any conclusions about potential biological decay under field conditions using TBA as an indicator. A comparison of the mixing experiments to previous mixing experiments of Kramer and Hayes (1987) and API (1991) is provided. Field data showing the behavior of MTBE and TBA in source area wells at gasoline retail outlets in New Jersey is provided. The mixing experiment explains the presence of TBA and MTBE at similar concentrations in groundwater at gasoline retail sites and confirms that TBA is present in gasoline and is a significant contributor to the total oxygenate content of the water-soluble phase. TAME and Methanol were detected in most samples, but at significantly lower concentrations than MTBE and TBA.

Introduction

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 several 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.

Previous Studies

In a study by Kramer and Hayes (1987) three grades of gasoline were collected from a service station in central New Jersey (a different oil company from those used in the current study). 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 six states for MTBE, TBA and other geochemical parameters. 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 MTBE:TBA concentration ratio. Correspondence from Wilson (2000) to the New Jersey Department of Environmental Protection summarizes the New Jersey component of this work. A complete summary of this work has yet to be published by USEPA.

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.

Oxygenate Production Process

Some knowledge of the oxygenate production process may help predict the types and relative amounts of oxygenates that may be present in gasoline.

One approach was to search for manufacture specifications on MTBE to look for an indication that TBA or other impurities may be present that would account for some of the groundwater concentrations of TBA observed in New Jersey. Limited information was found on specifications of 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. MTBE production can be grouped into four categories as described below:

Butane Dehydrogenation

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 Saudia Arabian MTBE production (USITC, 1999).

Fluid Catalytic Cracking Units

Mixed C4 streams generated by fluid catalytic cracking units during the refining process are reacted with methanol to form MTBE. The methanol reacts selectively with the isobutylene in the FCCU stream. Approximately 31 % of US MTBE production uses this process (USITC, 1999).

Tertiary Butyl Alcohol

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. Approximately 20% of US MTBE production uses TBA to generate MTBE (USITC, 1999). This process is used primarily by two US manufacturers, Huntsman and Lyondell (formerly Arco Chemical).

Steam Cracker Units

Mixed C4 streams generated by steam crackers (as a byproduct of ethylene production) are reacted with methanol to form MTBE. This method accounts for approximately 4% of US MTBE production (USITC, 1999).

Other Oxygenates

ETBE is derived from ethanol and isobutylene, while TAME is derived from methanol and isoamylene. (USITC, 1999).

Procedure

Regular unleaded Gasoline samples (87 to 89 octane) were collected at six different central New Jersey gasoline service stations between February and August 2000. All service stations were those of five major oil companies and one regional oil company. 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.

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.

Results

The results of the mixing experiment are shown in **Table 3** and are summarized below:

- Gasoline from 5 of the service stations sampled 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).
- At station # 005, samples collected in May 1998 and April 2000 showed ND (<2,500 ug/l) and ND (<500,000 ug/l) TBA respectively, significantly below the TBA levels seen at the other service stations in the February 2000 sampling events. A sample collected at station #006 on July 31, 2000 also showed ND levels of TBA (<500,000 ug/l). The samples collected in April, May and July showed low to ND levels of TBA whereas all samples collected in February showed TBA at concentrations close to MTBE concentrations.
- Ethanol was detected in 1 of 6 samples at Station # 003 at 17,300 ug/l.
- TAME was detected at all 6 service station 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 5 samples was 4,270 ug/l.
- Methanol was detected in all 6 service station samples ranging from 26,000 to 51,000 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)

Time to Reach Equilibrium

For one of the mixing experiments, water samples were collected at 16, 48 and 96 hours to evaluate the effect of mixing time on concentration and the time required to reach equilibrium (**Table 4**). BTX, MTBE and TBA concentrations more than doubled between 16 and 96 hours however the relative concentration of total BTX remained constant at 0.87% of total oxygenate concentration at 16, 48 and 96 hours. This is probably a result of the relatively gentle stirring of the gasoline and water. This was thought to be more representative of the mixing that goes on under field conditions.

Another sample collected in April 2000 (from Station # 005) was mixed in the separatory funnel and the water phase was sampled after 2, 4 and 8 days to evaluate the time to reach equilibrium. After 8 days, the following concentrations were reached benzene - 14,900 ug/l, toluene - 31,800 ug/l, xylene - 7,370 ug/l, MTBE - 5,080,000 ug/l, TBA - ND (<1,000,000 ug/l) and methanol - 31,600 ug/l. (**Table 5**). The MTBE concentration of 5,080,000 after 8 days is close to the value reported by API (1991) for a gasoline with 15% MTBE. MTBE and benzene concentrations doubled between 2 and 8 days. Toluene concentrations rose nearly 7 fold. Xylene was not detected until 8 days (7,370 ug/l) probably as a result of the detection limits of 10,000 ug/l in the 2 and 4 day samples. Methanol concentrations dropped from 71,300 ug/l at 2 days to 31,600 ug/l at 8 days. There was no TBA present in this gasoline sample.

Effect of Different Sampling Dates

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 had TBA concentrations similar to the other gasoline samples collected in February.

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). 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 8 days of mixing (**Table 5**), 5,080 mg/l MTBE was found in the water phase or a total mass of 4,064 mg in the 800 ml of water. This is close to the equilibrium value reported in API (1991) using a gasoline with 15% MTBE. Assuming an original MTBE content of 13% by volume in the gasoline, and that 1 ml of MTBE weighs approximately 0.74 gm., this equates to an MTBE mass of 19,240 mg in the 200 ml sample of gasoline used in the study. Therefore, after 8 days of mixing, about 21% of the MTBE mass in the original gasoline sample had transferred into the water phase.

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. Assuming all the TBA in the gasoline went into solution, that the 2,970,000 ug/l of TBA in **Table 4** represents an equilibrium concentration, and that the MTBE content of the gasoline was 13% by volume, it was estimated that the TBA content of the MTBE would be approximately 11% by volume or 1.5% by volume of the total gasoline. This is significantly higher than the levels of 0.5 to 2 % TBA contents reported in

MTBE by manufacturers. If not all the TBA went into the water phase or equilibrium had not yet been achieved at 96 hours, then the TBA content of the gasoline would be higher than estimated.

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 was 38 mg/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 30.4 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 0.2%. 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 to 8 days). 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 the study were estimated at 11% in MTBE or 1.5% of the total gasoline.

Although the service stations used in the study carried major oil company brand names, the actual source of the product sampled was not verified.

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. USEPA (1999) reports 0.04 to 0.05% TBA by volume in some gasoline test blends used to evaluate reformulated gasoline.

The estimated TBA contents of gasoline from the mixing experiments (1.5%) is significantly higher than values reported in USEPA reformulated gasoline samples from New Jersey in 2000 (**Table 6**). To assess whether or not the elevated TBA concentrations from the February 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 was valid.

Oxygenate Field Data from New Jersey gasoline retail sites.

Oxygenate behavior in groundwater at gasoline retail sites can be characterized as rapid rises and falls in concentrations resulting in "slug" behavior. TBA occurs in conjunction with MTBE at most sites in concentrations close to or exceeding MTBE concentrations. It is not unusual to detect only TBA in a well without BTEX or MTBE. This behavior has raised suspicions that the TBA may be in the gasoline as opposed to a degradation product of 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. Some sites show TBA concentrations lagging behind the arrival of MTBE concentrations.

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 highest TBA concentration observed by the authors 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. 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.

Summary

The mixing experiment explains the presence of TBA and MTBE at similar concentrations in groundwater at gasoline retail sites and confirms that TBA is present in gasoline and is a significant contributor to the total oxygenate content of the water-soluble phase. The other oxygenates were present 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 wide occurrence of TBA at similar concentrations to MTBE indicates that caution needs to be exercised in drawing any conclusions about potential biological decay 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 and to investigate the apparent discrepancy between literature values of TBA in gasoline and the higher contents estimated from the mixing tests.

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., Baehler, 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*

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 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 Managers 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.

Wilson, J. (2000) *Correspondence from USEPA to NJDEP Bureau of Underground Storage Tanks summarizing the New Jersey groundwater sampling results.*

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
BTEX / Oxygenate Ratio	0.0057	0.0046	0.0082	0.009	0.022	0.0088	0.0053	0.0087

ND = < 5,000 ug/l unless otherwise noted
 NA = Not Analyzed

Table 4
Effect of Mixing Time on Concentration
All results in ug/l

Service Station #	005		
Sampling date	2/17/00		
Water / Gasoline Ratio	4:1		
Product Type	87 Octane		
Station Location	Central New Jersey		
Mixing Duration	16 hr	48 hr	96 hr
Benzene	8,020	14,000	17,800
Toluene	12,200	21,600	30,100
Xylene	2,990	5,710	7,520
Ethylbenzene	609	1,300	1,690
Naphthalene	ND	ND	NA
Cumene	ND (<2,000)	ND	NA
MTBE	1,390,000	2,560,000	3,530,000
TBA	1,270,000	2,300,000	2,970,000
TBF	ND	ND	NA
DIPE	ND	ND	NA
Methanol	27,200	24,900	NA
Ethanol	ND (<500)	ND	NA
ETBE	ND	ND	NA
TAME	ND	ND	NA
BTEX / Oxygenate Ratio	0.0088	0.0087	0.0087

NA = Not Analyzed

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

Table 5
Effect of Mixing Time on Concentration
All results in ug/l

Service Station #	005		
Gasoline sample collected on	4/2/00		
Water / Gasoline Ratio	4:1		
Product Type	87 Octane		
Station Location	Central New Jersey		
Mixing Duration	2 DAYS	4 DAYS	8 DAYS
Benzene	6,960	11,600	14,900
Toluene	4,490	16,800	31,800
Xylene	ND (<10,000)	ND (< 10,000)	7,370
Ethylbenzene	ND (<10,000)	ND (<10,000)	ND (<20,000)
MTBE	2,080,000	2,888,000	5,080,000
TBA	ND (< 500,000)	ND (< 500,000)	ND (<1,000,000)
Methanol	71,300	43,600	31,600

Note the low TBA concentrations in this sample compared to TBA from the same station collected in February 2000. A sample from this same station in May 1998 also showed ND for TBA (Table 3) Test conducted at 58°F

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)