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Abstract: In order to assess the pathways for human exposure to methyl-*tert*-butyl-ether (MTBE) and to understand the extent of MTBE contamination in watersheds, a purge and trap gas chromatographic mass spectrometric method to measure *part-per-trillion (ppt)* concentrations of MTBE in environmental waters was developed. A variety of California's raw drinking waters were analyzed. No detectable MTBE was found in deep groundwater (>1000 feet). However shallow groundwater (<250 feet) contained MTBE concentrations of non-detect to 1300 ppt. MTBE concentrations measured in rivers and lakes ranged from non-detect to 3500 ppt. East (San Francisco) Bay area rain water contained approximately 80 ppt MTBE.

Introduction: The wide use of the gasoline additive methyl-*tert*-butyl-ether (MTBE) has raised public concern about the risk of exposure. For example, 9 billion kilograms of MTBE were produced in the U. S. in 1997[1]--nearly all of this MTBE was used as a gasoline additive. As a consequence, 109 million U.S. citizens live in the 32 regions and 18 states where MTBE is used.[2] A recent study by the U.S. Geological Survey detected MTBE in 27% of the urban wells and 1.3% of the agricultural wells it tested (reporting limit of 2 *parts-per-billion*).[2]

Although there has been no demonstrated connection between MTBE exposure at ambient/occupational concentrations and alleged acute health effects,[3] the health effects of long-term exposure to low concentrations of MTBE are unknown. The U.S. Environmental Protection Agency tentatively considers MTBE a "possible human carcinogen" and has set health advisory levels for MTBE in drinking water at 20-40 *parts-per-billion*.[4] Such high concentrations of MTBE are typically associated with leaking underground fuel tanks.

The high aqueous solubility of MTBE and its resistance to degradation[5] suggest that atmospheric MTBE will be deposited with precipitation and persist in aqueous systems. For this reason, and because of public concern about low levels of MTBE contamination, we developed a method to determine *part-per-trillion (ppt)* concentrations of MTBE in aqueous samples and initiated a survey of California surface, ground, and rain waters.

Experimental: Instrumentation. Purge and trap gas chromatography/mass spectrometry (GC/MS) was used to determine MTBE in aqueous samples. The purge and trap unit (model 4460A, OI Analytical, College Station, TX) was equipped with an autosampler (model PTA-30, Dynatech Precision Sampling Corp.) and was connected to a GC/MS (model 5970B, with UNIX operating system, Hewlett-Packard, Palo Alto, CA).

Method. A 25.00 mL water sample was measured into a pre-cleaned VOA vial, which served as the purge vessel, and a Teflon-coated stirrer was added. The sample was spiked with either 10 µL of 2.5 ng/µL bromofluorobenzene in methanol (for samples analyzed before d_{12}-MTBE became available) or with 10 µL of 0.40 ng/µL d_{12}-MTBE in methanol. The solution was purged, for 11 minutes at 40°C, with stirring, with 40 cc/min of Ultra High Purity helium (Air Liquide America Corp.). The analytes were collected on a trap containing charcoal, Tenax, and silica gel (#6, OI Analytical). After the purge was complete, the analytes were thermally desorbed from the trap at 180°C for two minutes and carried to the head of the GC column. The transfer line between the purge unit and the GC was kept at 110°C. The GC column used was a 60 m, RTX-502.2 column with a 0.32 mm i.d. and a 1.8 µm film thickness (Restek Corp., Bellefonte, PA). The GC was held at 35°C for 2 min, ramped at 5°C/min to 65°C, ramped at 10°C/min to 280°C, and held at 280°C for 5 minutes. Prior to subsequent analyses, the trap was baked at 180°C for 20 minutes to remove any residual contamination.

The GC/MS was operated in the selected ion monitoring mode. Ions of *m/z* 43, 57, and 73 were monitored for MTBE, ions of *m/z* 50, 66, and 82 were monitored for d_{12}-MTBE, ions of *m/z* 94, 96, and 176 were monitored for bromofluorobenzene (initial analyses only), and ions of *m/z* 75 and 76 were monitored to determine contamination from the VOA vial. All ions were monitored for a dwell time of 100 ms and the MS cycle time was 1.1 seconds. Positive identification of MTBE required a chromatographic peak at the expected retention time (*m/z* 73), with a signal to noise ratio greater than 5.

Sample collection. All samples were collected as "grab" samples. Samples were collected in VOA vials (leaving no headspace), immediately capped, and refrigerated (4°C) until analysis. Groundwater samples were collected, after sufficiently flushing the sampling lines, surface waters were sampled at approximately 1-2 feet below the surface, and rain samples were collected in a combustion cleaned, open, glass container.

Blank samples. Blank samples and trip blanks were analyzed to determine potential contamination of the system and the sample, respectively. Blank samples consisted of 18.2 MOhm water (Milli-Q, UV Plus system, Millipore, Bedford, MA) that was boiled for 30 min., allowed to cool, and immediately placed in sealed 40 mL VOA vials (leaving no headspace). Blank samples were used within two days of preparation and no MTBE was observed in blank samples prepared by this method.

No laboratory contamination of the samples with MTBE was observed. However, after several hours of exposure to ambient air, open vials of clean water became contaminated with atmospheric MTBE. Thus, extreme care must be taken when preparing blank samples. No MTBE was measured in any trip blanks; this indicates that no significant amount of MTBE was introduced into the samples during collection. The analysis of deep groundwater samples from Davis, California (*i.e.* groundwater found at depth >1000 feet which has not been exposed to the atmosphere for thousands of years[6]) did not contain MTBE; this suggests that the groundwater sampling procedure did not contaminate the samples with MTBE.

Storage Study. A liter of 18.2 MOhmwater containing 2 ppb MTBE was made and aliquotted into several, 40 mL VOA vials. These "samples" were stored at 4°C. Fresh, duplicate samples were analyzed periodically during the course of a month to determine if MTBE would degrade. Data suggest that samples are best analyzed for MTBE within a week of collection; but, approximately 80% of the MTBE still remained in the samples after 28 days of storage.

Results: Using purge and trap GC/MS, the detection limit for MTBE in 18.2 MOhm water was 15 *parts-per-trillion* (detection limit=$st_{(n-1)}$, where s=standard deviation of 7 measurements of 55.2 ppt MTBE, t=Student's t value for the 99% confidence level with (n-1) degrees of freedom, and n=number of replicates). When the GC/MS was functioning optimally, MTBE could be detected at 5-10 ppt in a 25.00 mL, spiked water sample. This detection limit is almost an order of magnitude better than the best detection limit, 100 ppt, reported to date.[7] For replicate analyses of the 55.2 ppt MTBE in 18.2 MOhm water performed on the same day, the standard deviation for 7 replicate measurements was 7%.

Figure 1 shows the locations where surface water samples were collected. MTBE concentrations measured in the Sacramento and San Joaquin River Basins in June 1998 ranged from 80-3500 ppt; see Table 1. Spatial and temporal variations in MTBE concentrations in these surface waters might be related to variations in the atmospheric source and variations in the concentrations of MTBE partitioned into rain,[8] or variations in transport of MTBE to rivers and lakes via runoff. In general, higher MTBE concentrations were observed in urban areas of the Basin. The highest MTBE concentration was observed in the Mokelumne River; this sample was collected near to a marina, where additional MTBE contamination might have been introduced into the water by motor boats.

Figure 1. Map of sampling sites.

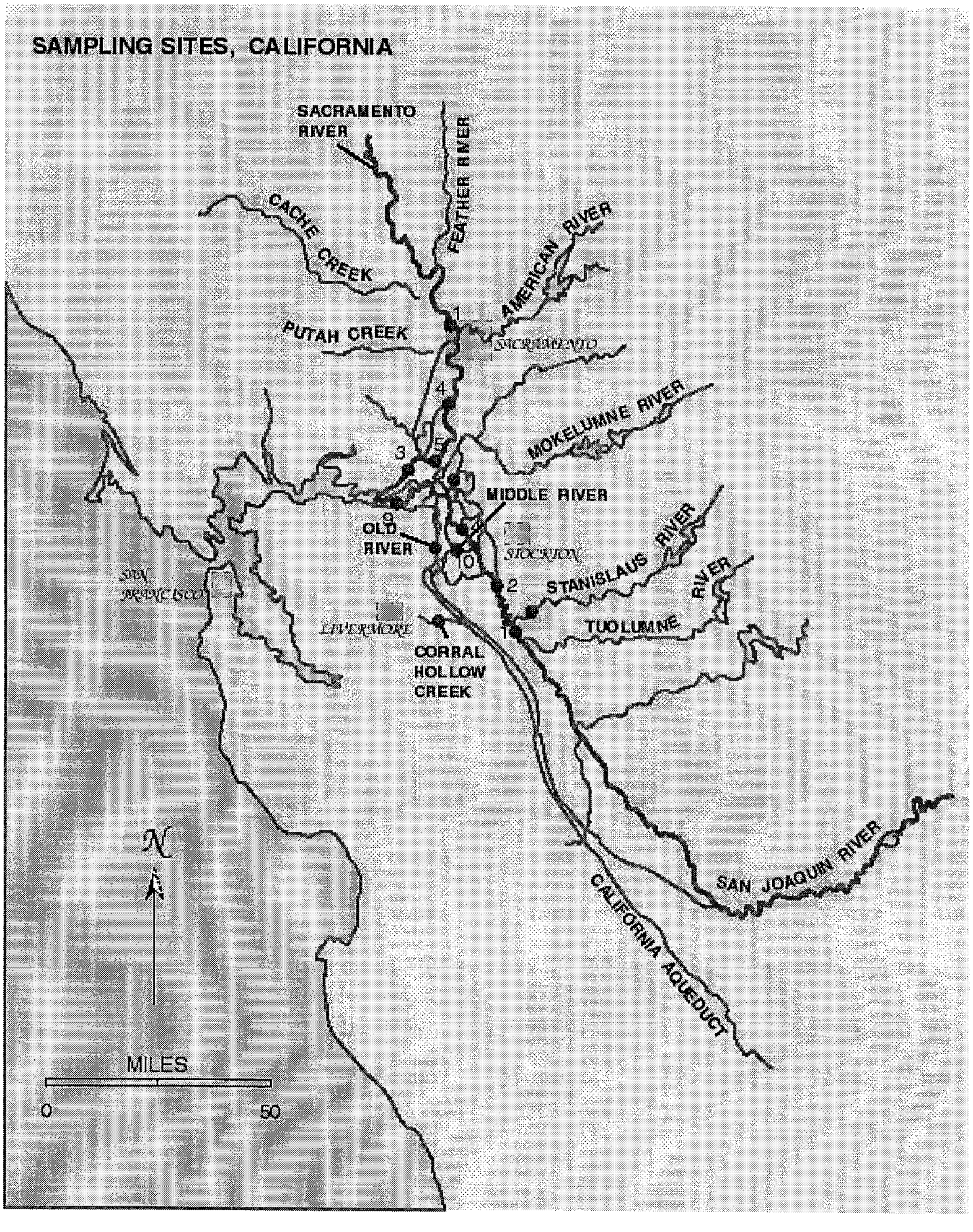


Table 1. MTBE concentrations in California surface rivers. Data collected in June 1998.

Sample Location	MTBE Concentration (ppt)
Corral Hollow Creek	81
Sacramento River, #1	1200
Sacramento River, #3	890
Sacramento River, #4	1500
Middle River	810
Mokelumne River	3500
Old River	560
Stanislaus River	220
San Joaquin River, #1	79
San Joaquin River, #10	520

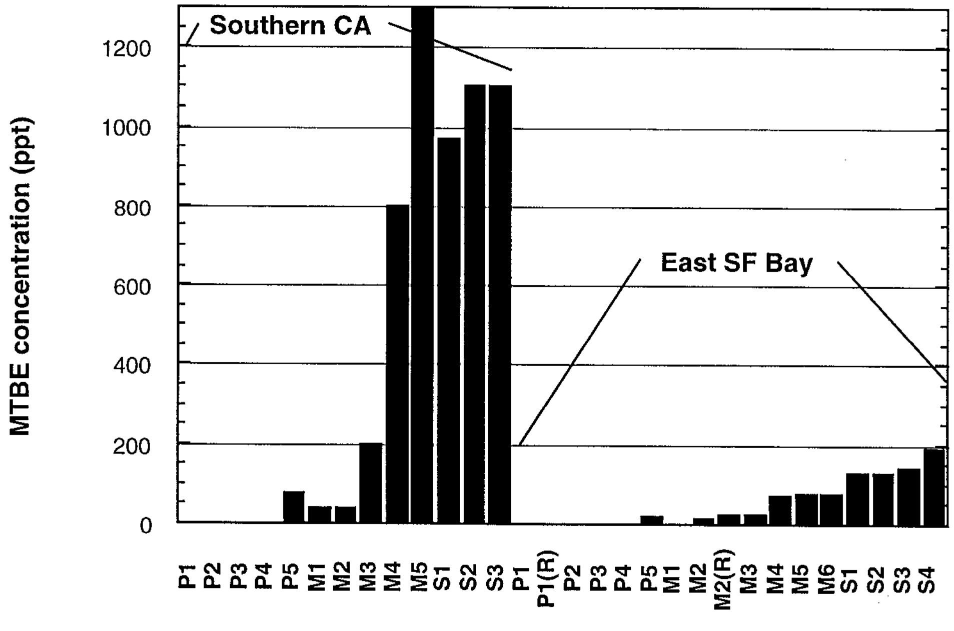
Water samples from the Sacramento River collected in June contained approximately 10 times higher MTBE concentrations than those observed in January of 1998; see Table 2. Perhaps very high runoff in January 1998 might have resulted in the dilution of MTBE in rivers. Furthermore, large reservoir releases into the Sacramento River in June might have resulted in increased MTBE concentrations--boating (with two-stroke engines) in reservoirs is likely to constitute a major source of MTBE. Further study is needed to determine the causes of variability in MTBE concentrations in surface waters.

Table 2. MTBE concentrations in California surface rivers. Data collected in January 1998.

Sample Location	MTBE Concentration (ppt)
Sacramento River, #1	80
Sacramento River, #3	220
Sacramento River, #5	260
San Joaquin River, #2	280
San Joaquin River, #9	40
San Joaquin River, #10	115

Ground and surface water samples were collected in Southern California and in the East (San Francisco) Bay region; see Figure 2. In general, ground waters from production and monitoring wells contained lower MTBE concentrations than surface waters. Many groundwater sources contain deep water which has been out of contact with the atmosphere for many years, and thus, has never been exposed to MTBE. Surface waters have more exposure to MTBE than groundwaters that are not impacted by leaking underground fuel tanks. The low concentration of MTBE in surface waters of the East Bay region suggest an atmospheric source of MTBE.

Figure 2. MTBE concentrations measured in various ground and surface waters in Southern California and in the East (San Francisco) Bay Region. Samples marked with "P" indicate production wells, with "M" indicate monitoring wells, and with "S" indicate surface waters. The surface waters were sampled near to the groundwater sampling sites.



Two rain samples were collected and analyzed for MTBE in January 1998. One sample contained 67 ppt MTBE and a second sample contained 90 ppt MTBE. This indicates an atmospheric source for MTBE. However, the lower concentrations of MTBE in rainwater, as compared to surface waters, suggest that other sources, such as boating, or transport processes in watersheds, contribute to MTBE contamination in rivers.

We have developed a method to measure 15 ppt of MTBE in environmental waters. MTBE has been found in low concentrations in several areas of California. To the best of our knowledge, these results represent the lowest MTBE concentrations reported to date and demonstrate that MTBE is ubiquitous in California's waters. Potential future applications of this method include examination of atmospheric and aqueous transport of MTBE and tracing groundwater recharged since the time of increased MTBE use.

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