Ground Water Monitoring & Remediation

TBA Production by Acid Hydrolysis of MTBE During Heated Headspace Analysis and Evaluation of a Base as a Preservative

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Abstract

At room temperature (20° ± 3°C), purge and trap samplers provide poor sensitivity for analysis of the fuel oxygenates that are alcohols, such as tertiary butyl alcohol (TBA). Because alcohols are miscible or highly soluble in water, they are not efficiently transferred to a gas chromatograph for analysis. To improve the efficiency of transfer, the water in a purge and trap sampler can be heated. Alternatively, the sensitivity for TBA can be improved by preparing the sample in a heated static headspace sampler. In a heated water sample, the acid used as a preservative may cause chemical hydrolysis of methyl tertiary butyl ether (MTBE) to produce TBA. This effect is well illustrated in this paper using data collected by the U.S. Environmental Protection Agency Office of Research and Development on a plume of MTBE in California. Samples were analyzed using a static headspace sampler heated to 80°C. The ground water samples were preserved in the field with HCl to a pH ≤ 2. The extent of MTBE hydrolysis to TBA during sample analysis varied from 19% to 87%; the average extent of hydrolysis was 59%. To confirm and document the importance of acid hydrolysis of MTBE at higher temperatures during sample preparation, the rate of hydrolysis of MTBE was measured at 80°C. At pH = 1, the rate of hydrolysis was 1.22/h, while the rate at pH = 2 was 0.15/h. Acid hydrolysis of MTBE during sample preparation in a heated headspace sampler can be avoided by preserving the sample with 1% (w/w) trisodium phosphate dodecahydrate (TSP) instead of using HCl, or by neutralizing the acid before analysis. In the presence of an acclimated microbial culture, TSP prevented biodegradation of MTBE, as well as benzene, toluene, ethylbenzene, and xylene compounds, in ground water at room temperature for 66 d. However, in a spike recovery experiment, TSP caused based catalyzed hydrolysis of bromomethane. It is not appropriate as a universal preservative.

Introduction

Tertiary butyl alcohol (TBA) is often present in gasoline containing methyl tertiary butyl ether (MTBE), and can be produced from MTBE in ground water from biological activity. Releases of gasoline from underground storage tanks can contaminate ground water with TBA. In 1999, the California State Department of Health Services established a drinking water action level of 12 µg/L for TBA (California Regional Water Quality Control Board, Santa Ana Region 2002).

The most common analytical method for fuel components in ground water is sample preparation by purge and trap—U.S. Environmental Protection Agency (EPA) Method 5030 (U.S. EPA 1997)—followed by analysis with gas chromatography with a flame ionization detector (EPA Method 8015 [U.S. EPA 1997]), or gas chromatography with a mass spectrometer detector (EPA Method 8260 [U.S. EPA 1997]). Halden et al. (2001) compared the performance of standard methods for analysis of fuel oxygenates, including TBA, in ground water. They compared purge and trap followed by analysis according to EPA Method 8260B (capillary column, gas chromatography/mass spectrometry) (U.S. EPA 1997) to a modification of American Society for Testing and Materials (ASTM) Method D4815 (purge and trap, two-dimensional gas chromatography, flame ionization detector) (ASTM 1990) and to purge and trap with analysis by EPA Method 8021B (gas chromatography/photo-ionization detector) (U.S. EPA 1997). They concluded that ". . . all three methods are sufficiently sensitive to monitor MTBE at the stringent primary (13 µg/L) and secondary (5 µg/L) action levels set forth by the state of California." They also found that EPA Method 8240B (U.S. EPA 1997) and ASTM Method D4815 were amenable to TBA analysis. However, the method detection limit for TBA with EPA Method 8260 when 10 mL of sample was purged at 20°C was 35 µg/L and

Received October 2002, accepted November 2003.

the method detection limit with ASTM Method D4815 was 27 µg/L. These detection limits are not adequate to monitor TBA at the California Department of Health drinking water action limit of 12 µg/L.

There are several successful approaches to determine TBA at concentrations near 12 µg/L with adequate sensitivity. Church et al. (1997) utilized a direct aqueous injection into a gas chromatograph equipped with a mass spectrometer. With a 10 µL injection, they achieved detection limits of 10, 0.10, and 0.02 µg/L, respectively, for the operation of the mass spectrometer in full scan, multiple ion monitoring, and single ion monitoring modes. While the sensitivity afforded by the ion monitoring modes is substantial, use of those modes reduces the ability to measure a broad suite of volatile organic compounds (VOCs) in one analysis and reduces the ability of the mass spectral detector to provide confirmation of the peak identifications.

Cassada et al. (2000) achieved a method detection limit for TBA of 1.8 µg/L using solid-phase microextraction and multiple ion monitoring. Pierini and Mastrogiacomo (2001) used solid phase microextraction and multiple ion monitoring to achieve a recovery of 84% and a relative standard deviation of 6% for a calibration standard of 0.1 µg/L.

Another approach to increase sensitivity for TBA without reducing the utility of the mass spectrometer is to heat the water sample. EPA Method 8260 recommends that a purge and trap vessel heated to 80°C be used to determine allyl alcohol, n-butanol, and propionitrile. Bianchi et al. (2002) determined the optimum conditions for recovery of MTBE, TBA, and benzene, toluene, ethylbenzene, and xzylene (BTEX) compounds by purge and trap. Optimal conditions were a purge time of 30 min from a sample heated to 60°C. Halden et al. (2001) compared the method detection limit for purge and trap analysis of a 5 mL sample purged at 20°C to a 10 mL sample purged at 40°C. The method detection limit was lowered from 35 to 3.0 µg/L. A method developed by the U.S. Geological Survey (Rose and Sandstrom 2003) achieved a method detection limit for TBA of 0.21 µg/L, with an interim reporting level of 0.43 µg/L, when the water sample was purged at 65°C. However, it is not necessary to heat the sample to achieve good sensitivity for TBA. Rosell et al. (2003) achieved a detection limit of 0.11 µg/L and a relative standard deviation of 5.5% for calibration standards at 1.0 µg/L when 15 mL of sample was purged at room temperature.

U.S. EPA recognizes a static headspace sampler—EPA Method 5021 (U.S. EPA 1997)—as an acceptable method for preparation of water samples for analysis of fuel components (U.S. EPA 2003). The authors have had good success with heated static headspace samplers for analysis of TBA in ground water. When the sample was prepared in a heated static headspace sampler and analyzed with a flame ionization detector, Pirkle and McLoughlin (2003) attained a reporting limit for TBA of 5 µg/L. When the samples were heated at 80°C for 30 min in a headspace sampler and then analyzed using a mass spectrometer detector, Lin et al. (2003) attained a method detection limit of 0.79 µg/L. In the work of Lin et al. (2003), an ion trap mass spectrometer was used and afforded the advantages of both full scan and ion monitoring. The relative standard deviation of a calibration standard at 2.5 µg/L was 10.2%.

Ground water samples collected for the analysis of VOCs are most often preserved with 2 to 5 drops of 6 N HCl. Method 6200C (APHA 1998) specifies, "For samples and field blanks that contain volatile constituents but do not contain residual chlorine, add HCl (4 drops 6N HCl/40 mL) to prevent biodegradation and dehydrohalogenation." EPA Method 8260 refers to Chapter 4 of the U.S. EPA SW–846 manual (U.S. EPA 1997), organic analyses where samples destined for EPA Method 5030 (U.S. EPA 1997) are to be preserved, and specifies, "Cool to 4°C and adjust pH to less than 2 with H_2SO_4, HCl or solid $NaHSO_4$." U.S. EPA Methods 524.2 (U.S. EPA 1995) and 502.2 (U.S. EPA 1995) specify, "Adjust the pH of all the samples to < 2 *at the time of collection*, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 mL of sample volume."

Typically, the pH is adjusted in the range between 1 and 2. O'Reilly et al. (2001) showed that MTBE in water samples in this pH range can hydrolyze to form TBA. The kinetics of hydrolysis in this pH range are relatively slow at room temperature; ~0.2% of the MTBE is hydrolyzed each day at pH = 2. If samples are stored at 4°C and analyzed within two weeks of collection by purge and trap at room temperature, there should be minimal effect of acid hydrolysis on the reported concentrations of MTBE or TBA (White et al. 2002). O'Reilly et al. (2001) also showed that the rate of hydrolysis increases sharply with an increase in temperature. In a sample that is at pH = 2 and held at 80°C for the preheat time typically required by a static headspace sampler, a substantial amount of MTBE should hydrolyze to TBA.

In an evaluation of the method reported by Rose and Sandstrom (2003), Marr et al. (2003) investigated use of that technique with both an ambient purge at 22°C and a heated purge at 80°C. They found no evidence of hydrolysis. They report TBA observation only in the samples spiked with 20,000 µg/L MTBE. In the samples analyzed with an ambient purge, the reported TBA concentration in the 20,000 µg/L MTBE sample ranged from 32 to 39 µg/L. In the samples analyzed with an 80°C purge, the reported TBA concentrations ranged from 24 to 31 µg/L. Marr et al. conclude that the observed TBA was probably from a trace contaminant in their MTBE standard and not from acid hydrolysis. Marr et al. suggest that hydrolysis is ". . . negligible during the analytical process, even when using heated-purge methods."

Wade (1998) was the first to recognize that MTBE could be hydrolyzed in water samples that were preserved with acid. If MTBE were hydrolyzed, it would lead to an underestimation of MTBE concentrations and an overestimation of TBA concentrations. If the amount of TBA produced by acid hydrolysis exceeds the regulatory standards for TBA, the use of acid could produce a TBA concentration that suggests a regulatory violation where there is none. Air stripping or carbon adsorption can treat MTBE effectively, but TBA is not treated effectively by these technologies. A treatment system designed to remove both MTBE and TBA will be more complex and more costly than a treatment system designed to remove MTBE alone. A false positive for TBA can result in money wasted for a treatment system that is more complex

and more expensive than is necessary (White et al. 2002). Finally, TBA is the first product of the natural biodegradation of MTBE in ground water (Church et al. 1997). A false positive for TBA may suggest undue significance of natural attenuation of MTBE at a site.

Kovacs and Kampbell (1999) developed an alternate preservative that uses a base instead of an acid. A convenient way to add base to a water sample is to add an excess of the salt of a weak acid. In the method of Kovacs and Kampbell (1999), 40 mL VOA vials are prepared by adding ~0.4 g of trisodium phosphate dodecahydrate (TSP) to each vial. The vial is then filled with the water sample and sealed without headspace. As the salt dissolves in water, it produces a basic solution with a pH > 11. Just as the low pH of an acidic solution hinders bioactivity, a high pH should also hinder bioactivity. Kovacs and Kampbell (1999) had good results with TSP as a preservative. However, the U.S. EPA (1997) specifically recommends the use of acid preservatives for VOCs, and the approach of Kovacs and Kampbell (1999) has not been widely applied.

This paper is a collection of interrelated studies concerning acid hydrolysis of MTBE during analysis, and the performance of trisodium phosphate as an alternative preservative to prevent hydrolysis of MTBE. We report the extensive acid hydrolysis of MTBE to TBA in ground water samples that were heated to 80°C during headspace sampling. To confirm the anecdotal observations, the experimental approach of O'Reilly et al. (2001) was used to directly determine the rate of acid hydrolysis of MTBE to TBA at 80°C at pH = 1 and pH = 2. The rate of hydrolysis at 80°C was 1000 times faster than the rate of hydrolysis reported by O'Reilly et al. (2001) at 26°C. When TSP was used as a preservative, MTBE was not hydrolyzed to TBA at 80°C. We evaluated the influence of acid hydrolysis during storage of samples by measuring the loss of MTBE in ground water samples that were preserved with HCl to pH < 2, and then stored for 237 d at 5°C. The loss was minimal. We present a case study where hydrolysis of MTBE during analysis with a heated headspace sampler produced a false picture of the distribution of TBA in an MTBE plume. We also report experiments that evaluate the efficacy of HCl and TSP as preservatives, as determined from their ability to inhibit the expression of biological oxygen demand (BOD), and to prevent the biodegradation of MTBE, benzene, toluene, ethylbenzene, and o-xylene in water samples. Finally, we report an experiment that tests the limitations of TSP and show that the recovery of bromomethane is reduced when spiked into ground water that is preserved with TSP.

Acid Hydrolysis of MTBE to TBA During Heated Headspace Analysis of Samples from an MTBE Plume in California

In 1984 and 1985, there was a release of motor gasoline from the Naval Exchange Service Station at the Naval Base Ventura County, Port Hueneme, California. The release produced a long plume of BTEX compounds and MTBE in the shallow water table aquifer. The plume of MTBE in ground water is currently being treated by in situ aerobic biodegradation. The flux of MTBE contamination from residual gasoline in the source area of the plume into the aerobic treatment systems is being monitored using a transect of wells installed just upgradient of the treatment system. In November 2000, water samples from these monitoring wells were acquired into 40 mL VOA vials and preserved with HCl to a pH < 2 following the usual field protocol at the time in California. The samples were shipped to the R.S. Kerr Environmental Research Center in Ada, Oklahoma, for analysis. This occurred prior to the report of O'Reilly et al. (2001) of the potential for hydrolysis.

The project data quality objectives called for a measurement of TBA that was sensitive to concentrations below 12 µg/L. There were several methodology choices available, but given the data quality objectives, the available equipment, and the information available at that time, it was chosen to use a heated headspace/gas chromatography/mass spectrometer methodology. Specifically, the samples were analyzed using a modification of EPA Method 5021/8260 (U.S. EPA. 1997). The samples were prepared by adding NaCl at 20% and heating at 80°C for 20 min in a static headspace sampler, and then analyzed by gas chromatography using a mass spectrometer detector. The samples were analyzed for concentrations of MTBE, TBA, and the BTEX compounds. It was necessary to dilute several of the samples to bring one or more of the target analytes within the range of the calibration. The acid used to preserve the samples was diluted along with the target chemicals. The analyst noticed that the reported concentration of TBA decreased as the amount of acid decreased. Following the relationships published by O'Reilly et al. (2001), the rate of hydrolysis should be directly proportional to the concentration of acid. As the sample was diluted 1:10 and 1:100, the rate of acid hydrolysis should slow by a factor of 1:10 and 1:100. Data on the reported concentrations of MTBE and TBA are presented in Table 1. The concentrations are corrected for dilution.

The corrected concentrations of TBA in the samples that were diluted 1:100 are the best available estimate of the true concentration of TBA in the ground water as originally collected. The concentration of TBA in these samples varied from 8% to 16% of the concentration of MTBE. The measured concentration of TBA in the presence of the undiluted acid was four- to eightfold higher than the true concentration. In the data presented in Table 1, the concentration of TBA produced by acid hydrolysis during headspace analysis would account for hydrolysis of 43% to 79% of the MTBE that was originally present in the sample. In 15 samples examined from the plume, the extent of hydrolysis of MTBE varied from 19% to 87%; the average extent of hydrolysis was 59%.

Rate of Acid Hydrolysis of MTBE at 80°C

O'Reilly et al. (2001) report the kinetics of hydrolysis of MTBE at pH = 1 and 2 at 26°C and 37°C, respectively. Their approach was used to determine the kinetics of hydrolysis at pH = 1.0 and 2.0 at 80°C. Two sets of water samples were prepared in 40 mL VOA vials using a pyrophosphate buffer system similar to that used by O'Reilly et al. (2001). The pH of the pyrophosphate buffers was determined with a research grade pH meter. Calibration buffers with pH = 4.00, pH = 7.00, and pH = 10.00 were used to adjust the slope factor of

Table 1
Effect of Dilution of the Sample (and Dilution of the Acid Used to Preserve the Sample) on the Concentration of TBA Determined in Four Ground Water Samples Using a Heated Headspace Sampler

Analyte		MTBE	TBA	TBA	TBA
Dilution of Sample		1 to 100	1 to 100	1 to 10	none
			Increasing Concentration of Acid →		
Concentration	Well A	7200	591	1310	4640
(µg/L) reported in	Well B	8550	740	1220	5100
four samples after	Well C	12,700	2000	2640	10,400
correction for dilution	Well D	13,200	1400	1480	6170

the electrode. The pH meter reading is considered accurate to ~ 0.03 pH unit. The pyrophosphate buffer in one set of vials was adjusted to pH = 2.00 with concentrated HCl, and a second set of vials was acidified to pH = 1.00. A third set of water samples was constructed with boiled deionized water and preserved by the addition of 1.0% TSP. All vials were spiked with MTBE to an initial concentration near 500 µg/L. Three vials from each set were analyzed immediately to establish the initial concentrations. The remaining vials were then placed in a water bath that was maintained at 80°C. After 30, 60, and 120 min of incubation, three vials from each set were removed and immediately quenched in a bath of cold water. Just prior to analysis, sodium hydroxide was added to the samples to bring them to an approximate pH of 7. The water samples were then prepared for static headspace sampling by adding NaCl at 20% and heating to 80°C for 20 min, and then analyzed using a gas chromatograph with a mass spectrometer detector. Data showing the loss of MTBE are presented in Figure 1. The extent of MTBE loss increased as the sample pH decreased. After only 30 min at 80°C, 7% of the MTBE hydrolyzed at pH = 2.00 and 61% hydrolyzed at pH = 1.00. In Figure 2, the loss of MTBE at pH = 1.00 is compared to the production of TBA. The production of TBA was directly commensurate with the loss of MTBE in the acid samples.

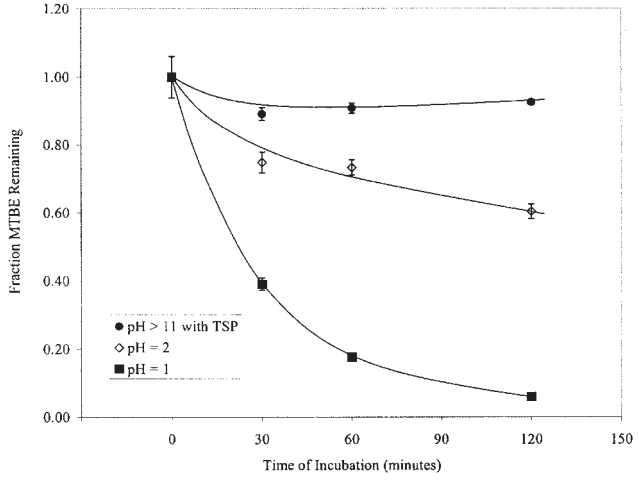

Figure 1. Effect of pH on the rate of hydrolysis of MTBE at 80°C. Presented are the mean and one standard deviation of the three replicate analyses.

The data on the loss of MTBE was used to calculate an empirical first-order rate constant for loss of MTBE at that particular pH. The following expression was used:

$$\frac{[MTBE]}{[MTBE]_0} = e^{-kt} \quad (1)$$

where [*MTBE*] is the concentration of MTBE at time, *t*; $[MTBE]_0$ is the original concentration of MTBE; and *k* is the observed rate constant for hydrolysis.

Realizing that the left-hand side of Equation 1 is the fraction of MTBE remaining, the curves in Figure 1 for pH = 1 and pH = 2 can be fit to Equation 1. Results are presented in Table 2.

As verified in Figure 2, one molecule of MTBE hydrolyzes to produce one molecule of TBA. When the extent of hydrolysis is limited, the first-order rate of MTBE hydrolysis can also be estimated by dividing the zero order rate of TBA production by the initial concentration of MTBE. The following expression can be used to solve for the first-order rate of MTBE hydrolysis to TBA:

$$\frac{[TBA] - [TBA]_0}{[MTBE]_0} = kt \quad (2)$$

This is the approach taken by O'Reilly et al. (2001) to estimate rates at 26°C and 37°C. Results obtained in this study are compared to the results of O'Reilly et al. (2001) in Table 2.

After 120 min of incubation at 80°C, the concentration of TBA was still less than the method detection limit (2.6 µg/L) in every sample that was preserved with TSP. The initial concentration of MTBE in the samples that were preserved with TSP was 476 µg/L. The detection limit for TBA and the initial concentration of MTBE were used in Equation 2 to estimate an upper boundary on the rate of MTBE hydrolysis in the samples preserved with TSP (Table 2). The rate was at least 50 times slower than the rate at pH = 2.00.

To make it easier to distinguish the effect of temperature from the effect of acid, the empirical first-order rate constants were divided by the hydrogen ion concentration. In this study, the hydrogen ion concentration was calculated from the measured pH, with the assumption that the activity coefficient of the hydrogen ion is unity. In the data presented in Table 2 of their report, O'Reilly et al. (2001) used the Debye-Huckel equation to calculate the activity of the hydrogen

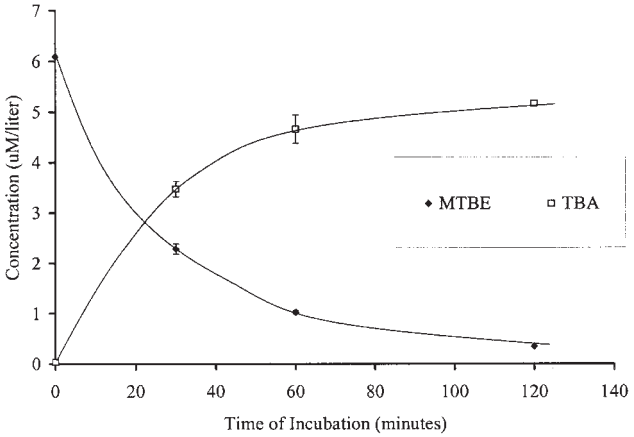

Figure 2. Concomitant production of TBA during hydrolysis of MTBE at 80°C and pH = 1. Presented are the mean and one standard deviation of the three replicate analyses.

ion from the measured pH. After the empirical rate constants are corrected for the concentration of the hydrogen ions, there is good agreement between the rate constants that are extracted at pH = 1 and at pH = 2 (compare the second column of rate constants in Table 2 for the rate at pH = 1 against the rate at pH = 2).

There was a large effect of temperature on the rate of hydrolysis. The rate at 80°C is ~1000 times greater than the rate at 26°C. The Arrhenius relationship (Atkins 1990) can be used to extrapolate a rate constant for hydrolysis at 80°C from the rates reported by O'Reilly et al. (2001) for hydrolysis at 26°C and 37°C. The rate of hydrolysis at 80°C that is extrapolated from their data is 11/h/[H+]. This is in good agreement with our measured rate constants at 80°C (Table 2).

Limited Acid Hydrolysis of MTBE During Storage

Ground water from the plume of MTBE at Port Hueneme was used to measure the rate of acid hydrolysis of MTBE in water samples during storage. Water was sampled in June 2001, and preserved in the field with HCl to pH < 2, following the recommended practice in California at the time. The samples were shipped to the R.S. Kerr Environmental Research Center, where they were stored at 5°C (range 4.5° to 7°C) until they were analyzed. Samples from 40 monitoring wells were analyzed 45 d after collection and preservation. Replicate water samples from the same 40 wells were analyzed 282 d after collection. The samples were made basic just prior to analysis by the addition of TSP to each sample, and the analysis was conducted using a heated headspace sampler with gas chromatography and mass spectrometry (Lin et al. 2003). The concentrations determined after 45 and 282 d of storage are presented in Figure 3.

There was minimal effect of the acid. In the figure, a line with perfect 1:1 correlation is plotted for comparison purposes. It can be seen that, while the relation is linear and the slope is nearly 1, a majority of the points lie below the line. In the samples from the 40 wells, the average loss during 237 d of storage at 5°C was 5.3% of the initial concentration (± 0.40% at one standard deviation). This corresponds to a rate of loss of 0.0000096/h. The rate of hydrolysis at 80°C is more than 100,000 times faster (Table 2).

Douthit et al. (2002) conducted a similar experiment where they spiked ground water with 200, 2000, or 20,000 µg/L MTBE, acidified the water to pH = 2, and stored the samples at 4°C for up to 31 d; < 3% of the MTBE was hydrolyzed to TBA. Rose and Sandstrom (2003) adjusted water to pH = 2, spiked water samples with 2 µg/L MTBE, and stored the water samples at 4°C for 46 d. The average relative recovery was 106% with a relative standard deviation of 4.8%.

If water samples are kept refrigerated at 4° ± 2°C until analysis, if they are analyzed in a reasonable period of time, and if the samples are analyzed at room temperature or neutralized before analysis, then the use of acid as a preservative should not compromise the quality of the data with respect to concentrations of MTBE. There is no compelling reason to change the current practice of preservation with HCl if the samples are stored at 4° ± 2°C and the pH is adjusted before analysis.

Current reports (Rose and Sandstrom 2003; Marr et al. 2003) indicate that a heated purge can be used without the incurrence of hydrolysis. Written methodologies are generally

Table 2
Effect of Temperature and pH on the Rate of Hydrolysis of MTBE to TBA in Aqueous Solution

Temperature (°C)	pH	Basis[a]	Rate of Acid Hydrolysis MTBE Per Hour[b]	Per Hour Per [H+]	Reference
80	1.0	MTBE	1.22 ± 0.121	12	This study
80	2.0	MTBE	0.15 ± 0.055	15	This study
80	> 11	TBA	<0.00342		This study
37	1.1	TBA	0.00327 ± 0.00019	0.046	O'Reilly et al. 2001
37	2.0	TBA	0.000383 ± 0.000045	0.049	O'Reilly et al. 2001
26	1.1	TBA	0.000768 ± 0.000040	0.0094	O'Reilly et al. 2001
26	2.0	TBA	0.0000752 ± 0.0000011	0.0088	O'Reilly et al. 2001
5	< 2	MTBE	0.0000096 ± 0.0000014		This study

[a]Calculated from loss of MTBE or production of TBA
[b]Rate ± twice the standard error of the rate

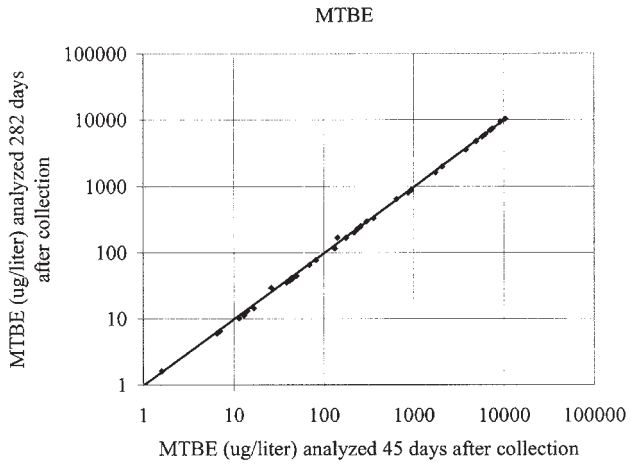

Figure 3. Effect of time of storage at 5°C on the measured concentrations of MTBE in water samples preserved with HCl to pH < 2. The solid line represents a perfect correlation.

very prescriptive. However, there is extensive variation in equipment and personnel available at each laboratory. This variability is such that an appropriate purge temperature cannot be universally established. Marr et al. (2003) attest to the improved performance of TBA under a mildly (45°C) heated purge. Reports (Rose and Sandstrom 2003; Marr et al. 2003) indicate that a heated purge can be used without incurring significant hydrolysis. However, if heating is used, it is incumbent upon the chemist to prove that the reported results are not adversely affected by hydrolysis. If data has been collected without using a heated purge, there is no reason to suspect that hydrolysis would have caused any problems in the analysis of MTBE or TBA concentrations.

Case Study: A False Positive for TBA in a Plume of MTBE

In May 2000, ground water samples were collected from a large plume of MTBE from a release of reformulated gasoline at a site in Lindenhurst, New York. Monitoring wells at the site were organized in well clusters. At each cluster, a separate well in the cluster was screened every 5 ft. Temporary push samples were also organized in clusters. At each cluster a separate sample was acquired every 4 ft. Each well cluster extended from the water table to a total depth of either 40 or 50 ft. The well clusters were arranged in a transect that was oriented along the direction of ground water flow and extended from the leading edge of the plume into clean ground water in front of the plume. Samples were collected into 40 mL vials and preserved with HCl to a pH < 2. The samples were then cooled to 4°C and shipped to Pittsburgh, Pennsylvania, for analysis.

The samples were collected and analyzed before the release of the report by O'Reilly et al. (2001). The New York State regulator wanted good reproducibility at concentrations at or below 12 µg/L. There were several methodology choices available, but given the data quality objectives, the available equipment, and the information available at that time, a heated headspace-gas chromatography was chosen for the analysis. Specifically, samples were placed in a heated headspace sampler and analyzed using gas chromatography with a flame ionization detector (Pirkle and McLoughlin 2003).

Results are presented in Figure 4. Ground water flow is from the left to the right in the figure. The well clusters at locations ML–12 and ML–3 encompassed the plume vertically. The maximum concentrations of MTBE exceeded 10,000 µg/L. The analyses revealed a plume of TBA that was roughly congruent to the plume of MTBE, with concentrations of TBA that were ~0.1 of the concentrations of MTBE.

After these data were collected, the authors of this paper became aware of the possibility of hydrolysis of MTBE during analysis by the acid used to preserve the water sample. In June 2001, a subsequent round of samples were collected from the same site using the same methods for collection and analysis of the samples, but TSP was used as the preservative rather than HCl.

The MTBE plume is contained in a sand aquifer on Long Island. The seepage velocity of the plume is near 1.8 ft/d. In the 13 months between sampling events, the plume would be expected to move ~700 ft. The results of the second round of sampling are presented in Figure 5. As expected, the MTBE plume extended farther downgradient. As was the case in the earlier round of sampling, the concentrations of MTBE exceeded 10,000 µg/L. However, TBA was not detected in any well in the plume at concentrations above the lower reporting limit (5 µg/L). This suggests the TBA plume observed in the earlier round of sampling was an artifact of

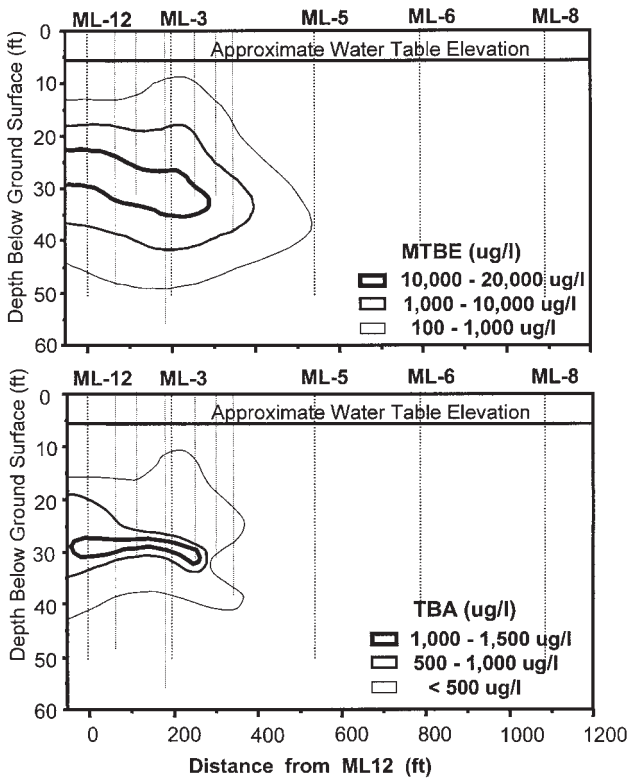

Figure 4. Apparent distribution of MTBE and TBA in a plume of gasoline contamination on Long Island, New York. The ground water samples were collected in May 2000 and were preserved in the field using HCl to pH < 2. Dashed vertical lines represent the location of permanently installed, multilevel monitoring wells and the location of temporary push point wells. The figure is redrawn from Pirkle and McLoughlin (2003).

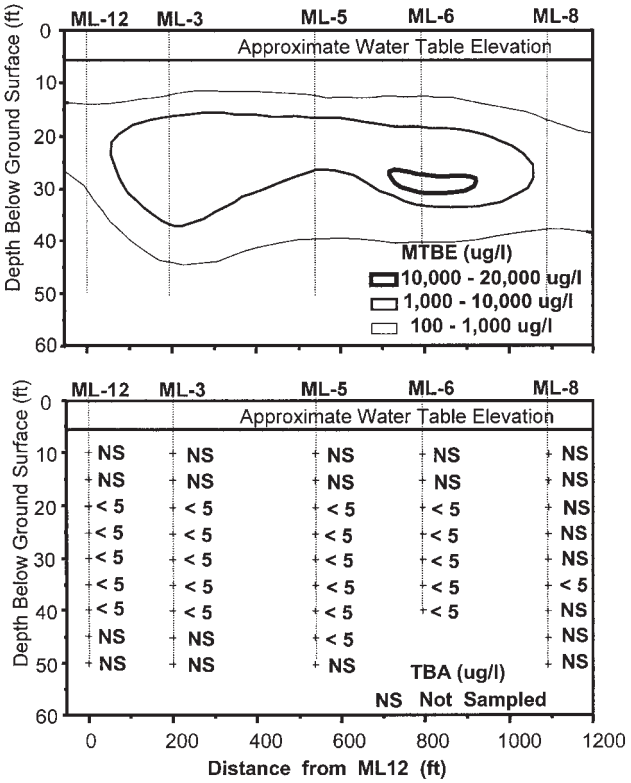

Figure 5. True distribution of MTBE and TBA in a plume of gasoline contamination on Long Island, New York, in samples collected in June 2001. The samples were preserved in the field using TSP to pH > 11. Dashed vertical lines represent the location of permanently installed, multilevel monitoring wells and the location of temporary push point wells. The figure is redrawn from Pirkle and McLoughlin (2003).

the preservative and of the use of a heated headspace sampler to prepare the samples for analysis.

To confirm that the TBA was being produced in the headspace sampler and not in the aquifer, replicate samples from the second round of sampling were acidified to a pH < 2 with 6 N HCl. The acidified samples were then analyzed using the same technique. Results are presented in Figure 6. The concentrations of MTBE were lower; no sample exceeded 10,000 µg/L. The distribution of TBA followed the same pattern seen in the earlier round of samples that had been preserved with HCl in the field. The apparent plume of TBA was roughly congruent to the plume of MTBE. Acidifying the samples reconstructed the codistribution of TBA and MTBE that was seen in the first round of samples, further confirming that the TBA was produced during sample preparation.

Comparison of the Performance of HCl and TSP as Preservatives

Three studies were conducted to evaluate HCl and TSP as preservatives. The first study documented the ability of the preservatives to inhibit general microbial metabolism by examining their effect on the expressed biological oxygen demand (BOD) of readily degraded organic compounds in a standard BOD test (APHA 1989). Deionized water was fully aerated; then a solution of glucose and glutamic acid (GGA) was added to produce an oxygen demand of 200 mg/L. The water was then amended with mineral nutrients, a phosphate buffer, and a microbial seed prepared from InterLab's Polyseed (The Woodlands, Texas). A BOD test was conducted following the procedure in Standard Methods 5210B (APHA 1989). Before incubation, and after the phosphate buffer addition, three of the samples were brought to pH < 2 with 6 N HCl and three of the samples were brought to a pH > 11 with TSP. Three samples were not preserved to act as controls. The BOD exerted in the controls without preservative was 210, 205, and 198 mg/L, corresponding to a spike recovery of 105%, 103%, and 98.7%, respectively. The BOD exerted in the treatments preserved with HCl to pH < 2 and in treatments preserved with trisodium phosphate to pH > 11 were all < 1.0 mg/L. HCl and trisodium phosphate were equally effective in inhibiting aerobic biological oxygen demand.

The second experiment compared the effectiveness of HCl and TSP as preservatives for selected compounds of regulatory interest at gasoline spill sites, specifically BTEX and MTBE. Three beakers of aerated water were inoculated with the BOD microbial seed, buffer, and mineral solutions as described previously. Water in one of the beakers was then acidified with 6 N HCl to a pH < 2, and TSP was added to water in a second beaker to pH > 11. These solutions were then transferred without headspace to 40 mL VOA vials. Six vials were filled with the HCl preserved solution, six vials were filled with the TSP preserved solution, and five vials

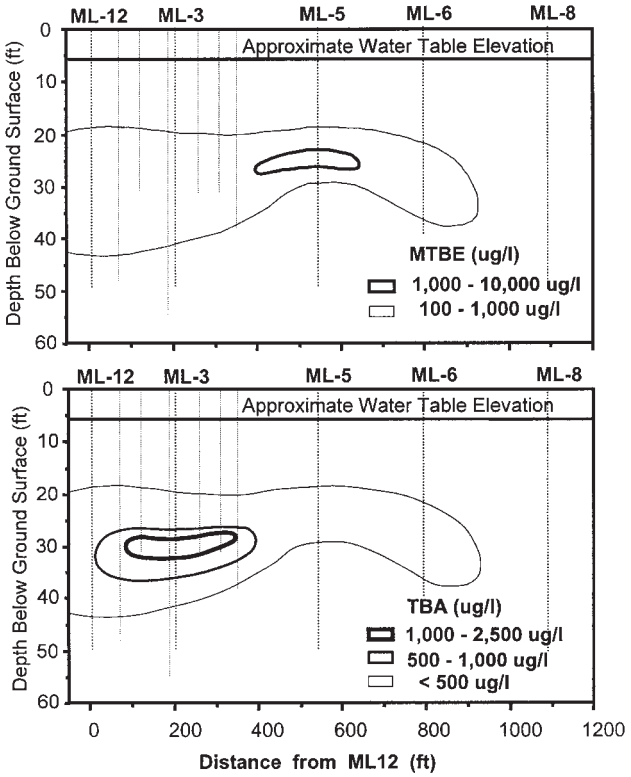

Figure 6. Reconstruction of the apparent distribution of TBA seen in May 2000 (Figure 4) created by adjusting the samples collected in June 2001 (Figure 5) to pH < 1 with HCl before sample preparation and analysis. Dashed vertical lines represent the location of permanently installed, multilevel monitoring wells and the location of temporary push point wells. The figure is redrawn from Pirkle and McLoughlin (2003).

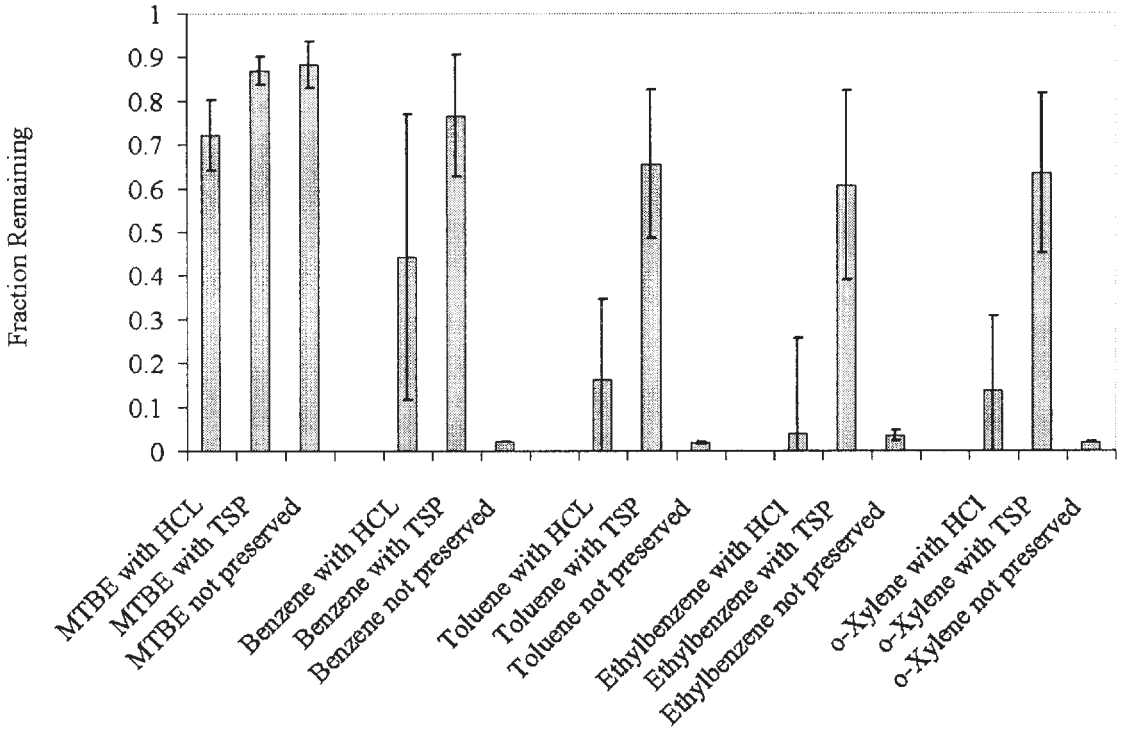

Figure 7. Stability of MTBE and BTEX in water samples after 66 d of storage at room temperature when the samples are preserved with HCl to pH < 2, when the samples are preserved with trisodium phosphate to pH > 11, and when the samples are not preserved. The error bars are one standard deviation on the mean.

were filled with the unpreserved solution. BTEX and MTBE were added to each vial as a concentrated solution in methanol to a final concentration in water of 50 µg/L. The vials were then stored at 20°C for 66 d; then they were analyzed for BTEX and MTBE using SW846–8021 (U.S. EPA 1997). Results are presented in Figure 7.

After 66 d of storage at room temperature, there was no significant difference between the recovery of MTBE in the samples that were preserved with TSP and the samples that were not preserved. The recovery was slightly less in the water samples that were preserved with HCl. In the samples that were not preserved, there was extensive biodegradation of benzene, toluene, ethylbenzene, and o-xylene after 66 d of storage.

It is necessary to preserve ground water samples that are intended for the analysis of BTEX compounds. There was also extensive removal of benzene, toluene, ethylbenzene, and o-xylene in the water preserved with HCl. The recovery of MTBE in the water samples that were preserved with TSP was good. There were lower recoveries of benzene, toluene, ethylbenzene, and o-xylene. This may be caused by sorption of these compounds to components of the VOA vial after 66 d of incubation (compare BTEX sorption in the study of Kovacs and Kampbell [1999]). It is recognized that the biota will vary from ground water sample to ground water sample, and that samples of ground water may not be well represented by the inoculum used in these experiments. However, in these controlled comparisons, preservation with TSP was at least as effective as preservation with acid at hindering biodegradation.

Because it promotes acid hydrolysis of MTBE, HCl cannot be considered a universal preservative for ground water samples. Because it avoids problems with MTBE hydrolysis, trisodium phosphate is a useful alternative preservative for fuel hydrocarbons and fuel oxygenates in ground water. However, as was the case with HCl, trisodium phosphate is not a universal preservative. Jeffers et al. (1989) determined Arrhenius constants for base catalyzed and neutral hydrolysis of selected chlorinated hydrocarbons. As calculated from their published constants for the conditions of a heated head space analysis (pH = 11.7, 80°C, 30 min incubation), > 80% of 1,1,2-trichloroethane; 1,1,2,2-tetrachloroethane; and 1,1,1,2-tetrachloroethane would hydrolyze and ~50% of chloroform would hydrolyze. However, < 6% of 1,1,1-trichloroethane and 1,2-dichloroethane, and < 1% of carbon tetrachloride; trichloroethylene; tetrachloroethylene; 1,1-dichloroethylene; 1,2-dichloroethylene; or 1,1-dichloroethane would hydrolyze.

In a third study, the performance of HCl and TSP was tested on a suite of halogenated hydrocarbons including dichlorodifluoromethane, chloromethane, vinyl chloride, bromomethane, chloroethane, and trichlorofluoromethane. VOA vials were prepared as previously described with preservative using organic-free reagent grade water; then each of the vials was spiked with a concentrated solution of the halogenated hydrocarbon in methanol that would produce a concentration in water of 100 µg/L for each of the halogenated hydrocarbons. The vials were stored at 20°C for 27 d; then they were analyzed for the halogenated organic compounds using SW846–8021. Results are presented in Table 3. There was extensive loss of bromomethane in the samples that were preserved with trisodium phosphate. Trisodium phosphate is useful for preservation of selected halogenated hydrocarbons, but not for the entire suite of analytes.

Table 3
Percent Recovery of a Spiked 100 µg/L of Selected Halogenated Hydrocarbons from Water Samples

Compound	HCl	Unpreserved	TSP
	Mean ± Standard Deviation (n = 3) as Percent of Spiked Concentration		
Bromomethane	77 ± 5.4	61 ± 16	5.0 ± 4.3
Chloroethane	112 ± 6.3	86 ± 13.2	95 ± 2.8
Chloromethane	138 ± 6.8	92 ± 11	95 ± 4.1
Dichlorodifluoromethane	99 ± 2.5	49 ± 2.2	68 ± 1.4
Trichlorofluoromethane	97 ± 5.2	78 ± 14.4	81 ± 7.4
Vinyl chloride	118 ± 1.4	89 ± 5.6	100 ± 1.3

After 27 days of storage at 20°C when the samples are preserved with HCl to pH <2, when the samples are not preserved, and when the samples are preserved with trisodium phosphate to pH >11

Additional studies are under way at the Kerr Center to evaluate alkaline hydrolysis during analysis using a heated headspace sampler when samples are preserved with 1% wt/vol trisodium phosphate. From 39% to > 99% of spiked concentrations of dibromofluoromethane; 1,1,2,2-tetrachloroethane; 1,2-dibromo–3-chloropropane; 1,1,2-trichloroethane; bromomethane; dibromochloromethane; bromoform; and 1,1,1,2-tetrachloroethane are lost when trisodium phosphate is present (data has been published and can be supplied by author upon request).

Summary and Implications for Sampling at Gasoline Spill Sites

If ground water samples are transported and stored at 4°C, and if they are analyzed within two weeks of collection, the use of HCl as a preservative will not cause a problem with hydrolysis of MTBE to TBA during transport and storage. Based on the relationship between the pH of the sample, the temperature of the sample, and rate of hydrolysis, there will not be a problem with hydrolysis during analysis of the samples using a purge and trap sampler at room temperature.

Often, conventional procedures for analysis of water samples by purge and trap at room temperature cannot determine TBA at California's drinking water action level of 12 µg/L. One approach to increase sensitivity for TBA is to heat the water sample during analysis. If water samples are heated during analysis, there may be a problem with hydrolysis of MTBE to TBA. In this study, samples were analyzed using static headspace samplers heated to 80°C, and ~33% to 50% of the MTBE hydrolyzed to TBA during analysis. This problem can be avoided by using trisodium phosphate as the preservative instead of acid, or by neutralizing the acid used as a preservative prior to sample analysis.

Trisodium phosphate is effective at preventing biodegradation of MTBE and fuel hydrocarbons. However, it is not appropriate for preservation of certain halogenated hydrocarbons. Bromomethane is extensively degraded in the presence of trisodium phosphate at room temperature. Extensive base catalyzed hydrolysis of 1,1,2-trichloroethane; 1,1,2,2-tetrachloroethane; 1,1,1,2-tetrachloroethane; and chloroform should be expected during analysis with a heated headspace sampler (calculations from data of Jeffers et al. [1989]). If trisodium phosphate is used as a preservative, dibromofluoromethane should not be used as a surrogate standard.

Acknowledgments

The authors would like to thank Joseph E. Haas II of the New York State Department of Conservation, Region II, for use of the New York site, for pertinent and encouraging discussions with the authors, and for partial support of this work. We would also like to thank Murray Einarson, Doug Mackay, and staff of the Naval Facilities Engineering Service Center for their interest and encouragement, and for providing water samples from the site at Port Hueneme, California. Jim Davidson with Exponent, Al Verstuyft with Chevron Texico Energy Research and Technology Co., and two anonymous peer reviewers identified the deficiencies in our review draft with candor and objectivity, and offered explicit and useful suggestions to improve the manuscript.

Authors' Note: The U.S. Environmental Protection Agency through its Office of Research and Development partially funded and collaborated in the research described here under inhouse task 5857 (Natural Attenuation of MTBE) at the Ground Water and Ecosystems Restoration Division of the National Risk Management Laboratory, and under task 5219 through contract number CR 68-C–98–138. It has not been subjected to agency review and therefore does not necessarily reflect the views of the agency. No official endorsement should be inferred.

Editor's Note: The use of brand names in peer-reviewed papers is for identification purposes only and does not constitute endorsement by the authors, their employers, or the National Ground Water Association.

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