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Concentrations, Sources, and Fate of the Gasoline Oxygenate Methyl *tert*-Butyl Ether (MTBE) in a Multiple-Use Lake

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Discovery of the fuel additive methyl *tert*-butyl ether (MTBE) in drinking water supplies is of concern to public health officials, water suppliers, and the public. Despite recent policy decisions, few published studies exist on the concentrations, sources, and fate of MTBE in surface waters. The purpose of this study was to determine (1) the relative contribution of motorized watercraft as a source of MTBE, (2) its seasonal distribution, (3) loss from the water column, (4) the extent of vertical transport, and (5) its persistence between years; this work was done in Donner Lake, California, a multiple-use lake in the Sierra Nevada Mountains. MTBE measurements were made at 9 individual depths from surface to bottom on 16 dates. Recreational boating was the most important source of MTBE. Statistically, 86% of the change in MTBE was explained by variation in motorized watercraft use. Neither highway runoff nor precipitation contributed significantly. MTBE concentration ranged from $<0.1\ \mu g \cdot L^{-1}$ to a high of $12\ \mu g \cdot L^{-1}$. Between July 1 and 7, 1997, MTBE content rose dramatically from 115 to 365 kg. By January, levels had declined to a minimum of 15 kg, suggesting little interannual persistence. The major loss of MTBE appeared to be volatilization at the air−water interface characterized by two distinct periods. During the boating season, MTBE decline was 1.2 $kg \cdot day^{-1}$ (193 day half-life). At the end of the boating season, MTBE loss increased to 8.1 $kg \cdot day^{-1}$ (14 day half-life). Thermal stratification acted to retard MTBE transport to deeper depths.

Introduction

Addition of fuel oxygenates to gasoline to enhance octane level, increase burning efficiency, and reduce the emission of atmospheric pollutants has become more common in recent years. The most frequently used fuel oxygenate is methyl *tert*-butyl ether (MTBE) (*1*). Other ether-based additives that are far less frequently used include ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME). As of 1992, urban areas classified as serious or moderate nonattainment for carbon monoxide (CO) under the 1990 Clean Air Act Amendments were required to sell oxygenated fuel containing a minimum of 2.7% oxygen by weight. For MTBE this would correspond to 14.8% by volume (*2*). Since October 1992 the state of California has required fuel to be oxygenated during the wintertime in areas of CO nonattainment. In 1995 California's South Coast region was using reformulated gasoline year round, and by June 1996 gasoline containing MTBE as the primary fuel oxygenate was at service stations statewide.

Discovery of MTBE in groundwater, lakes, and reservoirs used for drinking water has raised considerable concern among health officials and water suppliers. The U.S. Environmental Protection Agency has classified MTBE as a possible human carcinogen and has set a drinking water advisory at 20−40 $\mu g \cdot L^{-1}$ based on consumer acceptance. A California state drinking water interim action level of 35 $\mu g \cdot L^{-1}$ has been established. However, state legislation in California has required that primary and secondary drinking water standards be in place by 1999 and 1998, respectively. Currently under consideration are values of 5 $\mu g \cdot L^{-1}$ based on taste and odor concerns and 14 $\mu g \cdot L^{-1}$ as a public health goal. These concentrations are recommendations and not enforceable at this time. Because of MTBE's possible health effects and the fact that it is highly soluble in water and difficult to biodegrade, its potential persistence in water supplies has recently raised numerous research and management questions. In a nationwide survey of the occurrence and possible sources of MTBE and other volatile organic compounds (VOCs) in groundwater, the U.S. Geological Survey's National Water-Quality Assessment program reported MTBE as the second most frequently detected chemical in shallow groundwater from urban areas (*2*). Of the 210 shallow urban wells and springs sampled, 27% were found to contain MTBE at a concentration at or above a reporting limit of 0.2 $\mu g \cdot L^{-1}$. Three percent of the wells exceeded 20 $\mu g \cdot L^{-1}$ MTBE. In this study it was noted that because MTBE is mobile in groundwater, it may move from shallow to deeper aquifers, suggesting the possibility of its transport into subsurface drinking water supplies over time. Sources of MTBE in shallow groundwater include direct contamination from leaking storage tanks and indirect contamination from stormwater flow and urban precipitation (*3*−*5*).

Despite the fact that a body of literature on MTBE is now growing, very few published studies exist on the sources, fate, and transport in lakes and reservoirs. This is highlighted in a recent review that discusses the environmental behavior and fate of MTBE (*6*). With some notable exceptions, most of the investigations on MTBE in lakes to date focus on describing point-in-time, regulatory monitoring designed to determine whether MTBE is present. The results of these surveys are primarily accessible from agency monitoring files. Concentrations of MTBE measured in the open-water portions of a variety of reservoirs in California to date typically range from <1 to 20 $\mu g \cdot L^{-1}$ (*7*). The Metropolitan Water District of Southern California has conducted an extensive MTBE monitoring program in six surface water reservoirs of varying recreational activity. The occurrence of MTBE correlated with the general pattern of recreational use by

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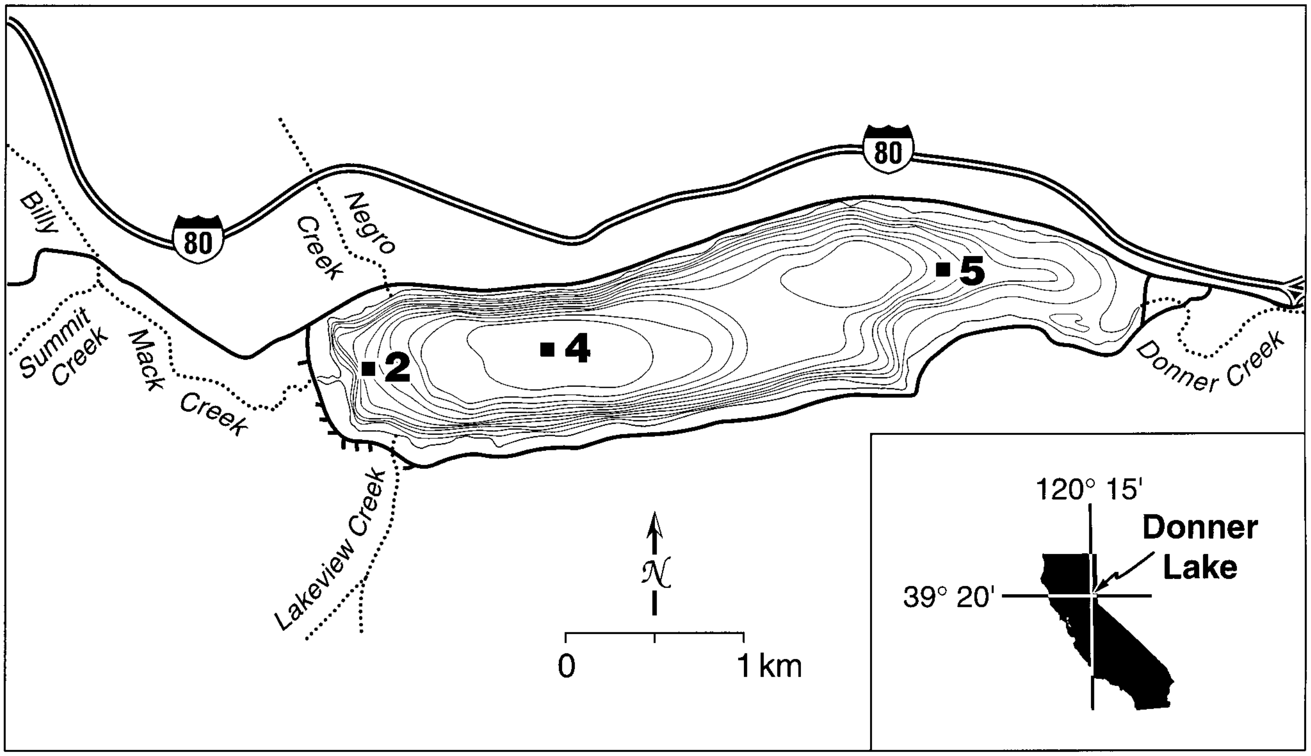

FIGURE 1. Map of Donner Lake, California, showing depth contours (6.1 m intervals), location of sampling stations 2, 4 and 5, Summit and Billy Mack Creeks (gaged inflow), and Donner Creek (gaged outflow). Redrawn from Dong (*27*).

motorized watercraft (*8*). These investigators determined seasonal trends at Lake Perris and found that epilimnetic concentrations of MTBE reached as high as 25 $\mu g \cdot L^{-1}$, the thermocline acted to retard transport of MTBE to deeper waters, and MTBE was diluted in the late fall as lake mixing commenced.

At the same time, concentrations of MTBE in and around marinas, or in other areas expressly used for boating, can be much higher. In Shasta Lake, a large hydropower and recreational-use reservoir in northern California, concentrations ranged from 9 to 88 $\mu g \cdot L^{-1}$ over the Labor Day 1996 weekend. Maximum values were associated directly with large boats entering a docking area or with engine exhaust from these same vessels (*9*). MTBE was also measured in a temporary lake constructed in southern California for a jetski event in the summer of 1996. After the 3-day event, concentrations ranged from 50 to 60 $\mu g \cdot L^{-1}$ and were well-mixed in this shallow water body (*10*). Concentrations of MTBE at Lake Tahoe in the vicinity of boating activity were often within the range of 20−25 $\mu g \cdot L^{-1}$, with a single maximum measured value of 47 $\mu g \cdot L^{-1}$ (*11*). Between July and September 1997, the U.S. Geological Survey conducted a preliminary survey of MTBE and other VOCs in Lake Tahoe. Concentrations ranged from 0.18 to 4.2 $\mu g \cdot L^{-1}$, with larger concentrations nearer sites with substantial boating activity (*12*). Despite the apparent link between the use of motorized watercraft and levels of MTBE, this source has not been widely acknowledged in the literature reviews on MTBE to date.

The work of Pankow et al. (*13*) provides a theoretical basis for predicting volatilization of MTBE from flowing surface waters. Rates were predicted as a function of mean flow velocity, mean flow depth, ambient temperature, and wind speed. Half-life values for MTBE were calculated to range from hours in shallow (0.3 m), high-velocity (3 $m \cdot s^{-1}$) waterbodies to tens of days in deep (10 m), slow-moving (0.1 $m \cdot s^{-1}$) waters. These calculations apply to streams and river that are assumed to be characterized by relatively defined flow velocities which roughly correspond to much of the channel. However, the direct application of these calculations in predicting MTBE volatilization in lakes and reservoirs is complicated by the fact that there is less likely to be a well-defined cross section of flow which applies to the entire waterbody (*13*). Models to simulate the transport and fate of MTBE in lakes and reservoirs are in various stages of development (*15*−*17*). However, comprehensive field studies that provide sufficient data to identify important physical−chemical processes and for use in calibrating and verifying these models are essential.

From March 1997 to January 1998 we extensively studied the concentrations, sources, transport, and fate of MTBE in Donner Lake, which is located at the summit of Interstate 80 as it passes through the Sierra Nevada Mountains in California (Figure 1). Donner Lake lies at an elevation of 1809 m above sea level with a surface area of 3.9 km^2. Its volume is $\sim 1.26 \times 10^8$ m^3 (102 000 acre-feet) with a maximum depth of 70 m and an average depth of 33 m. Among its designated beneficial uses, Donner Lake is a source of drinking water for lakeside residents and contributes to the water supply for downstream communities including Reno, NV.

This study was designed to address a number of important issues including (a) the relative contribution of motorized watercraft as a source of MTBE, (b) the seasonal distribution of MTBE, (c) the extent of MTBE transport from surface waters into deeper portions of the lake, (d) the loss rate of MTBE from the water column, and (e) carry-over of MTBE between years.

Methods

Study Site and Field Sampling. Water for MTBE measurements was collected on 16 dates during the period from March 26, 1997, to January 15, 1998. On each date, samples were typically taken at three stations and from multiple depths along the long axis of Donner Lake, California (Figure 1). Station 2 was located ~0.1 km off the mouth of Billy Mack Creek, which is directly fed by Summit Creek and the major tributary inflow; the bottom depth at station 2 was 39 m. Station 4 was over the deepest portion of the lake with a depth of 66 m. Station 5, at a depth of 33 m, was positioned 1.4 km from the eastern outlet of Donner Lake. Whereas the exact location of the individual sampling depths varied somewhat over the 10 month sampling period, the sampling design typically included 0, 3, 6, 9, 12, 15, 20, 25, and 30 m at station 2 and station 5 and 0, 3, 6, 9, 12, 22, 32.5, 45, and 57.5 m at station 4. In all cases, these depths extended from the surface to the bottom with extensive coverage of the upper, epilimnetic waters. For whole-lake calculations it was taken that stations 2, 4, and 5 accounted for 17, 47, and 36% of the lake surface, respectively. The contribution of each depth layer to the whole-lake content was calculated as the product of mean lake concentration and the volume of each layer as determined from the morphometric contours (Figure 1).

In situ temperature profiles were obtained at each station with a YSI temperature meter, which was calibrated on each date with a hand-held thermometer.

Sampling for MTBE in Donner Lake was conducted from a 14 ft aluminum fishing boat powered by a 12 hp outboard motor. To ensure no contamination from the vessel, an auxiliary electric trolling motor was used to travel the final distance to each collection site. All sites were approached from downwind, and the boat was anchored on location.

Water samples were collected from discrete depths using a Kemmerer well sampler. The 5 cm diameter stainless tube with polyurethane end seals was lowered to depth in the open position and tripped closed with a messenger. The 0.6 L volume was hauled to the surface and used to completely fill preacidified 40 mL amber glass vials with septum-sealed tops. These vials are used for volatile organic analysis (VOA) sampling and were acidified prior to use with two drops of 1:1 hydrochloric acid. Lake water was poured directly into these vials using the spring-loaded purge at the bottom of the Kemmerer sampler. They were completely filled to ensure that no headspace existed. Collected samples were kept in a cooler on ice and directly transported to the laboratory for analysis. Analysis of field blanks (laboratory deionized water passed through the Kemmerer sampler and other phases of the field collection process) were always below the 0.1 $\mu g \cdot L^{-1}$ estimated limit of detection (LOD).

Laboratory Analysis. MTBE was analyzed at Alpha Analytical, Inc. (Sparks, NV), in 25 mL aliquots first using purge and trap procedures for concentration followed by gas chromatography/mass spectrometer detection (MSD) (EPA Method 524.2). Laboratory instrumentation consisted of a Tekmar autosampler, a Tekmar LSC 2000 liquid sample concentrator with a VOCARB 3000 trap, and a Hewlett-Packard 5890 gas chromatograph with a 75 m, 0.45 mm (i.d.), J&W DB-VRX column and glass-jet separator interface to a Hewlett-Packard MSD. The standard LOD for this method is 0.5 $\mu g \cdot L^{-1}$; however, to achieve the estimated LOD of 0.1 $\mu g \cdot L^{-1}$ used for this study, several modifications were necessary. Donner Lake samples were analyzed as independent batches, that is, without other samples which could contain high levels of MTBE and possibly result in even the slightest sample-to-sample carry-over. The MSD was tuned for maximum sensitivity, and a five-point calibration curve from 0.25 to 5.0 $\mu g \cdot L^{-1}$ was generated. This curve was consistently linear through the origin and in essence a six-point calibration curve. The ability to quantify MTBE at concentrations between 0.1 and 0.5 $\mu g \cdot L^{-1}$ was verified for each batch run by analyzing MTBE laboratory control spikes at 0.1 and/or 0.5 $\mu g \cdot L^{-1}$. QA/QC protocol required that for the 0.1 $\mu g \cdot L^{-1}$ spike, if the results were not in the range of 0.07−0.13 $\mu g \cdot L^{-1}$, those samples out of compliance were reanalyzed. To verify that reported sample concentrations >0.1 $\mu g \cdot L^{-1}$ were not due to carry-over or contamination of the analytical system, the normal Method 524.2 blank was analyzed at the beginning of each batch with the inclusion of identical method blanks at several points during the analytical sequence. All of the method blank analyses during the entire time that low-level MTBE analyses were made for this study showed no indication of MTBE in the laboratory or analytical system or between samples.

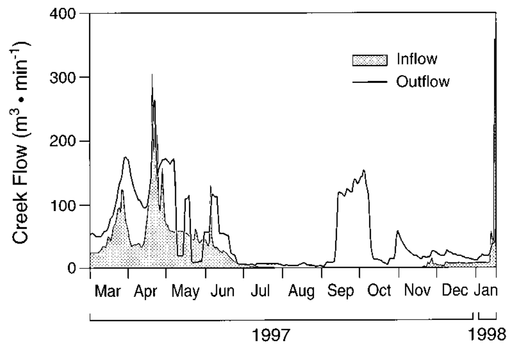

FIGURE 2. Stream discharge for major inflow and outflow from Donner Lake. Data are from U.S. Geological Survey database and reported as a daily flow. The USGS station number for Summit and Billy Mack Creeks is 10338100 and for Donner Creek it is 10338500. Notice the lack of significant inflow during the dry, summer period.

Results and Discussion

Seasonal Surface Hydrology. Sampling began prior to summer and during the period of annual spring snowmelt. Throughout March and early April, cumulative inflow to Donner Lake via its major tributary, Billy Mack and Summit Creeks, was moderate at 50−100 $m^3 \cdot min^{-1}$ despite a secondary peak in flow the last week in March (Figure 2). During that period, lake level and volume were relatively uniform at approximately 68 m and 1.19×10^8 m^3, respectively. From April 16 to 28 a major snowmelt event occurred, with creek discharge reaching as high as 305 $m^3 \cdot min^{-1}$. In the two month period from mid-April to mid-June the cumulative snowmelt discharge resulted in a 2 m increase in lake level and a 6% increase in lake volume. Both inflow and lake outflow were negligible by late June. Lake level declined steadily during the summer months of June−September at a rate of ~0.5 $cm \cdot day^{-1}$ as a result of evaporation in concert with no significant precipitation. Summers are extremely dry in the Sierra Nevada Mountains with the exception of occasional and brief thunderstorms that do not contribute significantly to the water budget of the medium to large subalpine lakes. Consequently, evaporative processes dominated the summer hydrology of Donner Lake until discharge began on September 12 for management purposes. This outflow is a regular feature of the lake's hydrology and is part of a release schedule that provides increased water supply for downstream use at the end of the dry summer and allows additional holding capacity in Donner Lake to accept fall rainstorms should they occur. Discharge on September 13 was 118 $m^3 \cdot min^{-1}$, and between September 3 and 30 the lake lost 2−3 and 6−7% of the whole-lake and epilimnetic volumes, respectively. Winter flow to the lake began on January 12, 1998. This was not part of the annual snowmelt period but rather was a short-lived precipitation event.

Sources of MTBE. On each of the 16 collection dates, MTBE was evenly distributed among the three sampling stations and presumably throughout the surface area of Donner Lake. The lake is characterized by an oval-shaped shoreline with no sheltered embayments or enclosed marinas. The long, east−west axis aligns with the prevailing wind direction, contributing to the spatially well-mixed conditions. On those dates when MTBE exceeded a concentration of 1 $\mu g \cdot L^{-1}$, the coefficient of variation (standard deviation ÷

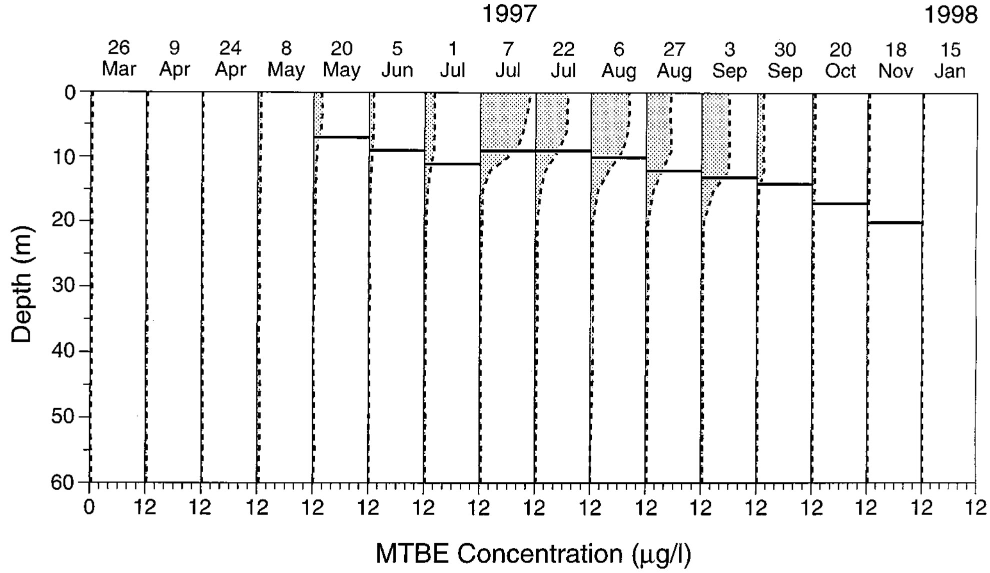

FIGURE 3. Depth profiles of MTBE concentration in Donner Lake on each of the sampling dates was 0.1 μg·L^{-1}. Depth of thermocline is denoted by the solid horizontal line. On March 26 and April 9, 1997, the water column was isothermal, as was the case again on January 15, 1998. On April 24, 1997 the water column was nearly isothermal and only weakly stratified on May 8, 1997.

mean) for measurements taken at the three sampling stations was low and typically <10%. MTBE concentrations ranged from a minimum of <0.1 μg·L^{-1} to a maximum of 12.1 μg·L^{-1} for the entire study. Because the objective of this study was to examine MTBE on the spatial scale of the entire water body, no attempt was made to collect samples in the immediate vicinity of boat-launching facilities, in the wake of passing watercraft engine exhaust, or at other locations that were not representative of whole-lake conditions.

Examination of the depth distribution of MTBE was facilitated by having measurements with a 0.1 μg·L^{-1} LOD. In March and April all measured concentrations ranged from 0.1 to 0.3 μg·L^{-1}. Mean concentrations on these three sampling dates from surface to bottom were 0.3, 0.2, and 0.2 μg·L^{-1}. The water column was isothermal on March 26 and April 9; on April 24 the difference between surface and bottom water temperatures was only 1 °C. This temperature structure allowed for wind-induced mixing to occur throughout the water column with no apparent vertical differences in MTBE distribution (Figure 3).

These low concentrations during the spring months show that precipitation or highway runoff during this period did not significantly contribute to the MTBE content in Donner Lake. The March and April sampling dates were in the period when annual snowmelt was underway (Figure 2). Maximum inflow occurred the week prior to the April 24 sampling. The partitioning of MTBE to precipitation in urban settings with MTBE use can result in concentrations as high as 2−4 μg·L^{-1} (*6*). Because the ratio of annual inflow to total lake volume is on the order of 1:10, even if the entire snowmelt volume from the rural and subalpine drainage basin of Donner Lake contained these types of urban concentrations, the lake concentration would increase by only 0.2−0.4 μg·L^{-1}. Preliminary data on MTBE content in snow was obtained on January 21, 1998, at three locations along Interstate 80 at Donner Lake. Analysis of fresh snowfall indicated that in all samples MTBE was <0.1 μg·L^{-1} (*18*). This is supported by data from fresh snow samples taken in the metropolitan Denver region, which showed MTBE concentrations to be very low at 0.011−0.088 μg·L^{-1} (*19*). On the basis of these considerations, precipitation as a source of MTBE to Donner Lake is of minor importance. Similarly, we suspect that because of the dry summer conditions in most of California, precipitation as a direct source of MTBE to reservoirs and lakes used as drinking water supplies should be of little consequence relative to advisories of 20−40 μg·L^{-1}.

Interstate 80 is the major commercial trucking, bus, and passenger car route through the Sierra Nevada Mountains. It is a four to six lane highway that runs for 5 km along the northern edge of Donner Lake (see Figure 1). At a minimum the roadway is 0.1 km from the lakeshore, and at most it is 0.7 km away. Because Donner Lake is directly downslope of the highway, all highway runoff ultimately discharges to the lake. Nationwide survey data on fuel oxygenates and BTEX compounds in urban runoff collected by the U.S. Geological Survey during the period 1991−1995 found MTBE in 41 of 592 stormwater samples (*3*). While it was the seventh most frequently detected VOC found in these samples, the range of detected limits was 0.2−8.7 μg·L^{-1}, with a median of only 1.5 μg·L^{-1}. Given that the hydrologic contribution of highway runoff to Donner Lake is negligible relative to snowmelt flows and that even the most elevated MTBE concentration in this runoff would not be expected to exceed 8−10 μg·L^{-1}, the contribution of highway runoff to the MTBE content of this lake would be minimal.

It is noteworthy that despite the low March−April MTBE levels in 1997, they were nonetheless above detection and higher than the lowest measured concentrations during this study. For example, during the summer months it was not uncommon to observe MTBE concentrations below a depth of 30−40 m to be 0.1−0.2 μg·L^{-1}, and in January 1998 MTBE throughout the water column was just above the 0.1 μg·L^{-1} LOD. This slight elevation in March−April might have been the result of a leak in a fuel pipeline, which was first observed on March 1. Released fuel containing MTBE flowed under the snow cover and into the headwaters of Summit Creek. Sampling in Billy Mack/Summit Creeks by state agencies, in cooperation with other responsible parties, revealed that just prior to entering Donner Lake, concentrations of MTBE in the inflow were only 1.0−1.5 μg·L^{-1} on March 26 when lake sampling began. During the period March 11−25, MTBE in Summit Creek declined uniformly from a concentration of 20−25 μg·L^{-1} to the lower level measured on March 26. Although the effects of this spill may have caused the 0.1−0.2 μg·L^{-1} elevation in MTBE concentrations in March and April, the relative impact was negligible.

Concentrations of MTBE began to increase slightly in the surface waters by early−mid May when levels rose to 0.5−

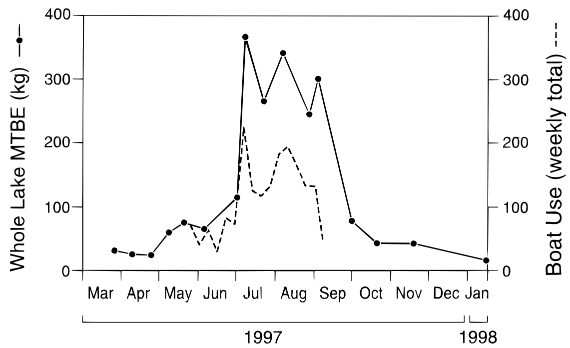

FIGURE 4. Calculated whole-lake MTBE mass based on individual depth concentrations and lake depth−volume curve for each sampling date (solid line). Also shown are boat use data for the week prior to MTBE collection (dashed line).

0.7 $\mu g \cdot L^{-1}$ in the upper 15 m. Even though there was not a well-developed thermocline at that time, thermal stratification was becoming established, as evidenced by a 5 °C decrease in water temperature between the surface and a depth of 30 m. This was sufficient to prevent complete mixing and allow MTBE to accumulate in the surface water (Figure 3). Coincident with the subsequent onset of warmer air and water temperatures, and the boating season, MTBE in the upper 10 m of the water column increased even further to 0.9−2.1 $\mu g \cdot L^{-1}$. This increase occurred between the end of May and the beginning of July. By July, a strong thermocline had developed at a depth of ∼9−11 m, which hindered the transport of MTBE to the deeper, hypolimnetic waters. Some entrainment of MTBE into the uppermost portion of the hypolimnion was observed when epilimnetic concentrations were the highest (Figure 3).

Sampling on July 1 and 7 allowed us to address the hypothesis that releases from motorized watercraft were a primary source of MTBE in Donner Lake. Maximum epilimnetic concentrations rose dramatically over this 7-day period as evidenced by the 6-fold increase in MTBE from 2.1 $\mu g \cdot L^{-1}$ on July 1 to 12.1 $\mu g \cdot L^{-1}$ on July 7. Because precipitation, snowmelt, and highway runoff were virtually nonexistent at that time and because stream inflow from Summit Creek was nearing its seasonal minimum, motorized watercraft associated with the July 4th holiday were the most likely source. During March and April, before the traditional seasonal boating activity began, Donner Lake contained between 20 and 30 kg of MTBE. The whole-lake MTBE level provides a volume-weighted value and is therefore more representative than depth-specific concentrations. By July 1 this had increased to 115 kg as concentrations rose. The sharp increase in concentration observed between July 1 and July 7 resulted in an additional increase of 250 kg MTBE to the lake.

The relationship between calculated values for whole-lake MTBE and boat use data obtained from day-use permit sales records taken at the sole public boat ramp on the lake shows the direct and strong relationship between MTBE and watercraft use throughout the study period (Figure 4). Of particular interest is the observation that the whole-lake MTBE level responded not only to large source events, that is, the significant July 4th event, but also to less dramatic variations in boating patterns during the summer. A strong statistical relationship was found between these two variables on the basis of regression analysis. The relationship was linear and had a high r-statistic of 0.93, indicating that 86% of the observed variation in whole-lake MTBE level was explained by boat use as measured by censusing at the boat-launching facilities. This analysis does not distinguish among the relative contributions of the various motorized watercraft that operate on Donner Lake; however, outboard motors on fishing boats, personal watercraft, and water-skiing are the most common motorized boat uses. For reference, a total of 193 boats utilized the ramp facility during the week ending July 6. There is a resident population of boats at Donner Lake that are active on the lake but which are not included in the boat ramp data. Visual observations and discussions with lakeshore residents indicate that the seasonal patterns of resident and nonresident boat use are similar. Consequently, whereas the relationship seen between boat use and MTBE level is accurate to describe the relative association, loading per boat based on lake MTBE content cannot be obtained solely on the basis of the available boat ramp data.

Although the data in Figure 4 strongly suggest that the changes in MTBE level in Donner Lake were primarily related to boat use and most probably engine exhaust, there are a number of activities associated with boating which could also contribute MTBE to surface waters and which must be considered. First, elevated MTBE in lakes and reservoirs has been found in the vicinity of protected marinas and gas-fueling stations. Because neither of these services is provided at Donner Lake, these were not sources of MTBE to the open lake. Second, gasoline can be spilled into the surface water upon engine startup, while switching between gas tanks, or during removal of bilge water. Over the period of July 1−7 we know that 250 kg of MTBE was loaded to the lake and 193 boats used the launching facility. Assuming that (a) the number of resident boats on the lake was equal to the number of nonresident boats (i.e., a total of 386 boats, a high-side assumption), (b) MTBE was 11 vol % in the gasoline, and (c) the density of gasoline is ∼0.75 $g \cdot cm^3$, we estimate that each boat on the lake would have had to spill ∼2 gal of raw gasoline directly to the lake over this period to account for the observed whole-lake increase. We consider this scenario highly unlikely. Direct exhaust of unburned fuel into surface waters during the operation of marine gasoline combustion engines appears to be a more likely source of increased MTBE. The greatest releases of VOCs come from two-cycle engines that have exhaust ports at or below the water surface (*20*). These engines are most commonly found in personal watercraft and outboard motors. Studies have shown that 4 to >50% of the fuel and oil mixture can pass uncombusted through a two-cycle engine and into the water (*21−23*). This wide range in values is due to different manufacturing considerations and engine-operating conditions (*24*). Data on the partitioning of MTBE in exhaust between air and water for the different watercraft motors is needed.

Fate of MTBE. From the maximum total lake content of 370 kg as measured on July 7, both MTBE content and concentration declined throughout the remainder of the year. The rate of MTBE loss from Donner Lake differed depending on whether motorized boating was still occurring, as in the very active summer season between July and August, or during the post-Labor Day holiday period in September and October when seasonal boating was significantly reduced. The mean concentration in the upper 10 m of the lake from July to September varied from 9.6 to 5.4 $\mu g \cdot L^{-1}$, with the higher levels on July 7, July 22, and September 3. The September 3 date immediately followed the Labor Day weekend (August 30−September 1). Overall the rate of decline over this period as determined by linear regression was 1.2 kg of MTBE$\cdot day^{-1}$ for a half-life of 193 days (assuming first-order kinetics). This represents the loss rate following the large July 4th input but still during the boating season when new sources of MTBE were present.

Following the Labor Day weekend, boat use decline dramatically (Figure 4). This marks the end of the active summer recreation period, and although some watercraft continued to use Donner Lake, the numbers were significantly reduced and, indeed, boat use censusing by municipalities stops. In the 27 day period between September 3 and 30, the whole-lake MTBE content dropped from 300 to 80 kg at a rate of 8.1 kg MTBE·day^{-1}. The corresponding half-life without significant boat use was ~14 days. This is supported by the observation that between July 7 and 22 when weekly boat use fell, the measured MTBE rate of loss was similar at 6.7 kg MTBE·day^{-1}.

Calculations show that only a minor portion of the observed MTBE loss between September 3 and 30 could be accounted for by the increase in Donner Lake outflow during this period. Total discharge from the lake at that time was 0.034×10^8 m^3. Even with a high-side estimate of a 5.0 μg·L^{-1} MTBE concentration during that entire time (actual levels declined from a high of 6.0 to a low of 1.4 μg·L^{-1}), the total MTBE loss would be ~15 kg or only 7% of the 225 kg loss. Volatilization appears to be the primary mechanism responsible for the major loss of MTBE from Donner Lake. MTBE volatilization also occurred during periods of watercraft activity but with a reduced net loss from the lake because of the continued source from new emissions. It is also very noteworthy that this MTBE loss occurred prior to complete lake mixing. On September 30 a strong thermocline still existed at a depth of 13–14 m and, indeed, even by November 18 the water column was still not isothermal.

Wind is an important meteorological forcing factor affecting the transfer velocity of MTBE at the air–water interface and, consequently, volatilization from the surface of lakes. For Donner Lake, mean daily wind speed data were available from nearby Truckee, CA, during the entire period of our MTBE study (*25*). Although the mean daily wind speed varied from day-to-day, the magnitude of this variation was relatively low. From March to November 1997, the range of the monthly average for daily mean wind speed was only 1.7–2.1 m·s^{-1}. In comparison, these values declined to 1.1–1.5 m·s^{-1} in the winter months (November–February). Visual comparison of the mean daily wind speed data to whole-lake MTBE content for Donner Lake clearly showed that (a) the MTBE increase during the late spring–summer period was not the result of a season decline in wind speed which could have allowed a buildup of this compound and (b) reductions in boat use and not changes in wind speed were most closely related to the observed pattern of MTBE content. Because MTBE data were collected on a biweekly or monthly schedule, it is not possible to ascertain the affect of wind on the daily change in MTBE during the period September 3–30.

Between September 30 and October 20, the mean MTBE concentration in surface waters (0–10 m) declined from ~1.4 to 0.5 μg·L^{-1} (Figure 3) with a fall in whole-lake MTBE content from 80 to 45 kg (Figure 4). During September–November, MTBE concentration in the deeper waters (=20 m) ranged from 0.2 to 0.4 μg·L^{-1}. Complete mixing had not occurred by November 18, and surface water concentrations were still slightly above those found in the deeper waters. By the last sampling on January 15 (1998), the water column was isothermal at 3.9–4.0 °C, and MTBE was uniformly distributed from surface to bottom at concentrations slightly above the 0.1 μg·L^{-1} LOD (Figure 3). Total-lake MTBE in January was at a seasonal low of 15 kg. For reference, if all measured values in the water column were at the 0.1 μg·L^{-1} analytical detection, total-lake MTBE content would be 12 kg. The minimal concentrations measured in January strongly indicate that in Donner Lake there was no interannual carry-over of MTBE.

Motorized watercraft were clearly the most important source of MTBE in Donner Lake; unfortunately, the censusing data were not sufficient to separate the relative contribution of the various makes and models (e.g., personal watercraft, outboard engines). The importance of these watercraft as a significant source of MTBE to lakes and reservoirs has not been emphasized in many of the early reviews on sources and environmental behavior of this compound (*4*, *6*). However, a number of datasets that are only now being collected from drinking water reservoirs, including this Donner Lake study, the work of the Metropolitan Water District in Southern California (*8*), the preliminary survey at Lake Tahoe by the U.S. Geological Survey (*12*), and a recent survey by the Association of California Water Agencies (*26*), show the importance of this source. Although many of the observations from Donner Lake may be applicable elsewhere, many lakes and reservoirs have unique features that must be accounted for in an analysis of MTBE transport and fate. When management options for individual lakes or reservoirs are considered, these features include, but are not limited to, thermocline stability, volume, lake hydrodynamics, water-use schedules, depth of water intake system, etc. Given the concern regarding MTBE in drinking water supplies, it is important that simulation models are developed for the purpose of lake management and environmental planning. Comprehensive monitoring is needed for a wide range of lake and reservoir types.

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