



Seasonal and daily variations in concentrations of methyl-tertiary-butyl ether (MTBE) at Cranberry Lake, New Jersey

Laura Toran^{a,*}, Charles Lipka^a, Arthur Baehr^b, Timothy Reilly^b, Ronald Baker^b

^a Department of Geology, Temple University, 1901 N. 13th Street, Philadelphia, PA 19122-6081, USA

^b US Geological Survey, West Trenton, NJ 08628, USA

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Abstract

Methyl-tertiary-butyl ether (MTBE), an additive used to oxygenate gasoline, has been detected in lakes in northwestern New Jersey. This occurrence has been attributed to the use of gasoline-powered watercraft. This paper documents and explains both seasonal and daily variations in MTBE concentrations at Cranberry Lake. During a recent boating season (late April to September 1999), concentrations of MTBE typically exceeded 20 µg/L. MTBE concentrations varied daily from 12 to 24 µg/L over a 2-week period that included the Labor Day holiday. Concentrations were highest on weekends when there is more boat traffic, which had an immediate effect on MTBE mass throughout the lake. MTBE concentrations decreased to about 2 µg/L shortly after the end of the summer recreational season. The loss of MTBE can be accounted for by volatilization, with a half-life on the order of 10 days. The volatilization rate was modeled with the daily decrease in MTBE then the modeled rate was validated using the data from the seasonal decline.

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1. Introduction

Methyl-tertiary-butyl ether (MTBE) is an additive used to oxygenate gasoline to improve air quality by reducing tailpipe emissions of carbon monoxide and ozone precursors. The US Environmental Protection Agency (USEPA) initially approved the use of MTBE to reduce ground-level ozone concentrations in 1979, and the compound currently is the most widely used oxygenate across the country, particularly in the northeastern United States. During the period of data collection for this study, a program in effect in the State of New Jersey required blending 14.8% MTBE by volume to gasoline from November to February, and

blending 11% MTBE by volume during the rest of the year.

MTBE has been detected throughout the hydrologic cycle. Most notable are incidents of high-level groundwater contamination associated with fuel spills and leaks. For example, ground water at approximately 10,000 sites in California is contaminated with MTBE [1]. Half of the Santa Monica public-water-supply wells were closed because MTBE concentrations were as high as 600 µg/L [2]. As part of the National Water Quality Assessment (NAWQA) program conducted by the US Geological Survey (USGS), Squillace et al. [3] found that MTBE was the second most frequently detected volatile organic compound (VOC) in ground water in nine areas across the country. MTBE also has been found in urban storm runoff and streams [4], lakes [5–9], and improper disposal of used motor oil [10]. MTBE in the atmosphere over southern New Jersey was monitored from 1996 to 1998 [11,12]. Typical atmospheric

*Corresponding author. Tel.: +1-215-204-2352; fax: +1-215-204-3496.

E-mail address: ltoran@temple.edu (L. Toran).

concentrations were in equilibrium with aqueous concentrations of about 0.1 µg/L.

In addition to its enormous production and widespread use, MTBE has properties that make it mobile and a threat to water supplies. It is a suspected carcinogen [13,14], is highly soluble in water (50,000 mg/L), does not sorb readily to soils, and is generally believed to be less degradable than other gasoline components (i.e., BTEX, or benzene, toluene, ethylbenzene, and xylene). Based on MTBE's documented occurrence in the environment and its anticipated fate in aquifers, a Blue Ribbon Panel commissioned by the USEPA [15] recommended that its use be phased out. Several states have enacted legislation to phase out use of MTBE, but as of this writing, only Colorado and Alaska have banned MTBE.

The occurrence of MTBE in lakes is a result of unburned fuel and exhaust introduced routinely to water simply by operation of gasoline-powered watercraft. Gabele and Pyle [16] found that concentrations of MTBE and BTEX in emissions from outboard engines are higher in two-stroke engines than in four-stroke engines. Also, their study of emissions of engines operating at different rates showed that an engine operating in trolling mode would release more fuel than a speeding engine.

MTBE occurrence has been documented in lakes in Nevada and California [6–9] and in northern New Jersey [5]. Concentrations of MTBE in Lake Tahoe, Nevada (500 km² or 123,000 acre), ranged from 0.18 to 4.2 µg/L, and the compound was found throughout the 30-m vertical profile [6]. Reuter et al. [8] found that 86% of the variation in MTBE concentration in Donner Lake (3.9 km² or 950 acre) in California could be attributed to monitored variations in boat traffic, on the basis of sampling approximately monthly from March 1997 to January 1998. Concentrations increased from 2 to 12 µg/L on July 4, holiday. The decline in concentrations during the fall was attributed to volatilization on the basis of mass-balance calculations, which showed that stream discharge was not a large enough sink to account for the decrease. A half-life of 14 days was estimated from the concentration decline and an average wind speed of 1.8–2.3 m/s (4–5 mph).

A similar half-life (10 days) was calculated by Stocking and Kavanaugh [9] for Lake Perris (9.1 km² or 2240 acre), also in California. Using a two-layer diffusion model, they fit monthly MTBE concentration decline after the boating season to a model in which a 4.5-m/s (10-mph) wind speed (close to the measured average) was assumed. The observed concentration fell from 25 to 1 µg/L, and the MTBE dissipated in about 20–25 days once the source (boat traffic) ceased. Dale et al. [7] compared Lake Perris to several lakes in the same region and found no detectable MTBE where watercraft traffic was prohibited. The greatest variation

in MTBE concentrations was observed in lakes with the highest boat traffic and increased traffic was linked to higher concentrations.

Among the highest MTBE concentrations reported for ambient conditions (not associated with a spill) have been in the New Jersey lakes. Concentrations reported for Cranberry Lake and Lake Lackawanna during the summers of 1998 and 1999 ranged from 20 to 30 and 5 to 14 µg/L, respectively. MTBE concentrations in Lake Hopatcong, New Jersey's largest lake, were as high as 20 µg/L during the summer of 1999 [17].

This paper documents daily and seasonal variations in MTBE concentrations determined from analysis of lake-water samples at Cranberry Lake and explains the relation between watercraft use and the major attenuation mechanism—volatilization of MTBE from the lake surface. This work is part of a larger study by the USGS that seeks to identify the mechanisms of MTBE migration to wells at Cranberry Lake and other lakeside communities. Furthermore, understanding the fluctuation in MTBE concentration in this lake helps predict conditions at other lakes and aids in monitoring design. Although the link between MTBE concentration and watercraft use has been reported previously, the daily sampling conducted during this study provides additional information on the rates of change from boat use and subsequent MTBE volatilization.

2. Study area

The lakes region in northern New Jersey is in the New England and Valley and Ridge physiographic provinces. Cranberry Lake occupies about 0.76 km² (187 acre) in Sussex County and, like other large lakes in the region, it is man-made, with its level maintained by dams. The deepest parts of the lake are about 5 m deep and the average depth is about 2 m. The Cranberry Lake community consists of about 500 residences (Fig. 1). This community derives its water supply from wells that draw water from the fractured crystalline rock aquifer [5]. Density stratification is observed in the deep portions of the lake in early summer, but after the beginning of August the lake waters are vertically mixed [17].

Strawberry Point (Fig. 1) divides the lake into a northern and a southern section. This report focuses on the northern section. The inlet side of the lake, south of Strawberry Point, receives less boat traffic than the northern part because it is shallower water and contains lakebed obstructions. Consequently, MTBE concentrations are lower [17]. The northern part of the lake has an estimated volume of 1.13 km³, or 74% of the lake's total volume, and a corresponding 54% of its total area (0.409 km²). The volume of the lake was estimated from

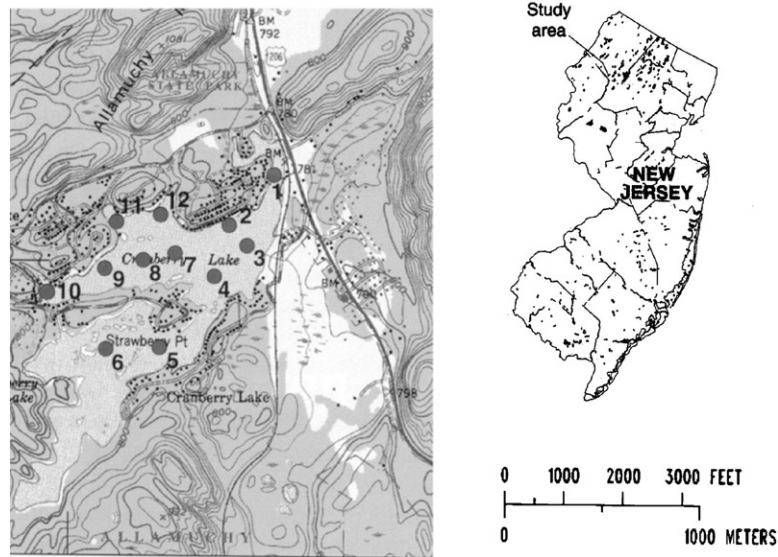


Fig. 1. Topographic map showing locations of Cranberry Lake and lake-sampling sites in previous study [17]. Site 1 is the footbridge used as a sampling location in this study. Basemap is from USGS 1:24,000 and the footbridge is located at $40^{\circ}52'13''$ latitude, $74^{\circ}56'16''$ longitude.

bathymetry and monthly measurements of lake-water level.

MTBE was detected in samples from 13 of the 14 wells sampled at Cranberry Lake in fall 1998 and summer 1999 [17]. The wells were selected to monitor ambient ground-water quality and had no history of contamination. During the fall 1998 synoptic sampling, MTBE concentrations in the wells ranged from 0.12 to 19.8 $\mu\text{g/L}$ (median concentration 0.43 $\mu\text{g/L}$). During the summer 1999 synoptic sampling, MTBE concentrations in the wells ranged from 0.14 to 13.2 $\mu\text{g/L}$ (median concentration 0.38 $\mu\text{g/L}$). Lake/well interaction is a feasible explanation for the near-ubiquitous occurrence of MTBE in ground water. The movement of water from the lake to wells is physically feasible because many static water levels and nearly all pumped water levels in the wells were below the level of the lake. Therefore, an understanding of the time-dependence of the source (the lake) is needed to predict and protect the ground-water quality.

3. Methods

To determine the seasonal variability of MTBE concentrations, Cranberry Lake was sampled four times in 1998 (6/24 to 12/16) and 12 times in 1999 (4/7 to 11/22). In 1999, both shallow and deep samples were collected from the lake, with the shallow sample at 1 m and the deep sample at 3 m when the lake level was sufficiently high and at 2 m when the lake level was

lower. The deep sample was below the thermocline when the lake was stratified.

Results of previous lakewide synoptic sampling at as many as 11 other locations showed that the concentrations measured at a footbridge across the northern arm of the lake are representative of concentrations throughout the northern portion of the lake [17]. Furthermore, the concentrations at the footbridge are about three times the concentrations in the southern portion of the lake [17]. For this reason, the northern arm was considered separately from the rest of the lake, and the concentrations, masses, and volumes reported are those in the northern arm. Stratification of the lake was measured through use of temperature profiles.

The footbridge was used as the sampling location for all water samples reported here. A peristaltic pump and plastic tubing were used to draw samples into 40-mL glass vials on the bridge about 3.6 m above the water surface. Analysis of a duplicate sample collected from a boat beneath the bridge showed that MTBE mass was not lost as a result of this sampling procedure [17].

To determine daily variability, Cranberry Lake was sampled from the footbridge nine times over a 2-week period (8/26/99–9/8/99) that included the Labor Day holiday. MTBE concentration also was measured in two streams and two stormwater drains entering Cranberry Lake in the summer and fall of 2000. Runoff samples were collected during the seasonal sampling in 1999. Although precipitation was not directly measured at the site, data on MTBE in precipitation elsewhere in New Jersey were used [12].

MTBE and BTEX concentrations in about 40% of the water samples were quantified at the USGS Water Quality Laboratory, Arvada, CO, using USGS Method Schedule 2022. This standard USGS method uses purge-and-trap isolation and concentration followed by capillary-column gas chromatography/mass spectroscopy (GC/MS) and is described in detail by Connor et al. [18]. About 60% of the samples were analyzed in the New Jersey District Laboratory, West Trenton, NJ, by purge-and-trap isolation and concentration followed by capillary-column gas chromatography with a flame ionization detector (GC/FID). The analytical instrumentation consisted of a Varian 3600 gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA), a Tekmar 3000 concentrator with a Tenax[®] trap, and a Tekmar Precept II autosampler (Tekmar-Dohrman, Cincinnati, OH). A 30-m-long DB-MTBE column (0.45 mm internal diameter and 2.55 mm film thickness) (J&W Scientific, Folsom, CA) was used with a zero-grade helium flow rate of 5 mL/min. This column is specifically designed for separating MTBE from hydrocarbons with similar elution times. Sample purge time was 11 min using helium at a purge rate of 40 mL/min, and sample volume was 5 mL. The GC temperature program used was 35 isothermal for 7 min, 4°C/min to 140°C, rapid increase to 200°C, and 200°C isothermal for 4 min. An analytical standard stock solution was prepared by dissolving 20 µg reagent-grade MTBE and BTEX compounds into a glass 2-L spherical flask completely filled with deionized, organic-free water, yielding analyte concentrations of about 10,000 µg/L. Dilutions of the stock solution were made in 40-mL VOC vials completely filled with water. A minimum of six standard concentrations were used, ranging from about 1 to 40 µg/L. Standard curves (linear regressions) were prepared using standard concentrations and peak areas. MTBE and BTEX compounds were identified in chromatograms by peak retention times. Nineteen samples were split and analyzed by both labs providing GC/MS confirmation of peak identifications. At least one organic-free-water blank and one standard was included in each batch of 8–12 samples. The mean difference between duplicate samples (25 sets) was 6.0%. Method minimum reporting levels were less than 1 µg/L for both methods.

The concentrations of MTBE in the lake can be used to estimate the number of gallons of gasoline loaded into the lake on the basis of the weight of MTBE in gas and the volume of the lake. Again, the northern arm was considered separately from the southern arm because watercraft traffic (and thus gasoline discharge) differs between the two portions. The northern arm of Cranberry Lake was well-mixed during the period of daily sampling. The lake volume used in calculations is that of the northern arm, 1.13 billion L (assumed to be constant for calculation purposes). For example, the

MTBE concentration was 15.8 µg/L on 9/3/99, which is 17,854 g of MTBE in the northern arm of the lake. Each gallon of gasoline contains about 312 g of MTBE based on an 11% fuel mixture. Thus, on this sampling date the volume of gasoline accumulated was calculated as 17,854 g divided by 312 g/gal, or 57.2 gal of gasoline. This estimate does not account for differential volatilization of gasoline components, and does not represent free product. It merely provides a bound on loading in units related to usage (gallons).

Watercraft traffic and wind are additional parameters that can be used to interpret results. Although these were not directly measured at Cranberry Lake during the course of the study, some assumptions can be made. Watercraft traffic tends to be greater in the summer and on the weekends than at other times. The Labor Day weekend included in the daily sampling was an extended period of recreation on the lake (with potential MTBE inputs). Although wind speed was not measured directly, data from an airport weather station 32 km (20 miles) away were examined for variations during the daily sampling period. These data provide bounds on typical wind speed and changes in wind speed during the study.

4. Results

4.1. Seasonal variations

Summertime MTBE concentrations in Cranberry Lake were between 15 and 30 µg/L for the shallow samples (Fig. 2). These concentrations are not associated with a spill. For both years of the study, the concentrations decreased from a high of 25–30 µg/L in mid-summer to 3 µg/L or less in November. Stratification of both MTBE concentrations (Fig. 2) and temperature occurs in May, June, and July, the warmer months as expected. The thermocline occurs at a depth of 2.4 m.

From these data, the mass of MTBE in the northern arm can be estimated for those dates when the lake was mixed (Table 1). Bi-weekly temperature profiles indicate that the lake was not stratified from late August to early spring, and the total volume of the northern part of the lake is applicable for mass calculations. Furthermore, concentrations in the samples collected at depths of 1 and 3 m were nearly identical from August to May, indicating mixing. The peak mass when the lake was mixed reached 19.4 kg, or the equivalent of 62 gal of gasoline. (Higher concentrations were observed when the lake was stratified, but the volume estimate was not done for individual lake layers.) There are no marinas on the lake, and this amount of gasoline is too large to have been spills from refueling by individual boaters. The source of the MTBE therefore is believed to be exhaust emissions and unburned fuel from

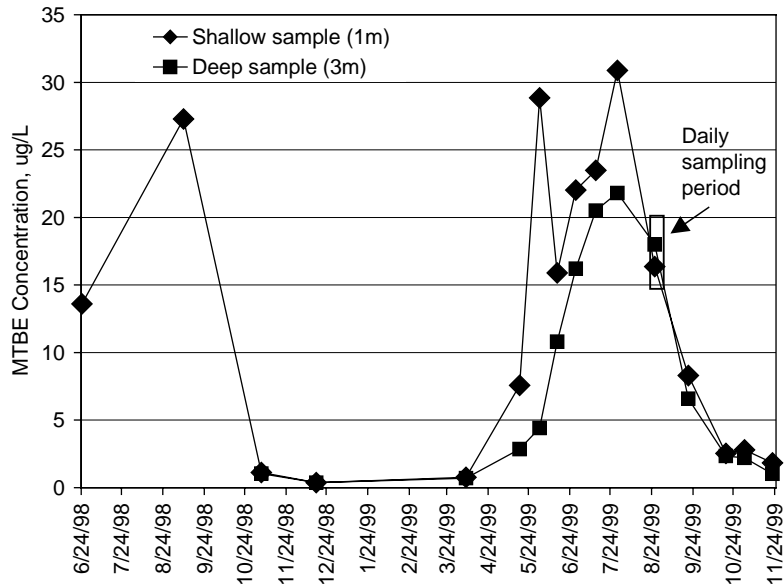


Fig. 2. Seasonal variation in MTBE concentrations in shallow and deep samples collected at the footbridge, Cranberry Lake, NJ, 6/24/98–12/3/99. Daily sampling period is shown in detail in Fig. 3.

Table 1

Seasonal variation in MTBE concentrations and equivalent volume of fuel in shallow and deep samples from the northern arm of Cranberry Lake (June 1998–November 1999)

Sampling date	MTBE concentration ($\mu\text{g/L}$)		MTBE (kg) ^a	Fuel (gal) ^b
	1 m	3 m		
6/24/98	13.6	—	7.7	S
9/8/98	27.3	—	15.4	49.4
11/5/98	1.1	1.0	1.2	3.9
12/16/98	0.4	0.4	0.4	1.4
4/7/99	0.8	0.7	0.8	2.7
5/17/99	7.6	2.9	5.9	S
6/1/99	28.8	4.4	18.8	S
6/14/99	15.9	10.8	15.1	S
6/28/99	22.0	16.2	21.6	S
7/13/99	23.5	20.5	24.8	S
7/29/99	30.9	21.8	29.8	S
8/26/99	16.4	18.0	19.4	62.2
9/20/99	8.3	6.6	8.4	26.9
10/18/99	2.5	2.4	2.8	8.9
11/1/99	2.8	2.2	2.8	9.1
11/22/99	1.8	1.0	1.6	5.2

—: no sample collected because lake too shallow.

S: Lake stratified; volume of gasoline not calculated.

^aMass of MTBE in Northern arm only, based on average MTBE concentration in shallow and deep samples.

^bEquivalent gallons of fuel calculated by assuming 11% MTBE by volume (312 g MTBE/gal fuel).

watercraft [5]. The decline in MTBE concentration in cooler months (Fig. 2), when boating on Cranberry Lake is minimal, provides additional evidence for this source.

4.2. Daily variations

MTBE concentrations during the period of daily sampling ranged from 12 to 24 $\mu\text{g/L}$ (Table 2, Fig. 3), which corresponds to a mass of MTBE in the northern part of the lake of 15–25 kg (48–80 gal of gasoline). The temperature profile indicates that the lake was mixed during this time. The shallow and deep samples typically differed by 0–3 $\mu\text{g/L}$, or as much as 20%, although on weekends the maximum difference was as much as 6 $\mu\text{g/L}$, or 25%. The concentration of MTBE in the shallow sample was higher on the weekend most likely because watercraft traffic contributed to contamination of the shallow part of the lake, and subsequently mixing distributed the MTBE throughout the lake.

The MTBE concentration was highest on the weekends and then declined approximately 6 $\mu\text{g/L}$ over 2 days. The decrease in MTBE mass indicates net mass loss of MTBE, not merely cessation of input. The daily loss rate is significant and has not previously been reported. Modeling of the mechanism of loss is presented below. Concentrations were higher during the Labor Day weekend than during the previous weekend. Anecdotal evidence suggests watercraft traffic also was greater. The total volume of gasoline increased

Table 2

Daily variation in MTBE concentrations in shallow and deep samples from the northern arm of Cranberry Lake. Mass and equivalent volume of fuel for each day, daily change, change calculated from volatilization, and estimated watercraft input

Sampling date	Day of the week	MTBE concentration ($\mu\text{g/L}$)		MTBE mass (kg) ^d	Fuel volume (gal) ^e	Change ^a in volume (gal) ^c	Calculated volatilization ^b (gal) ^c	Estimated watercraft input ^c (gal) ^e
		1 m	2 m					
8/26/99	Thursday	14.3	16.2	17.2	55.2			
8/29/99	Sunday	17.5	16.0	18.9	60.7	5.4	-5.3	10.3
8/30/99	Monday	16.2	16.7	18.6	59.6	-1.1	-5.2	4.1
8/31/99	Tuesday	13.9	12.6	14.9	47.9	-11.7	-4.1	—
9/1/99	Wednesday	13.6	14.2	15.7	50.3	2.4	-4.3	6.7
9/3/99	Friday	15.8	15.8	17.8	57.2	6.9	-5.0	(2 days) 11.9
9/5/99	Sunday	23.2	17.3	22.9	73.3	16.0	-6.6	(2 days) 22.6
9/6/99	Labor Day	23.4	18.9	23.9	76.6	3.4	-6.6	10
9/7/99	Tuesday	24.1	19.9	24.9	79.7	3.1	-6.7	9.8
9/8/99	Wednesday	20.8	17.0	21.3	68.5	-11.2	-6.1	—
9/9/99	Thursday	17.9	18.4	20.5	65.7	-2.7	-5.7	3
9/10/99	Friday	15.7	19.3	19.8	63.4	-2.4	-5.7	3.3

^a Change from previous sampling date. Negative sign indicates loss.

^b Daily volume calculated from Eq. (2) using previous measured concentration of MTBE.

^c Estimated from sum of change in fuel volume and volatilization volume where change is positive. Estimated from the difference between change and volatilization where change is negative and volatilization is larger than change in volume. Not calculated when the volatilization (using constant wind speed) underestimates the change in volume.

^d Calculated from average MTBE concentration in shallow and deep samples using volume of northern arm only.

^e Calculated from kg in northern arm by assuming 11% MTBE by volume (312 g MTBE/gal fuel).

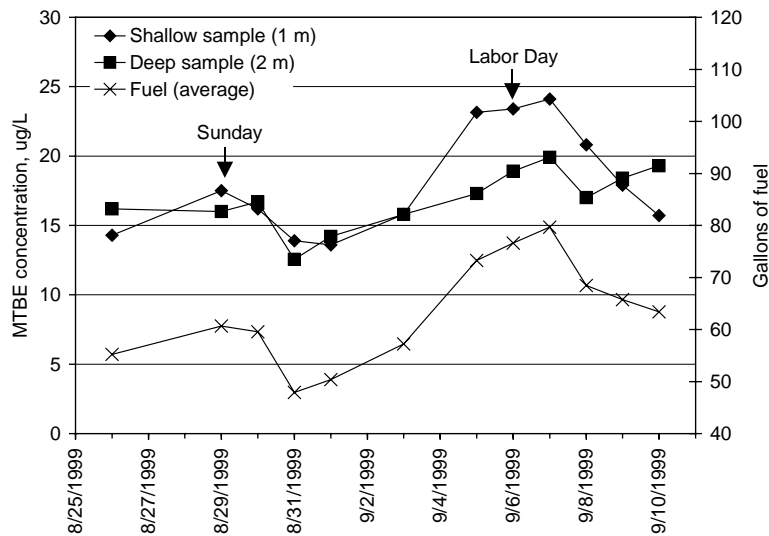


Fig. 3. Daily variation in MTBE concentrations in shallow and deep samples collected at the footbridge, 8/26/99–9/11/99, and equivalent volume of fuel in the northern arm of Cranberry Lake, NJ (volume of fuel calculated from average of the concentrations of MTBE in the shallow and deep samples).

most on the Sunday of the holiday weekend. This was the day with the least wind and clearest skies of the weekend, according to the airport records.

The monthly sample for this time period has a concentration of 17 $\mu\text{g/L}$ (average of shallow and deep).

The daily concentrations varied from 13.6 to 24.1 $\mu\text{g/L}$. The monthly value missed the peak by 30%. If the monthly sample had been collected at the minimum (Wednesday), it would have missed the peak by 44%. Monthly samples were collected on Monday about half

the time and mid-week (T through Th) half the time, which is close to the minimum of the week. Thus, the seasonal sampling may be biased toward lower concentrations.

5. Attenuation processes

Although the data collected during this study do not allow for the development of a detailed model of lake dynamics, the simple model discussed below confirms the importance of the volatilization pathway and provides an estimate of the rate of MTBE input from gasoline-powered watercraft. The processes causing a decline in MTBE concentration for both the daily sampling and the seasonal period from August to November are considered here.

Sources of MTBE to a lake generally include boat and personal watercraft input, plus MTBE contributed from typical input components of the lake's hydrologic budget: stream and overland flow, precipitation, and ground-water discharge to the lake. These hydrologic sources can be omitted from the model because the volume of the source is small or the contribution of MTBE from the source is small. Surface water was not a significant source of inflow for the daily sampling period, and furthermore, no MTBE was detected in streamflow. Although one storm sample contained 0.2 µg/L, concentrations in most samples of stormwater runoff were undetectable. The concentration of MTBE in precipitation was less than 1 µg/L [12]. Thus, the remaining source of MTBE is boat and personal watercraft traffic. As discussed above, the estimated volume of MTBE and the variation in MTBE concentrations in the lake are too large to be the result of unreported spills.

Sinks of MTBE from the lake include volatilization, in-lake biodegradation, and dilution. The model to calculate the mass of MTBE in the lake over time is

$$\frac{dVC}{dt} = B(t) - J_v A - \lambda CV. \quad (1)$$

The lake volume, V , shows changes due to dilution. C is the concentration of MTBE, $B(t)$ is the input into the lake of MTBE due to boats and personal watercraft, in units of mass per time (varying with time). J_v is the volatilization rate (concentration multiplied by L/T) from lake surface, which in turn is multiplied by the lake area. λ is a first-order biodegradation rate ($1/T$). The first term on the right-hand side of this equation is the source term and the last two are sink terms. Dilution is evaluated first below, then the two sink terms are discussed.

5.1. Dilution

Dilution by direct precipitation or streamflow would have resulted in a change in lake volume because no

outflow at the dam occurred during the sampling period. Furthermore, the lake volume did not change significantly. The lake volume changed only 1.3% over the daily sampling period and less than 2% over the period of seasonal sampling. One exception was a large storm associated with Hurricane Floyd (9/16–9/17/99). The lake volume was 20% higher after the storm; this potential dilution is discussed further below. Ground-water inflow and outflow were not measured directly. However, pumping of water-supply wells at the lake cottages results in a gradient from the lake to the aquifer, so this withdrawal of water would not have changed concentrations of MTBE in the lake.

Dilution due to mixing within the lake can also be omitted from the model. MTBE concentrations in the daily samples from the shallow and deep depths (1 and 3 m) differed by 0–4 µg/L. Although these daily variations may indicate temporary stratification, mixing does not cause MTBE concentrations to decline after the weekend. Concentrations in both the shallow and deep samples first decreased, then increased at nearly the same rate during the period of the weekend watercraft traffic. Thus, only biodegradation and volatilization need to be considered further as sinks for MTBE.

5.2. Biodegradation

The first-order biodegradation rate has not yet been measured in an open lake. Biodegradation in unsaturated soil was estimated by means of a one-dimensional model of MTBE transport in the unsaturated zone. Observed MTBE concentrations from an unsaturated-zone field study in New Jersey calibrated to a decay rate of approximately 10^{-8} 1/s [19]. Rates in oxic surface-water sediments [20] and laboratory microcosms [21] are on the order of 10^{-7} 1/s. These rates would result in decay for Cranberry Lake on the order of 18.72–187.2 g/day (0.06–0.6 gal/day) if the initial concentration was 20 µg/L. This loss is small in comparison to the observed changes at Cranberry Lake. To obtain 3 kg/day of degradation, the rate would need to be 2×10^{-6} 1/s, which is higher than previously reported values. Furthermore, the degradation rate in an open lake is likely to be lower rate than the rate of microbial decay on a sediment substrate. Although decay may play some role in reducing MTBE concentrations, it can account for only a small portion of the observed declines and therefore is neglected in the calculations that follow.

5.3. Volatilization model

Volatilization from the lake was calculated with the two-layer film equation for air–water exchange. The flux of a chemical across the air–water interface

[22, Eqs. (10–10) and (10–12), 9 Eq. (5)] is given by

$$J_v = v_l C - v_g \frac{C_a}{H}, \quad (2)$$

where v is the transfer velocity in centimeters per second for liquid and air, C as before is the concentration in the lake water, C_a is the concentration in air, and H is the Henry's Law constant (dimensionless). The volatilization rate is thus concentration multiplied by a rate. The two terms on the right side of the equation are the mass transfer for water and air. This equation is applicable where the fetch (the square root of area) is significantly larger than the depth (h). The recommended ratio is greater than 50, and the ratio for Cranberry Lake is 140. C_a is negligible because MTBE readily diffuses away from the water surface, given that the Henry's Law constant is greater than 0.01 (0.0169 at 20°C for MTBE). The C for each day was the average value in the lake. What remains is to find the transfer velocity for water, v_l . It is not easy to calculate v_l , as it is a function of a variety of environmental factors that are transient, such as wind speed, diffusion rate, film thickness, in addition to Henry's Law constant. The film thickness is particularly difficult to determine in environmental settings. However, empirical equations have been developed to calculate v_l as a function of wind speed and Henry's Law constant for a variety of organic compounds [22]. The v_l for MTBE at a wind speed of 1 m/s (2.2 mph) is estimated to be $10^{-3.6}$ cm/s [22, Fig. 10.9]. The v_l is less than 10^{-3} cm/s for wind speeds less than about 1.8–2.3 m/s (4–5 mph), then increases approximately linearly [22, Fig. 10.5].

The simplification of the rate-limiting volatilization factors leads to a more specific mass-balance equation

$$V \frac{dC}{dt} = B(t) - v_l C A. \quad (3)$$

This equation can be used to calculate daily volatilization, although it does not calculate the daily concentration unless the $B(t)$ can be estimated (input from watercraft). It can also be used to calculate the recovery of the lake in terms of MTBE concentrations after input from watercraft ceases.

Because daily sampling occurred under simpler hydrologic conditions (no significant change in lake volume) than those in effect during the period of seasonal decline in MTBE concentration, the losses due to volatilization for the daily sampling period are presented first. If the match between observed and calculated declines for the daily samples is good, the prediction then can be used to (1) estimate the net input from watercraft including losses due to volatilization, and (2) predict seasonal declines when input from watercraft ceases or decreases substantially. Through modeling of both short- and long-term effects, this data

set provides validation of the modeled volatilization rate.

5.4. Daily volatilization rate

Eq. (3) was used to predict the rate of volatilization of MTBE, which was then compared with observed declines on specific days. Eq. (3) was estimated with a finite-difference approximation where $dt = 1$ day. An average of the concentrations in the shallow and deep samples on the previous day was used to predict the volatilization rate on the following day. Volatilization was calculated only for consecutive days. The wind speed was assumed to be constant (1 m/s or 2.2 mph), and therefore the volatilization rate ($10^{-3.6}$ cm/s) also is constant. The mass of MTBE volatilized in these calculations varies only because the initial concentration varies.

The calculated volatilization results in a loss of 1.2–2.2 kg per day (4–7 gal of gasoline per day) in the northern part of the lake. On three of the days when the lake budget showed a decline in gasoline, volatilization is sufficient to account for losses (Table 2). Exceptions are 8/31/99 and 9/8/99, when the volume of gasoline declined 3.4–3.7 kg (11–12 gal), larger than the volatilization loss estimated here. The large decline in MTBE could result from an increase in wind speed (which in turn increases volatilization). If the wind speed is doubled, volatilization increases the estimated loss of MTBE from the lake to about 3.4 kg (11 gal), which could account for observed loss. No measurements of wind speed were made at the lake; however, data from a weather station about 32 km (20 miles) from the lake showed that 8/31/99 was the windiest day in the 2-week period.

To estimate the daily input of MTBE due to watercraft (B), the loss due to volatilization must be added to the observed change in fuel volume (Table 2). Accounting for loss due to volatilization increases the daily boat and personal watercraft input by 1.2–1.9 kg/day, which is the equivalent of 4–6 gal/day (Table 2). For example, the input over the Labor Day weekend (9/4–9/6/99) calculated from concentration differences was 6 kg or 19.4 gal; 3 days of volatilization would approximately double the input (19.9 gal or more than 6 gal per day volatilized for this period). For days when MTBE concentration declined, the input from watercraft is more difficult to estimate. When the volatilization estimate is higher than the observed change in volume (8/30/99, 9/9/99 and 9/10/99), the difference could be due to watercraft input. The data show 9–1.2 kg (3–4 gal) difference between volatilization and observed declines on these days. The uncertainty in the volatilization rate (e.g., due to wind correction) is illustrated by the 2 days with larger observed declines than estimated (8/31/99 and 9/8/99). This uncertainty translates to

1.6–2.2 kg/day (5–7 gal/day) if the wind is variable. Nonetheless, the data show that the estimated inputs on weekdays are about half that of the weekends (Table 2), and the daily inputs are significant.

The loss of MTBE due to volatilization was about 1.2 kg/day (4 gal/day), at Cranberry Lake immediately after the end of the boating season (September). This rate is smaller than that observed on Donner Lake by Reuter et al. [8], which was 8 kg/day, and is similar to that observed on Perris Lake [9], which was 1.6 kg/day. The surface areas of the lakes differ, however, and Perris Lake has the highest rate when its surface area is accounted for. The rate in $\text{kg}/\text{m}^2/\text{day}$ for Cranberry Lake is 3×10^{-6} ; for Donner Lake it is 2×10^{-6} , and for Perris Lake it is 9×10^{-6} .

5.5. Seasonal volatilization rate

To confirm the model showing volatilization is the major sink for MTBE in the lake, the MTBE concentration was predicted for several months, using the same rates used in modeling the daily declines. The seasonal model used the assumption that input from watercraft stopped after Labor Day weekend. Thus, with no inputs, the concentration would be expected to decline (exponentially) as a result of volatilization, using Eq. (3). The modeled rate of decline was compared to the rate calculated from actual monthly measurements, and the two follow the same trend (Fig. 4). The MTBE concentration decreased from $18 \mu\text{g}/\text{L}$ in early September to less than $2 \mu\text{g}/\text{L}$ in November. The

modeled values showed a similar decrease. However, the final concentration resulting from volatilization in the model reaches zero rather than leveling off between 1 and $2 \mu\text{g}/\text{L}$. This persistent, low-level concentration may be caused by occasional boat traffic. An additional model was calculated by assuming a steady input of 1.6 kg/day (0.5 gal/day) during the decline, and the resulting curve also matches the observed decline but does not reach zero.

The possible effects of dilution by the large storm associated with Hurricane Floyd (9/16–9/17/99) can be estimated from the lake-level measurements made 3 days after the storm. This measurement showed that the lake volume had increased 20%. Simple dilution of the MTBE concentration calculated for 9/16/99 ($11.6 \mu\text{g}/\text{L}$, Fig 4) would result in a concentration of $9.3 \mu\text{g}/\text{L}$ after the storm. The concentration on 9/18/99 calculated on the basis of volatilization was $10 \mu\text{g}/\text{L}$. These values are nearly the same, which shows that the dilution from the storm had nearly the same effect as volatilization and would not significantly change subsequent calculations of the volatilization rate.

6. Conclusions

Large daily fluctuations in MTBE concentrations were observed in a New Jersey Lake that receives gasoline input from boat and jet-ski exhaust. This study showed that concentrations of MTBE varied daily between 13 and $24 \mu\text{g}/\text{L}$ over a 2-week period that

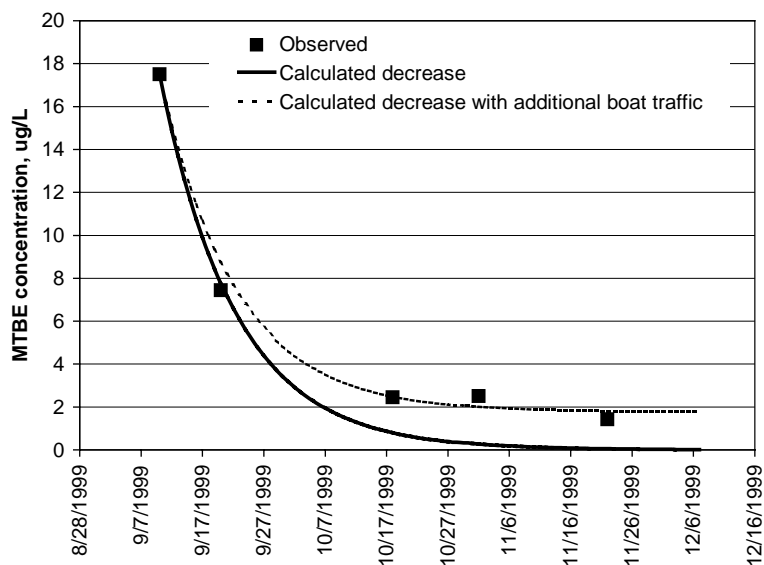


Fig. 4. Observed and calculated decrease in MTBE concentration in the northern arm of Cranberry Lake, NJ, September–November 1999. Calculated decrease determined by assuming the same constant volatilization rate used in the daily calculations (Table 2). Solid line calculated by assuming no input from watercraft after 9/11/99; dashed line calculated by assuming a low-level input from watercraft (1.5 kg/day or 0.5 gal/day) after 9/11/99.

included Labor Day weekend. A similar decline (about 10 µg/L) was observed in the samples collected 1 month apart (from the end of August to the end of September). This variation indicates that timing the collection of monthly or quarterly samples may not account for possible daily variations. The August monthly sample underestimated the peak MTBE concentration by 30%. Awareness of day of the week in relation to watercraft traffic can help account for bias in monthly samples. The observed increase in concentration on the weekends, when watercraft traffic is greatest, indicates that fuel input from boats and personal watercraft has an immediate effect on MTBE concentrations in the lake.

Furthermore, volatilization as a mechanism for MTBE losses from the lake was confirmed with both daily and seasonal modeling of declines. Volatilization (with wind speed correction) can account for the observed daily losses after the weekend watercraft traffic, which varied from 3.1 to 37 kg/day (1–12 gal/day). On days when there is little change in MTBE concentration, the total daily input from watercraft likely balances the potential loss of MTBE to volatilization. Volatilization can also account for the seasonal loss of MTBE from 18 µg/L in September to 2 µg/L in November, if a simple constant volatilization rate estimated from the daily variations is assumed.

The rate of MTBE loss due to volatilization is similar to rates observed in the California lakes mentioned earlier, Donner Lake and Perris Lake (1.2–8 kg/day or $2\text{--}9 \times 10^{-6}$ kg/m²/day). These rates can be used to estimate the dissipation of MTBE contamination in the lake once boat traffic ceases or MTBE use is curtailed. On Cranberry Lake, the concentration of MTBE decreased from 18 µg/L on Labor Day weekend to 2.5 µg/L 5 weeks later.

The results of this study show that daily sampling can improve our understanding of sources and sinks of MTBE in a lake environment in the following ways. The monthly samples may be biased depending on the day of the week collected. The input of MTBE from watercraft was greater than that indicated by the MTBE concentrations in the lake because significant volatilization occurs daily. And finally, the modeled declines from the daily sampling provided further evidence that volatilization was the primary attenuation mechanism, and confirmed predictions of seasonal decreases in MTBE concentration.

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