Atmospheric Methyl Tertiary Butyl Ether (MTBE) at a Rural Mountain Site in California

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ABSTRACT

Methyl tertiary butyl ether (MTBE) was measured in air samples collected at hourly intervals near Blodgett Forest Research Station on the western slope of the Sierra Nevada, California, in July 1997, October 1998, and June through September 1999. Mixing ratios ranged from below the detection limit (< approximately 0.01 ppbv) to 0.5 ppbv, but were generally less than 0.3 ppbv. At these mixing ratios partitioning of MTBE into surface waters would lead to MTBE concentrations of less than 0.2 $\mu g\ L^{-1}$. As expected, MTBE mixing ratios were highly correlated with other anthropogenically emitted hydrocarbons. Based on the observed diurnal cycle of MTBE and its ratio to 2-methyl-butane (isopentane), we estimated the average regional daytime oxidant concentration to be (9 to 13) $\times 10^6$ OH radicals per cubic centimeter, consistent with our earlier estimates for this region. Furthermore, MTBE ratios to toluene, another ubiquitous anthropogenic hydrocarbon, were generally consistent with regional transport and dilution, as well as atmospheric oxidation. Exceptions, pertaining to MTBE mixing ratios below or close to the detection limit, were associated with the influence of marine air masses that did not experience anthropogenic hydrocarbon input from California. With all these constraints in place, evidence for an additional atmospheric loss process, such as nonreversible deposition of MTBE, could not be established, and we conclude that any deposition is slow compared with removal from the atmosphere by the OH radical.

Methyl tertiary butyl ether (MTBE) is widely used as a fuel additive in the USA to achieve the oxygen level required by the Clean Air Act Amendments of 1990, in order to reduce tailpipe carbon monoxide emissions. In California, MTBE is an important component in reformulated gasoline, accounting for 11 to 15% of the fuel by volume. Due to its high water solubility, MTBE is readily transferred into surface and ground water, and the observed contamination of drinking water supplies (California Environmental Protection Agency, 1997, p. 675–680; USEPA, 1999) has drawn national concern. While MTBE has been found in significant amounts in surface and ground waters (Squillance et al., 1997), measurements of MTBE in air are still sparse and often confined to urban areas. The USEPA compiled data from urban locations throughout the USA in 1990 and 1991. Means ranged from 0.2 to 0.4 ppbv (California Environmental Protection Agency, 1997, p. 675–680). In Porto Allegre, Brazil, where MTBE makes up 15% of the gasoline (Grosjean et al., 1998a,b), much higher mixing ratios were found, ranging from 0.2 to 17.1 ppbv, with an average of 6.6 ± 4.3 ppbv. In California, the California Air Resources Board (CARB) measured MTBE in urban regions in 1995–1996, reporting a range of 0.4 to 13.2 ppbv in the Los Angeles area, 0.5 to 7.5 ppbv in the San Francisco bay area, and 1.2 to 3.1 ppbv in the Central Valley (California Environmental Protection Agency, 1997, p. 675–680). More recent measurements in the Central Valley, reported on the agency's web pages (California Air Resources Board, 2001), are consistently in this low ppbv range.

Generally, MTBE is emitted into ambient air through tailpipe exhaust, and evaporation and spillage of gasoline (Kirchstetter et al., 1999; Poulopoulos and Philippopoulos, 2000). At fuel stations, which are major point sources, concentrations and exposure to MTBE are generally higher than farther away from these sources (Vainiotalo et al., 1998, 1999; R.L. Corsi, University of Texas, Austin, personal communication, 2000). Once airborne, MTBE can be transported to more rural and remote locations before it is removed by atmospheric oxidation and rainout (Squillance et al., 1997), or dry deposition to the ground. It is not known whether the latter permanently removes MTBE from the environment (e.g., due to bacterial or plant metabolism), or has to be considered strictly as an equilibrium process that creates a certain background concentration of MTBE in surface waters. If the latter is true, concentrations in surface waters, uncontaminated by direct emissions such as from boat engines, can be estimated from the atmospheric mixing ratio of MTBE and its Henry constant.

We measured atmospheric MTBE mixing ratios at Blodgett Forest Research Station on the western slope of the Sierra Nevada, California, approximately 80 km downwind of Sacramento, and report mixing ratios from July 1997, October 1998, and June to September 1999. The MTBE mixing ratios are compared with other measured anthropogenic hydrocarbons emitted in the densely populated region of the Central Valley of California to address questions of MTBE climatology (abundance, diurnality, seasonality), including dilution with background air masses, oxidation by OH radicals during transport, and potential non-equilibrium ground deposition.

MATERIALS AND METHODS

The measurement site near Blodgett Forest Research Station (38°53′42.9″ N, 120°37′ 57.9″ W, 1315 m elevation; Fig. 1) and the hydrocarbon measurement details are thoroughly described in Lamanna and Goldstein (1999) for 1997, Schade et al. (1999) for 1998, and Schade and Goldstein (2001) for 1999. Hydrocarbons and other volatile organic compounds

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Abbreviations: MTBE, methyl tertiary butyl ether; ppbv, parts per billion by volume (1 ppbv MTBE = 3.61 $\mu g\ m^{-3}$).

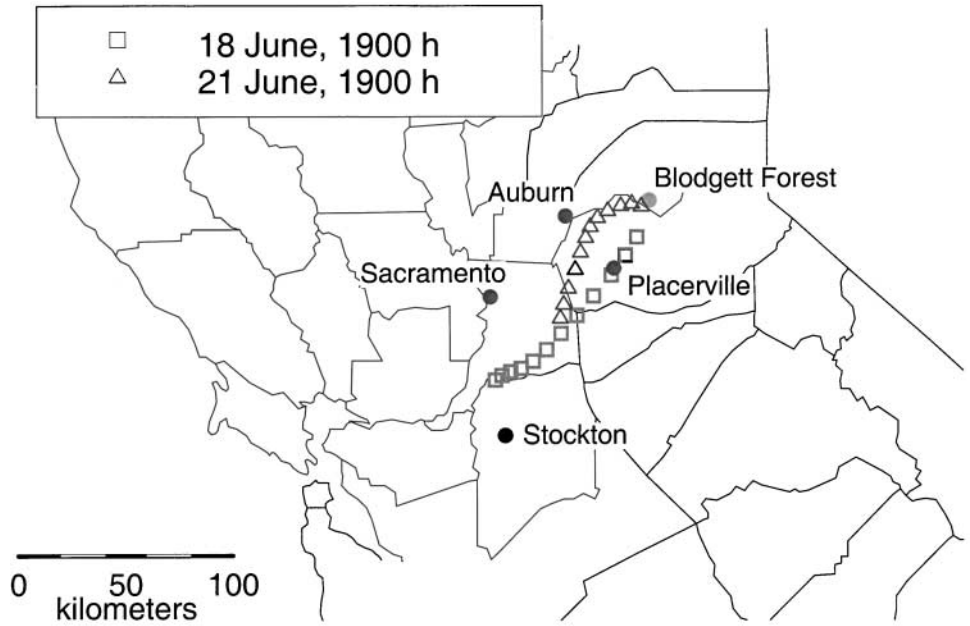

Fig. 1. County map of northern California showing the site as well as some major cities from which advection of anthropogenic hydrocarbons can occur. Also shown are two 12-h isentropic back-trajectories calculated with HYSPLIT (National Oceanic and Atmospheric Administration Air Resources Laboratory, 1997) for 18 and 21 June 1999, arriving at Blodgett at 1900 h (first symbol at −1 h).

(VOCs) were measured from a walk-up tower above a young ponderosa pine (*Pinus ponderosa* P. Lawson & C. Lawson) plantation. Meteorological data and trace gas fluxes (CO_2, H_2O, O_3, hydrocarbons) were measured from approximately 5 to 6 m above the average tree height. The hydrocarbon measurement setup consisted of Teflon sampling lines, through which ambient air was continuously drawn into a temperature-controlled building next to the tower. Subsamples from the air stream were preconcentrated onto Carbopack B and Carbosieve SIII (both from Supelco [Bellefonte, PA]; approximately 12 mg each) in Silcosteel microtraps (Restek Corp., Bellefonte, PA), embedded in a cold block. After sample collection, the hydrocarbons were thermally desorbed on-column, separated by a 60-m Rtx-WAX column (Restek Corp.), and detected with a flame ionization detector. The system was calibrated by automatic dilution of primary gas standards (Scott Marrin, Riverside, CA) into the tower sampling lines. The setup was fully automated (HP [Palo Alto, CA] Chemstation and Campbell Scientific [Logan, UT] data logger) and measured 30-min average samples in situ once every hour. Laboratory tests showed that no breakthrough occurred for most compounds of interest at trap temperatures below −2°C for a sample size of 210 mL. In the field, the cold block temperature was kept between −5 and −10°C, and sample sizes were generally smaller than 210 mL. The most volatile alkane for which no breakthrough was found in the described setup was *n*-butane.

In June 1999, we used a 60-m, 1-μm film DB-624 column (J&W Scientific, Folsom, CA) for separation. The MTBE retention time on each column was identified by spiking ambient air samples with MTBE. As no quantitative gas standard was available for MTBE, the flame ionization detector response was estimated based on the percentage carbon in the compound (Goldstein et al., 1995) relative to isoprene, a technique feasible for a number of oxygenated hydrocarbons (Lamanna and Goldstein, 1999). The measurement accuracy was approximately 30%, and the flame ionization detector response factors—corrected for sample size—varied by less than 5% over the three years. Under these conditions, the detection limit for MTBE was approximately 10 pptv.

RESULTS AND DISCUSSION

Atmospheric Methyl Tertiary Butyl Ether Abundance

Figure 2 shows the MTBE mixing ratio distributions for the different measurement periods. All periods were remarkably similar. The highest MTBE mixing ratios at Blodgett Forest never exceeded 0.5 ppbv, and were generally less than 0.3 ppbv. At these atmospheric levels of MTBE and given a dimensionless Henry's Law constant of 0.011 (Pankow et al., 1997; Lopes and Bender, 1998), the equilibrium concentration in surface waters

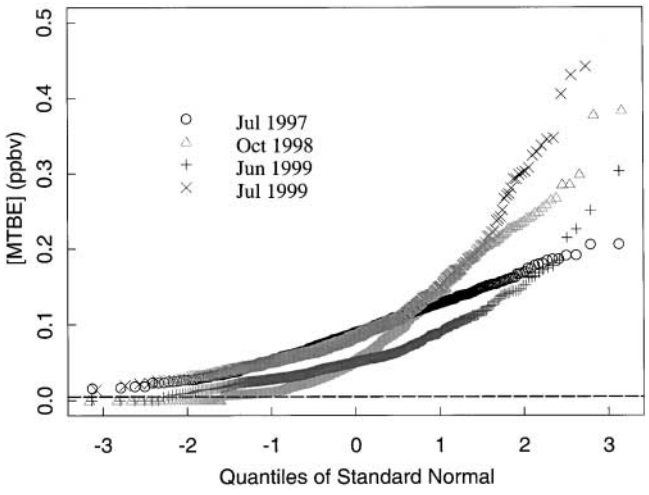

Fig. 2. Methyl tertiary butyl ether (MTBE) mixing ratio distributions (quantification for 1997 is tentative) near Blodgett Forest Research Station. The dashed line represents the detection limit.

Table 1. Correlations between methyl tertiary butyl ether (MTBE) and other anthropogenic volatile organic compounds (VOCs) in June 1999.

VOC	Slope	r^2
n-Pentane	0.40	0.71
Isopentane	1.08	0.75
2-methyl-pentane	0.38	0.53
Toluene	0.55	0.61

would be lower than 0.2 μg L^{-1}. This is consistent with the findings of Reuter et al. (1998) for lake water in the Sierra Nevada north of Lake Tahoe before summer contamination by motor boat activities. Reuter and coworkers also calculated that precipitation runoff would not have contributed significantly to the (contaminated) surface water MTBE levels they measured, even if atmospheric levels had been high. In this respect it is interesting to note that during rain events at our site the observed atmospheric MTBE mixing ratio was not notably depleted (data not shown), as would be expected (Squillance et al., 1997). Assuming that a 1% rainout still occurred (Squillance et al., 1997), at MTBE levels of 0.4 ppbv only 0.14 to 0.29 g MTBE ha^{-1} would be supplied from a 1- to 2-km atmospheric boundary layer. This suggests that at the low MTBE mixing ratios measured at this rural site, rainout would have only a small effect on whole-lake concentrations.

Methyl tertiary butyl ether was correlated to other anthropogenic hydrocarbons, such as *n*-pentane, 2-methylbutane (isopentane), and toluene (Table 1). Therefore, it is useful as a tracer of anthropogenically influenced air masses (Schade and Goldstein, 2001). We exploit this feature to estimate the daytime regional abundance of the OH radical, the atmosphere's cleansing agent, in the Estimate of Hydroxide Oxidation section, below. These estimates were only possible on days when air was transported to the site from the Central Valley. When the regional air mass trajectory changed so that we received air that had not been contaminated by emissions in the Central Valley, MTBE was generally below the detection limit, and we discuss these changes in a following section (Is Methyl Tertiary Butyl Ether Deposited?) with respect to possible MTBE deposition.

Comparison with Other Anthropogenic Hydrocarbons

Estimate of Hydroxide Oxidation

For the following analysis we will concentrate on data from the DB-624 column in June 1999, measured under the typical regional meteorological conditions. Meteorology on the western slope of the Sierra Nevada is driven by diurnal heating and cooling leading to a regular daytime up-slope and nighttime down-slope air flow pattern. In the morning, the wind shifts over a 1- to 3-h period from a northeast to southwest direction. During the daytime, winds from the SW transport anthropogenically influenced air masses from the Central Valley to the site. Winds shift back around sunset, and air descends to the site from higher elevations throughout the night (Dillon et al., 2002). These meteorological conditions are extremely consistent during the summer. We have chosen five days in June 1999 to demonstrate these conditions (Fig. 3). The MTBE mixing ratios showed a regular diurnal pattern, increasing abruptly around noon and, to a smaller extent, again in the late

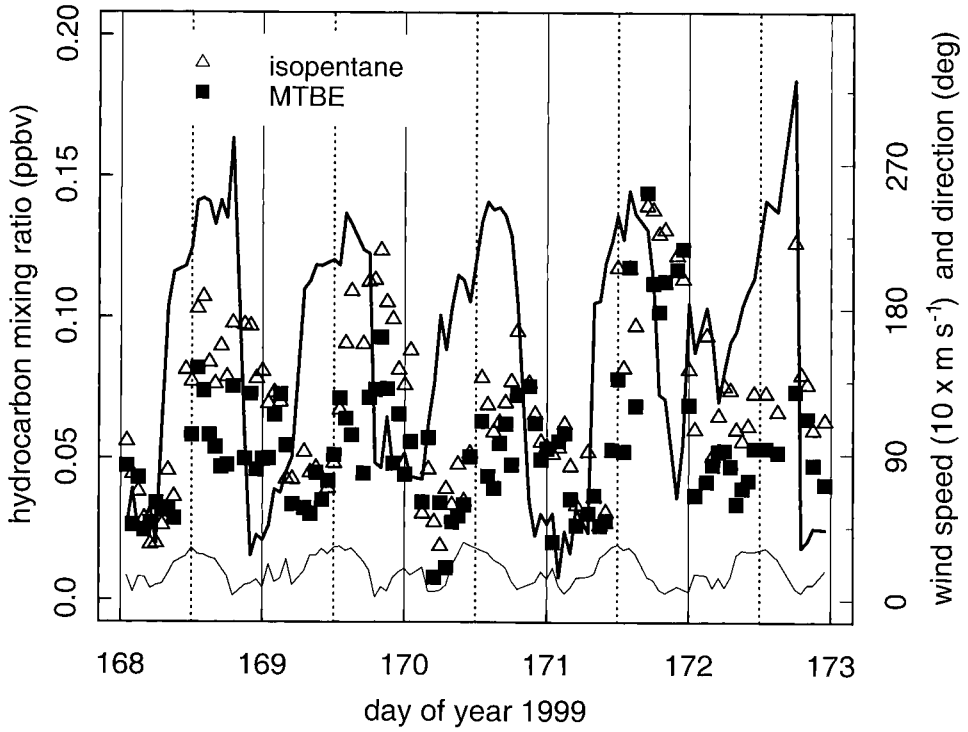

Fig. 3. Mixing ratios of isopentane and methyl tertiary butyl ether (MTBE) during 17–21 June 1999, along with the wind speed (thin line, multiplied by 10) and direction (thick line) (see also Fig. 1).

afternoon. That pattern was broken on the last day shown, as was the general wind direction pattern.

The nearest urban centers to the site are Placerville, 35 km south-southwest, Auburn, 40 km west, both in the Sierra Nevada foothills, and Sacramento, 80 km southwest in the Central Valley of California (Fig. 1). Major highways lead from Sacramento to both Placerville (US-50) and Auburn (I-80). Anthropogenically affected air masses, such as air influenced by the morning commute (e.g., in the Placerville area), are blown toward the site at wind speeds of 1 to 3 m s^{-1} in the morning and 2 to 5 m s^{-1} in the afternoon. Therefore, anthropogenic hydrocarbons at elevated mixing ratios arrive at the site approximately 4 to 5 h after the wind shift. Another increase in mixing ratio generally occurs later due to transport from stronger sources in the Central Valley (Sacramento). During the night, the mixing ratios of all measured anthropogenic hydrocarbons decrease due to the dilution with cleaner background air from higher elevations. A minimum is reached after sunrise, just before or after the wind shifts again. We defined the lower 0.1 quantile of the data during those hours (0500–1000 h PST) as the regional background for each hydrocarbon, similar to Goldstein et al. (1995). Figure 4a depicts the median mixing ratios above this background for three hydrocarbons during the four days shown above. The noon-time increase is clearly visible and appears approximately 5 h after the wind shift. The second increase occurred approximately 11 h after the wind shift. Comparing these MTBE data with the mixing ratios measured by the California Air Resources Board in the Central Valley (approximately 1–5 ppbv) shows that by the time the air mass has traveled into the Sierra Nevada a dilution of one to two orders of magnitude has occurred. Due to this dilution and the abundance of biogenically emitted hydrocarbons, the OH reactivity at Blodgett Forest is not influenced by anthropogenic hydrocarbons to a considerable extent (Lamanna and Goldstein, 1999). A more detailed investigation of the dilution aspect will be published elsewhere (Dillon et al., 2002).

If the source emission ratio for anthropogenic hydrocarbons—emitted from the same or similar sources—is reasonably well known, ratios between them can be used as an indirect measure of air mass age or photochemical activity. Most anthropogenic hydrocarbons are removed from the atmosphere solely or dominantly by the OH radical, the atmosphere's main oxidizing agent. Therefore, an estimate of the average OH abundance is possible if the transport time from a major point or line source and the mixing ratios of the respective hydrocarbons in the diluting background are known:

$$\overline{[OH]} \approx \frac{\ln\{[([HC_f] - [HC_f]_{bg})/([HC_s] - [HC_s]_{bg})]/ER_{source}\}}{(k_s - k_f) \times \Delta t} \quad [1]$$

Equation [1] (similar to McKeen and Liu, 1993) calculates [OH] from a faster reacting (f) and a slower reacting (s) hydrocarbon (HC) corrected for their regional background (bg), their respective reaction coefficients with OH (k), estimates of the source emission ratio, ER_{source}, and the processing time Δt. Equation [1] can also be used to estimate Δt, an average air mass age, presuming an average diurnal OH abundance. Here, we

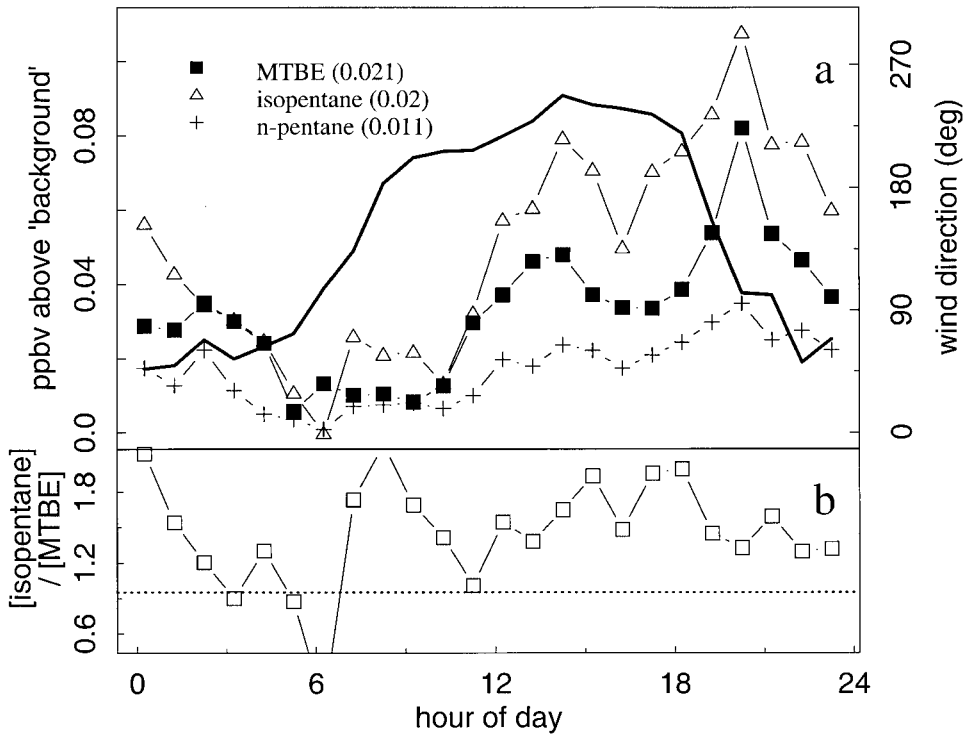

Fig. 4. (*a*) Median diurnal mixing ratio variation of methyl tertiary butyl ether (MTBE), isopentane, and *n*-pentane above their regional background levels (see legend), together with the median wind direction pattern for 17–20 June 1999 (thick line). (*b*) Median diurnal change of the isopentane to MTBE ratio for that time, including the background ratio (dotted line).

estimate a time-averaged OH abundance using mixing ratios of MTBE and isopentane, both major components of gasoline evaporation and automobile exhaust. Their source emission ratio was estimated from a recent study in the Caldecott tunnel in the San Francisco bay area (Kirchstetter et al., 1999). In order to constrain the regional dilution with background air during transport, we also estimated the corresponding isopentane to *n*-pentane ratio of automotive tailpipe exhaust from that study to be 3.9 in 1997. The respective ratio for gasoline evaporative emissions was approximately 4.8. Isopentane to *n*-pentane ratios measured in the Sacramento area in 1997 were around 3.6 (Dillon et al., 2002). As isopentane and *n*-pentane have near identical OH removal rates in the atmosphere, any change from the emission ratio (approximately 4) reflects dilution with background air of a different ratio. As the latter is around 1.9, and the average amount of Sacramento air reaching Blodgett Forest in summer is typically 32% (Dillon et al., 2002), the expected isopentane to *n*-pentane ratio is approximately 2.6. The measured isopentane to *n*-pentane ratio in the late afternoon at Blodgett Forest was 2.6 ($r^2 = 0.9$) in June 1999. Hence, our isopentane and *n*-pentane measurements are consistent with the dominant regional emission sources and mixing processes. Using MTBE mixing ratios and its source emission ratio relative to isopentane to estimate nondilution processes in the investigated air masses shown in Fig. 4a appears justified.

The source emission ratio for isopentane to MTBE was 2.6 ± 0.5 (one standard deviation) for tailpipe exhaust and 2.5 for gasoline head space concentrations (Kirchstetter et al., 1999). The latter, however, is probably altered by a non-negligible contribution from diesel engines, emitting isopentane but no MTBE. Whereas diesel-fueled engines made up less than 2% of the vehicle fleet in the Caldecott tunnel (Kirchstetter et al., 1999), a higher contribution can be expected in the Central Valley of California, consequently leading to a slightly higher isopentane to MTBE source ratio. We estimate the effective source emission ratio to be 2.8 ± 0.2. A subsequent, short-term decrease in this ratio in the atmosphere is presumed to reflect the difference in loss of MTBE and isopentane during transport due to reaction with the OH radical. Methyl tertiary butyl ether reacts 25% slower with OH ($k_{298} = 2.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; Bennett and Kerr, 1990) than isopentane ($k_{298} = 3.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; Atkinson, 1990).

Figure 4b shows the diurnal variation of the isopentane to MTBE ratio using the data from Fig. 4a. It is consistent with older air masses in the morning and younger air masses during the afternoon. Assuming OH reaction as the most significant daytime loss process for both hydrocarbons, we calculated kinetic ratios for different OH abundances using Eq. [1] (Table 2). The measured isopentane to MTBE ratio is consistent with an average daytime OH abundance of (9 to 13) × 10^6 molecules cm^{-3} for a travel time Δt of 9 to 11 h. While this is consistent with the earlier estimate for this region in summer (Dillon et al., 2002), the uncertainties due to a variable emission ratio (the use of MTBE in California gasoline has been highly variable in the past: 7.4 ± 4.3% in 1998 and 8.0 ± 4.0% in 1999; R. Harley, University of California at Berkeley, personal communication, 2000) or variable transport times, are significant.

Table 2. Theoretical (background-corrected) isopentane to methyl tertiary butyl ether (MTBE) ratios for different source emission ratios (ER_{source}), and assuming OH removal as the only relevant loss process from the atmosphere.

[OH]	Δt = 9h, ER_{source} = 2.6	Δt = 9 h, ER_{source} = 2.8	Δt = 9 h, ER_{source} = 3.0
molecules cm^{-3}			
3×10^6	2.36	2.54	2.72
5×10^6	2.21	2.38	2.55
7×10^6	2.07	2.23	2.39
9×10^6	1.94	2.09	2.24
11×10^6	1.82	1.96	2.10
13×10^6	1.71	1.84	1.97

Is Methyl Tertiary Butyl Ether Deposited?

The Estimate of Hydroxide Oxidation section, above, identified the two processes, dilution with a constant background and atmospheric oxidation, which are responsible for the change of MTBE mixing ratios relative to another anthropogenic hydrocarbon. If these processes are dominant, the ratio between two anthropogenic volatile organic compounds will deviate from the emission ratio only in favor of the longer-lived compound. When the opposite effect is observed, another significant process besides the two above may exist.

Some evidence for an additional process might be inferred from the mixing ratio distribution in October 1998, shown in Fig. 2. Transport processes change in the fall compared with summer conditions, and tropospheric OH radical levels are lower. While the latter may be responsible for higher than summer mixing ratios during "normal" transport patterns from the Sacramento Valley, a different process has to be invoked to explain the lowest mixing ratios including the complete absence of MTBE in older air masses. We analyzed rapid decreases of the MTBE mixing ratio throughout the available data sets of 1998 and 1999, and found that they were always associated with air mass changes and often rainy and humid periods. Back trajectory analysis (National Oceanic and Atmospheric Administration Air Resources Laboratory, 1997) showed that the initial change was brought on by descending air from higher elevations (Fig. 5) and generally of marine origin, which had not passed over source regions in the Central Valley at the ground. While toluene, a ubiquitous aromatic hydrocarbon not known to deposit, was still detectable in these air masses, MTBE regularly dropped below the detection limit. Consequently, the MTBE to toluene ratio was significantly lower (<0.5) compared with air masses reflecting transport from the Sacramento Valley (>1). As shown in Fig. 6, the MTBE to toluene ratio decreased with decreasing MTBE abundance. As expected, under most circumstances the ratio is higher than the estimated source emission ratio, because the atmospheric lifetime of toluene toward removal by the OH radical is half that of MTBE (2 versus 4 d; Atkinson, 2000). As MTBE is not a ubiquitous, long-lived hydro-

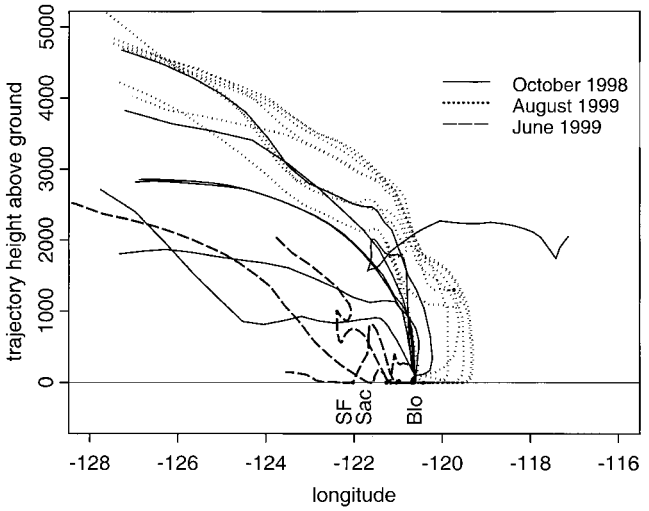

Fig. 5. Example of three-day back trajectories from 24 Oct. 1998 and 30 Aug. to 1 Sept. 1999 during which methyl tertiary butyl ether (MTBE) at Blodgett Forest (Blo) was at or below the detection limit, while toluene was still detectable. SF and Sac indicate the longitude of the urban centers Sacramento (Central Valley) and San Francisco (west coast). Three additional trajectories from June 1999 with "normal" flow through the Central Valley are depicted as well.

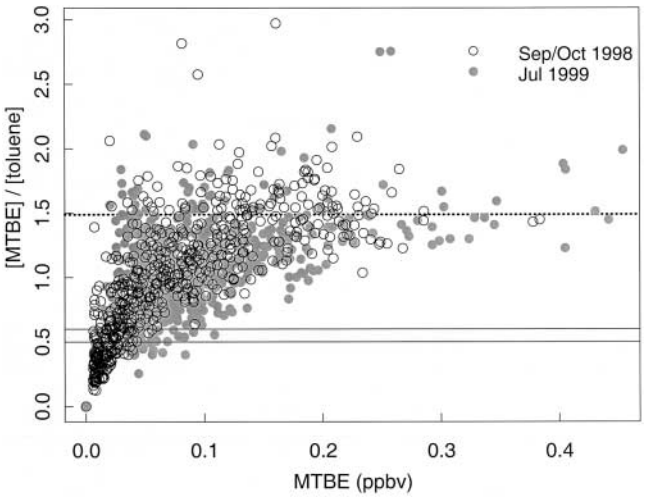

Fig. 6. Dependence of the methyl tertiary butyl ether (MTBE) to toluene ratio on MTBE abundance for fall 1998 and summer 1999. The horizontal gray bar depicts the estimated emission ratio from the Caldecott tunnel experiments (Kirchstetter et al., 1999), the dotted line is a calculated, background-corrected ratio at Blodgett Forest assuming source emission ratio (ER_{source}) = 0.5, [OH] = 1.1×10^7 molecules cm^{-3}, and Δt = 9 h.

carbon, air masses that did not experience anthropogenic hydrocarbon input prior to reaching Blodgett Forest, such as the ones described above, are not likely to contain measurable amounts of MTBE. Hence, the MTBE background mixing ratio diluting local air masses cannot be considered constant on longer time scales. Observations below the estimated MTBE to toluene emission ratio are most likely due to atmospheric mixing with air that had very low MTBE background levels, as demonstrated by the back-trajectory analysis in Fig. 5.

The alternative process would be a removal of MTBE from the atmosphere by irreversible deposition. However, we were unable to identify any periods with evidence for a significant MTBE deposition. All periods with observations of anthropogenically influenced air masses from the Sacramento Valley showed MTBE to toluene ratios higher than 0.5 and generally approached levels expected from the above estimated regional OH radical levels (Fig. 6). For MTBE mixing ratios higher than 0.1 ppbv, typical for afternoons with transport from the Central Valley, the observed MTBE to toluene ratio clusters around the expected value of approximately 1.5. Thus, our observations are consistent with the regional transport processes and estimated OH radical levels, which infers that MTBE deposition is slow compared with OH loss.

With atmospheric removal by the OH radical as the dominant MTBE loss process, MTBE equilibrium levels in surface waters are likely to decrease rapidly as a function of the distance from the atmospheric source. As OH radical levels in regions downwind of major pollution sources, such as downwind of Sacramento, are generally higher, atmospheric MTBE is not likely to represent an important source to surface waters away from its major source regions.

CONCLUSIONS

The MTBE mixing ratios are low by the time polluted air masses reach the mid-elevation of the Sierra Nevada, mostly due to dilution with low background mixing ratios. Furthermore, the MTBE mixing ratio and its ratios to other anthropogenic hydrocarbons are consistent with our understanding of regional transport and OH chemistry. An average daytime OH abundance of (9 to 13) $\times 10^6$ molecules cm^{-3} was estimated using the measured isopentane to MTBE ratio, in agreement with previous calculations for the region (Dillon et al., 2002). The MTBE levels in clean air masses with marine origin were generally below the detection limit, most probably due to the fact that MTBE is not ubiquitous and its emissions are concentrated in urban areas of California. Though low MTBE background levels compared with toluene might indicate that a significant portion of MTBE is lost from the atmosphere by deposition processes, the effect cannot be discerned from dilution processes with air masses that did not experience MTBE input in the first place. However, as air masses undergoing transport from the Central Valley generally showed the expected variation of MTBE to toluene ratios both qualitatively and quantitatively, we infer that, if irreversible MTBE deposition indeed occurs, it is slow compared with the main atmospheric removal process, oxidation by the OH radical.

Nevertheless, partitioning from the atmosphere without subsequent biological breakdown is probably responsible for the very low MTBE levels found in natural aquatic environments downwind from its sources. Though we have concluded that this process is slow compared with MTBE's removal from the atmosphere by the OH radical, a slowly developing equilibrium between gaseous and liquid phases would establish a liquid phase concentration in surface waters that is consistent with earlier findings from a Sierra Nevada lake (Reuter

et al., 1998). Though atmospheric levels would not be significantly affected, this process would lead to a distribution of MTBE in surface waters throughout regions downwind of major emission sources in states that use MTBE in gasoline (Squillance et al., 1997). However, the contribution from atmospheric deposition to the amount observed in lakes remains small compared with the influence of direct emission activities, such as motor boating (Reuter et al., 1998; Gabele and Pyle, 2000).

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REFERENCES

Atkinson, R. 1990. Gas-phase tropospheric chemistry of organic compounds: A review. Atmos. Environ. 24A(1):1–41.

Atkinson, R. 2000. Atmospheric chemistry of VOCs and NO_x. Atmos. Environ. 34:2063–2101.

Bennett, P.J., and J.A. Kerr. 1990. Kinetics of the reactions of hydroxyl radicals with aliphatic ethers under simulated atmospheric conditions: Temperature dependence of the rate constants. J. Atmos. Chem. 10:29–38.

California Air Resources Board. 2001. Annual summaries of toxics data from California's ambient toxics air quality monitoring network. Available online at http://www.arb.ca.gov/aqd/toxics/sitelists/mtbesites.html (verified 21 Feb. 2002). California ARB, Sacramento.

California Environmental Protection Agency. 1997. Toxic air contaminant identification list summaries, "Methyl Tert.-Butyl Ether". California Environ. Protection Agency, Air Resour. Board, Stationary Source Div., Sacramento.

Dillon, M.B., M.S. Lamanna, G.W. Schade, A.H. Goldstein, and C.C. Cohen. 2002. Chemical evolution of the Sacramento urban plume: Transport and oxidation. J. Geophys. Res. 107(D5):ACH3-1–ACH3-15.

Gabele, P.A., and S.M. Pyle. 2000. Emissions from two outboard engines operating on reformulated gasoline containing MTBE. Environ. Sci. Technol. 34:368–372.

Goldstein, A.H., B.C. Daube, J.W. Munger, and S.C. Wofsy. 1995. Automated in-situ monitoring of atmospheric non-methane hydrocarbon concentrations and gradients. J. Geophys. Res. 100(D10): 21023–21033.

Grosjean, E., D. Grosjean, R. Gunawardena, and R.A. Rasmussen. 1998a. Ambient concentrations of ethanol and methyl *tert*-butyl ether in Porto Allegre, Brazil, March 1996–April 1997. Env. Sci. Technol. 32:736–742.

Grosjean, E., R.A. Rasmussen, and D. Grosjean. 1998b. Ambient levels of gas phase pollutants in Porto Allegre, Brazil. Atmos. Environ. 32:3371–3379.

Kirchstetter, T.W., B.C. Singer, R.A. Harley, G.R. Kendall, and J.M. Hesson. 1999. Impact of California reformulated gasoline on motor vehicle emissions, 2. Volatile organic compound speciation and reactivity. Environ. Sci. Technol. 33:329–336.

Lamanna, M.S., and A.H. Goldstein. 1999. *In-situ* measurements of C_2-C_{10} VOCs above a Sierra-Nevada ponderosa pine plantation. J. Geophys. Res. 104(D17):21247–21262.

Lopes, T.J., and D.A. Bender. 1998. Nonpoint sources of volatile organic compounds in urban areas—Relative importance of land surfaces and air. Environ. Pollut. 101:221–230.

McKeen, S.A., and S.C. Liu. 1993. Hydrocarbon ratios and photochemical history of air masses. Geophys. Res. Lett. 20(21):2363–2366.

National Oceanic and Atmospheric Administration Air Resources Laboratory. 1997. HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model. Available online at http://www.arl.noaa.gov/ready/hysplit4.html (verified 21 Feb. 2002). NOAA, Washington, DC.

Pankow, J.F., N.R. Thomson, A.L. Baehr, and J.S. Zogorski. 1997. The urban atmosphere as a non-point source for the transport of MTBE and other volatile organic compounds (VOCs) to shallow groundwater. Environ. Sci. Technol. 31:2821–2828.

Poulopoulos, S., and C. Philippopoulos. 2000. Influence of MTBE addition into gasoline on automotive exhaust emissions. Atmos. Environ. 34:4781–4786.

Reuter, J.E., B.C. Allen, R.C. Richards, J.F. Pankow, C.R. Goldman, R.L. Scholl, and J.S. Seyfried. 1998. Concentrations, sources, and fate of the gasoline oxygenate methyl *tert*-butyl ether (MTBE) in a multiple-use lake. Environ. Sci. Technol. 32(23):3666–3672.

Schade, G.W., and A.H. Goldstein. 2001. Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation. J. Geophys. Res. 106(D3):3111–3123.

Schade, G.W., A.H. Goldstein, and M.S. Lamanna. 1999. Are monoterpene emissions influenced by humidity? Geophys. Res. Lett. 26: 2187–2190.

Squillance, P.J., J.F. Pankow, N.E. Korte, and J.S. Zogorski. 1997. Review of the environmental fate of methyl *tert*-butyl ether. Environ. Toxicol. Chem. 16:1836–1844.

USEPA. 1999. Achieving clean air and clean water: The report of the Blue Ribbon Panel on Oxygenates in Gasoline. EPA/420/R-99/021. USEPA, Washington, DC.

Vainiotalo, S., Y. Peltonen, and P. Pfäffli. 1998. MTBE concentrations in ambient air in the vicinity of service stations. Atmos. Environ. 32:3503–3509.

Vainiotalo, S., Y. Peltonen, A. Ruonakangas, and P. Pfäffli. 1999. Customer exposure to MTBE, TAME, C_6 alkyl ethers, and benzene during gasoline refueling. Environ. Health Persp. 102:133–140.