Concentrations of methyl-*tert*-butyl ether (MTBE) in inputs and receiving waters of Southern California

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ABSTRACT

The occurrence and concentration of methyl-*tert*-butyl ether (MTBE) was measured in dry-weather runoff, municipal wastewater and industrial effluents, and coastal receiving waters in southern California. MTBE was detected in the effluents of refineries and publicly owned treatment works (POTWs) discharging to coastal waters in southern California. Combined, these point source discharges release approximately 214 kg/day of MTBE into the marine environment. Santa Monica Bay receives most (98%) of the MTBE discharged from point sources, with the majority from POTW effluent discharges. This situation is the result of most refineries in Los Angeles County discharging wastewater to the municipal sewer system, rather than through industrial outfalls. Dry-weather urban runoff was analyzed for samples collected from 25 streams and rivers. Dry-weather stream flow accounted for less than 0.5% of the mass of MTBE discharged to coastal waters. The amount of MTBE contributed by stormwater discharges was estimated to be approximately 5% of the amount discharged by point sources. Receiving water samples were collected from 23 stations in Santa Monica Bay, Los Angeles Harbor, Mission Bay, and San Diego Bay. MTBE was detected at low concentrations near effluent discharges; however, no evidence was found of bay-wide MTBE contamination related to these outfalls. Marinas and areas used intensively for recreational boating had the highest average MTBE concentration (8.8 µg/L). Surface water contamination was most widespread in San Diego Bay and Mission Bay, areas with no refinery or POTW inputs.

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INTRODUCTION

Methyl-*tert*-butyl ether (MTBE) is a synthetic fuel additive that makes up approximately 11% of each gallon of gasoline sold in California. MTBE increases the oxygen content of gasoline, thereby making the fuel burn more efficiently and thus reducing the exhaust emissions of carbon monoxide and benzene (a known human carcinogen). The State of California started regulating the addition of MTBE to gasoline as part of an emission reduction policy in 1987.

MTBE has several chemical characteristics that result in a high potential to contaminate surface and groundwater systems. This volatile organic compound is highly soluble in water, binds weakly to soil, and does not readily biodegrade in the environment (Squillace *et al.* 1997). These characteristics, together with the widespread use of MTBE, have resulted in the contamination of groundwater and surface water in California.

Since 1996, when mandatory monitoring went into effect, at least two public water supply systems have closed portions of their drinking water wells due to MTBE contamination. The South Tahoe Public Utilities Districts closed 13 of its 36 groundwater wells, while the City of Santa Monica lost 50 percent of its total water supply at a cost of $3.5 million for replacement water. Leaking underground fuel tanks are the major source of groundwater contamination by MTBE (Oswalt 1997). MTBE has also been detected in reservoirs and lakes used for drinking water supplies throughout California. The most significant source of surface water contamination is motorized boating activities (Reuter *et al.* 1998).

The coastal marine environment is also at risk of contamination by MTBE. In addition to emissions of gasoline from motorized watercraft, California's coastal waters receive discharges from multiple sources that potentially contain MTBE, including urban runoff, effluent from petroleum refineries, and treated municipal wastewater

from publicly owned treatment works (POTWs) (Oswalt 1997). The volume of POTW and stormwater discharges is large; relatively little is known about the concentrations and mass emissions of MTBE discharged to California's coastal waters from these sources. While MTBE concentrations have been measured for some discharges, the data are limited and have not been assessed to determine their potential for contamination and toxic effects on marine life. Consequently, the extent of MTBE contamination and the degree to which it adversely affects marine water quality in California is not known.

This study has two objectives. The first objective is to assess the contribution of MTBE to the coastal environment resulting from point source discharges (refineries and POTWs) and nonpoint sources (urban streams). Documenting the sources and relative mass emission of MTBE to the marine environment will assist managers in determining the potential for adverse effects by identifying locations where exposure is likely to be greatest. The second objective is to measure the concentration and extent of MTBE contamination in coastal receiving waters. Receiving water concentrations reflect the fate of MTBE and help to establish the significance of different input types. In addition, these data are valuable for estimating the toxic effects of MTBE by defining the contamination levels to which marine life is exposed.

METHODS

Point Source Discharge Data Analysis

The input of MTBE from POTW and refinery discharges was estimated using data from a statewide study conducted from May through September 1999 of MTBE concentrations in municipal wastewater and industrial effluents. All NPDES facilities throughout the state discharging over 1 million gallons per day analyzed four effluent samples for MTBE during the study period. The raw data from the survey were compiled and summarized for each region. Data for facilities discharging into southern California marine waters were isolated from the results and combined with the discharger's daily flow data to estimate the daily mass emission.

Stream Sampling

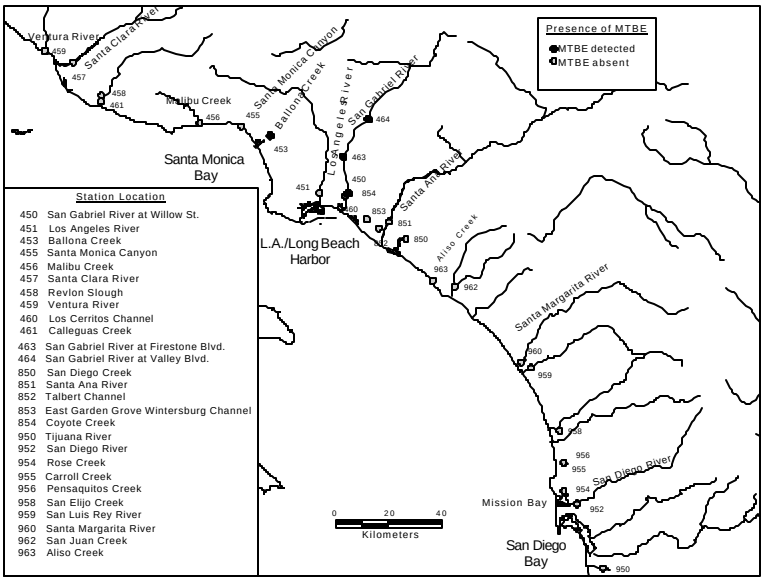
Selected streams (including creeks and urban rivers) were sampled to determine the concentration of MTBE in dry-weather discharges to southern California. The sampling sites were selected based upon three criteria: (1) flow in dry weather, (2) proximity of urban land uses, and (3) availability of prior monitoring/flow data.

Samples were obtained from 25 streams (Figure 1). These sites included the region's largest urban rivers (Ballona Creek and the Los Angeles, San Gabriel, and Santa Ana Rivers); smaller concrete channels draining high-density residential areas (e.g., Talbert Channel and Coyote Creek); and streams draining mostly undeveloped areas (e.g., Malibu Creek, Ventura River, and Santa Margarita River). Streams draining the San Diego Bay watershed could not be sampled because no flow was present, or the sampling locations were tidally influenced.

A two-tiered sampling strategy was employed. In the first tier, multiple creeks in each region were sampled once during June 1999 to determine the occurrence and concentration of MTBE. The second tier of sampling consisted of repeated sampling at those sites found to contain MTBE in the first tier. Three of the sites were revisited 2-4 times in July-August.

All sampling was conducted from the creek bank or from bridges. Different methods were used to collect samples, depending upon water depth and site accessibility. A glass jar attached to one end of a telescoping pole was used to collect a surface water grab sample at most of the sites. Samples from bridges were usually collected using a stainless steel bucket lowered by a rope. A portion of the sample was immediately transferred to 40 mL VOA vials containing an acid preservative, and kept on ice. Temperature and conductivity were measured on the remaining sample. Flow data were obtained from U.S. Army Corps of Engineers gauging stations or calculated using onsite

FIGURE 1. Southern California sampling locations for dry-weather runoff collected from June to August 1999.



measurements of surface velocity and stream cross-sectional area.

FIGURE 2. Santa Monica Bay and Los Angeles Harbor sampling locations for receiving water collected between June and July 1999.

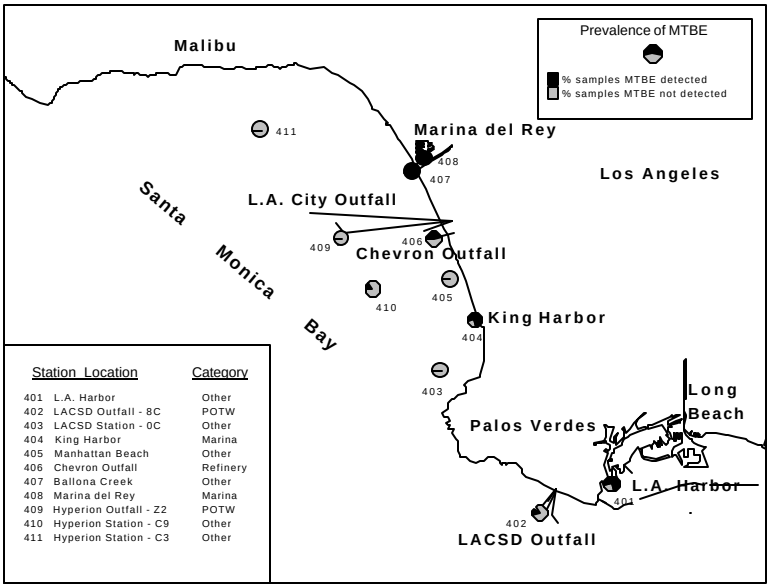
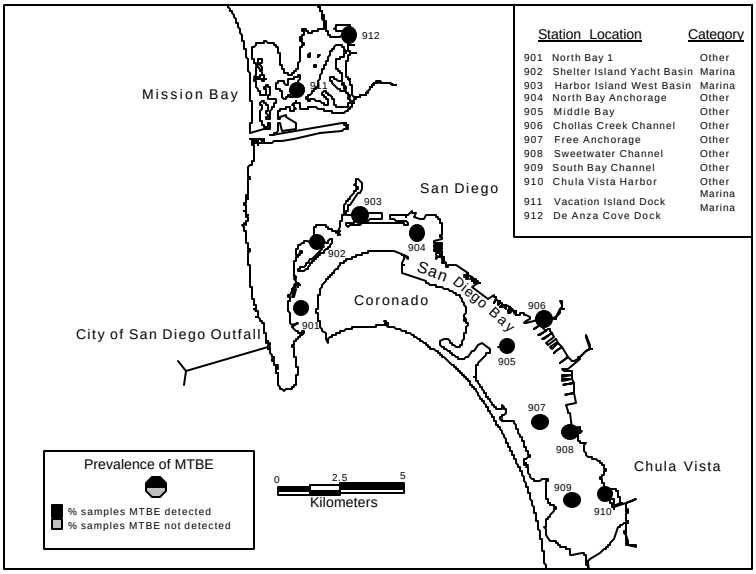


FIGURE 3. Mission Bay and San Diego Bay sampling locations for receiving water collected between June and July 1999.



Receiving Water Sampling

Water column samples from Santa Monica Bay, Los Angeles Harbor, Mission Bay, and San Diego Bay were analyzed to determine MTBE concentrations near suspected discharge sources as well as in areas representative of ambient conditions. Some of the sampling stations were near known MTBE-containing discharges (refinery or POTW effluent) or uses with the potential to release MTBE (marina/recreational boating). Additional stations represented ambient conditions throughout each bay. The ambient stations, termed "other" in this study, represented either stations with multiple uses or reference stations distant from MTBE contamination sources. These stations often included locations used in previous monitoring programs.

Receiving water stations in Santa Monica Bay (Figure 2) were located at the discharges for two POTWs and within two marinas. Ambient stations were located at similar depths to the POTW and refinery sites, as well as near the mouth of Ballona Creek. One station was located in the main channel of Los Angeles Harbor. This station was selected to represent ambient conditions in the harbor.

San Diego Bay sampling represented just one potential source category, marinas (Figure 3). No POTWs discharging to the bay and no industrial dischargers with effluent likely to contain MTBE were identified. Additional stations within San Diego Bay included areas adjacent to boat anchorages and areas expected to have relatively high commercial/recreational boat traffic, as well as three stations characteristic of ambient conditions. Two stations within Mission Bay were sampled. Both were adjacent to boat docks.

Each receiving water site was sampled twice during June-July 1999. Except for Mission Bay, all sampling was conducted from boats in water depths of at least 2 m. Samples were collected at the surface and near the bottom. Additional samples were taken below the thermocline, when present, and also at the depth corresponding to the effluent plumes in Santa Monica Bay. Samples were collected using a 1.2 L stainless steel Kemmerer grab sampler. The sampler was lowered on a nylon line, triggered to close at the appropriate depth using a messenger, and then retrieved for sample dispensing on board the boat. A portion of the sample was transferred to 40 mL VOA vials containing a preservative, and kept on ice. Temperature and conductivity/salinity were measured on the remaining sample.

The detection of thermoclines and effluent plumes was accomplished using a conductivity-temperature-depth (CTD) profiler. The CTD profiler was equilibrated with ambient seawater and then lowered through the water column to obtain a continuous record of temperature, conductivity, and salinity (calculated) with depth. The

resulting temperature and salinity profiles were viewed on board the boat and used to determine whether additional sampling depths were needed to capture samples beneath the thermocline or within the discharge plume.

Various CTD instruments were used in the study. A Hydrolab MiniSonde with a Surveyor 4 Datalogger was used during the June sampling period in San Diego Bay. A Sea-Bird Electronics SBE 911 was used to collect water quality data from Santa Monica Bay during the June sampling period. Water quality sampling in Santa Monica Bay and San Diego Bay during July was conducted using an SBE 19 CTD. All CTDs were factory or laboratory calibrated just prior to use.

Chemical Analysis

The stream and receiving water samples were analyzed for MTBE and benzene, toluene, ethylbenzene, and xylene (BTEX), volatile compounds also present in gasoline following U.S. EPA (1996) SW-846 Method 8260B. This is a purge-and-trap method with quantitation by gas chromatograph/mass spectrometer.

Quality assurance procedures employed during sampling included the analysis of field blanks from sampling equipment and travel blanks. Laboratory quality control procedures included the analysis of method blanks, recovery surrogates, 50 µg MTBE/L matrix spike/matrix spike duplicates, and a 5 µg MTBE/L low-level check standard for each set of samples analyzed.

Most samples were analyzed within 5 d after collection (maximum 8 d). All blanks were found to be below the detection limit, and high recovery was obtained for the matrix spikes (102%) and low-level standards (104%). Matrix spike duplicates and low-level standards had low variability, indicating that the instrumental analysis procedure had high precision.

RESULTS

Point Sources

Data were obtained for 16 POTWs, 2 petroleum refineries, and 8 other facilities discharging to southern California's marine environment. Many of these facilities (42%) detected MTBE in their discharge at least once during the survey period (Table 1). Throughout southern California, large point sources discharged approximately 214 kg/day of MTBE to coastal waters (Table 1).

Most of the mass of MTBE was discharged to Santa Monica Bay. Over 98% (210 kg) of the MTBE entering southern California coastal waters from refineries and POTWs is discharged to this water body. MTBE was not detected in large point source discharges to the San Diego Bay.

Discharges from petroleum refineries contained the highest concentrations of MTBE. Effluent from the Chevron El Segundo Refinery, which discharges to Santa Monica Bay, contained the highest mean concentration of MTBE of any discharge in this study (1,878 µg/L). The average concentration in effluent from the Equilon Refinery, discharging to the Los Angeles Harbor, was 88 µg/L. Combined, the daily mass emission from these facilities was estimated to be 46.53 kg/day.

Although refinery effluents generally contained the highest concentrations, discharges from POTWs accounted for the greatest proportion (78%) of the daily mass emission of MTBE (Table 1). Many (54%) of the POTW effluents discharged to the coastal environment contained detectable levels of MTBE. Most notable of these inputs is the Los Angeles County Sanitation District's Joint Water Pollution Control Plant (LACSD JWPCP) discharge in Santa Monica Bay, which had a greater mass emission (164 kg/day) of MTBE than any other facility (including refineries) discharging to the coast.

Dry-Weather Stream Discharge

A total of 41 surface water samples were collected from 25 streams during the field sampling program. MTBE was only detected in streams draining urban areas in Los Angeles County. Within this region, MTBE was detected at low levels in Ballona Creek and San Gabriel River (Figure 1). The tier one sample from the San Gabriel River contained the highest concentration (52.0 µg/L) of MTBE of any stream measured in this study. This river receives discharges from POTWs as well as urban runoff. Two additional San Gabriel River stations upstream of the Willow Avenue sampling site were added during tier two in an attempt to locate the source of the high MTBE measurements. Subsequent samples were much lower in concentration and did not show a strong spatial pattern. No other volatile organic compounds were detected at the site that would indicate a recent fuel spill. The mean MTBE concentration for this river was 11.53 µg/L. Mass emission calculations were based upon the median concentration of 1.4 µg/L to minimize the effect of the extreme value, resulting in a value of 0.84 kg/day. The mean MTBE concentration in Ballona Creek for five sampling events was 0.66 µg/L, with an estimated daily mass emission of 0.05 kg/day.

A mass emission estimate for MTBE in dry-weather stream discharges in the region was made. Nearly all of the estimated 0.89 kg/day discharged from streams during the study period was supplied by the San Gabriel River (Table 2).

TABLE 1. Concentrations and mass emissions of MTBE in POTW and industrial discharges to bays and coastal waters. Sampling was conducted from May to August 1999. Concentrations below the reporting limit were assigned a value of 0 µg/L for all calculations.

Discharge Location/Category	Number of Facilities Reporting Data	Percentage of Facilities with Detectable MTBE	MTBE (µg/L) Mean	MTBE (µg/L) Range	MTBE (kg/day) Mass
Statewide					
POTW	68	49	3.8	< 0.5 – 123.3	175.31
Refinery	6	100	395.6	34.3 – 1,877.5	52.36
Other	10	30	2.6	< 0.5 – 13.0	0.11
Southern California					
Santa Monica Bay					
POTW	2	100	63.6	3.9, 123.3	163.99
Refinery	1	100	1,877.5	–	45.79
L.A. Harbor					
POTW	1	100	15.3	–	0.96
Refinery	1	100	87.8	–	0.74
Mission Bay					
Other	1	100	13	–	0.11
San Diego Bay					
Other	2	0	0	< 5, < 20	0
Other Coastal Waters					
POTW	13	31	0.5	< 20 – 2.2	2.8
Other	5	20	2.5	< 20 – 12.5	< 0.01

TABLE 2. MTBE concentrations measured in dry-weather stream inputs to coastal waters of southern California. Samples were collected between June and August 1999. Concentrations below the reporting limit (0.5 µg/L) were assigned a value of 0 µg/L for all calculations. Mean concentrations are for all streams within a region. Mean concentrations from individual streams were used for concentration ranges.

Discharge Location	Number of Streams	Percent of Streams with Detectable MTBE	Concentration (µg/L) Mean	Concentration (µg/L) Range	Mass (kg/day)
Santa Monica Bay	3	33	0.2	< 0.5 – 0.7	0.05
Los Angeles Harbor	1	0	0	< 0.5	0
Mission Bay	1	0	0	< 0.5	0
Other Coastal Waters	20	5	0.6	< 0.5 - 11.5	0.84

Occurrence of MTBE in Bays and Harbors

A total of 23 receiving water stations were sampled in 4 water bodies. MTBE was detected at 83% of all stations and in each of the water bodies. However, the other volatile compounds present in gasoline (benzene, toluene, ethylbenzene, and xylenes) were only rarely detected. Although MTBE was detected in at least one sample from each of the study areas, the prevalence and concentration of MTBE varied among locations (Table 3).

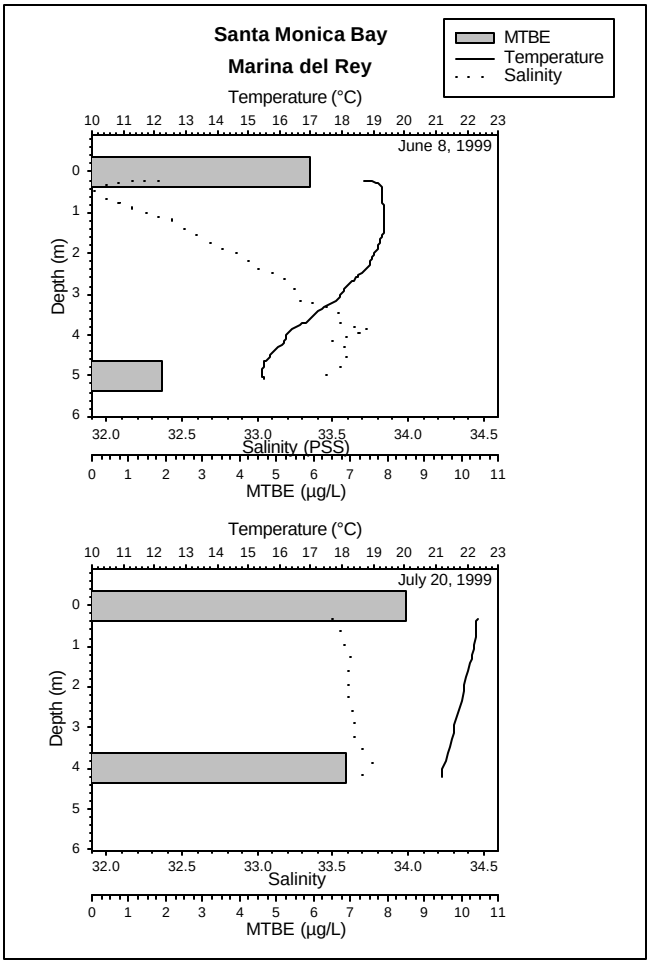
Santa Monica Bay

MTBE was detected at 6 stations in Santa Monica Bay (Figure 2). The greatest frequency of detection was found in marina areas (Marina del Rey and King Harbor) or offshore Ballona Creek (another location with relatively high boat traffic). Among these sites, MTBE concentrations were greatest in Marina del Rey, where average concentrations for the June and July sampling events were 3.9 and 7.7 µg/L, respectively. Higher concentrations of MTBE were measured in surface water samples than in samples collected near the bottom (Figure 4).

TABLE 3. Average MTBE concentrations in different receiving water use categories of southern California bays and harbors. Values are mean concentrations ± standard deviations. Concentrations below the reporting limit (0.5 µg/L) were assigned a value of 0 µg/L. Dash indicates samples not analyzed for the category. Stations in the "Other" category represent reference or areas with mixed uses.

	MTBE (µg/L)			
Location	Refinery	POTW	Marina	Other
Santa Monica Bay	1.4	< 0.1 ± 0.1	3.5 ± 3.3	0.2 ± 0.5
Los Angeles Harbor	-	-	-	0.6
Mission Bay	-	-	20.1 ± 8.3	-
San Diego Bay	-	-	2.9 ± 0.2	1.8 ± 0.5

FIGURE 4. Distribution of MTBE with depth for Marina del Rey (Station 408). Higher concentrations of MTBE were found in surface waters in both June and July.



MTBE was also detected near the Chevron El Segundo Refinery discharges during both the June and July sampling events. A thermocline was present in the offshore waters during both sampling cruises (Figure 5) and MTBE was only detected in samples collected beneath the thermocline, the zone where the refinery plume would be expected to be trapped. The greatest MTBE concentration (9.9 µg/L) was measured in July, in a sample collected in a region of the water column showing a relatively large decrease in salinity, which may indicate the presence of the diluted freshwater refinery plume.

A single sample collected near the LACSD outfall in July was also found to contain MTBE (Figure 6). Similar to the Chevron outfall samples, this sample was also collected below the thermocline in a region showing variable salinities that may have been influenced by the wastewater effluent plume. The MTBE concentration in this sample was 0.7 µg/L. A similar concentration of MTBE (0.5 µg/L) was measured in a single sample collected from a reference location (Station 410) at a depth of 10m (above the thermocline).

Los Angeles Harbor

MTBE was detected at the ambient station in Los Angeles Harbor during both June and July (Figure 2). The concentration at the surface in the June sample (0.6 µg/L) was slightly above the reporting limit (0.5 µg/L), while MTBE was not detected near the bottom. Higher concentrations were measured in July, with both surface and bottom samples containing 1.0 µg/L MTBE.

Mission Bay

MTBE was also consistently detected in Mission Bay (Figure 3). Surface water samples collected from boat docks at two locations within the bay (Vacation Island and De Anza Cove) contained the highest receiving water concentrations measured in this project (7.4 - 34.0 µg/L). Average concentrations at each station were 14.2 and 26.0 µg/L MTBE for Vacation Island and De Anza Cove, respectively. Concentrations were again approximately two times higher in the July collection, when a larger number of personal watercraft (i.e., jet skis) were observed in Mission Bay. Low concentrations (1.4-1.9 µg/L) of toluene and xylene were detected in one sample from the Vacation Island station (July) and one sample from De Anza Cove (June).

San Diego Bay

MTBE was detected in every sample collected from every station in San Diego Bay (Figure 3). Average concentrations between the marina and other sites showed little difference (Table 3). The water column was well mixed within the bay, as indicated by similar temperature and salinity values between surface and bottom water samples. The MTBE concentrations were approximately two times higher at the surface at one-half of the stations; the remaining stations showed little difference in concentra-

FIGURE 5. Distribution of MTBE with depth at the Chevron El Segundo Refinery outfall system (Station 406), Santa Monica Bay. Asterisks (*) indicate sampled depths with MTBE concentrations below the detection limit (0.5 µg/L).

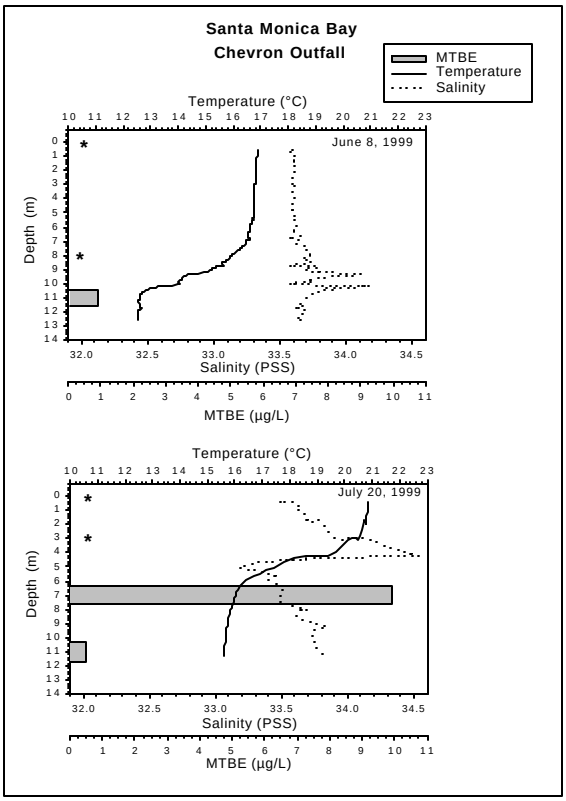
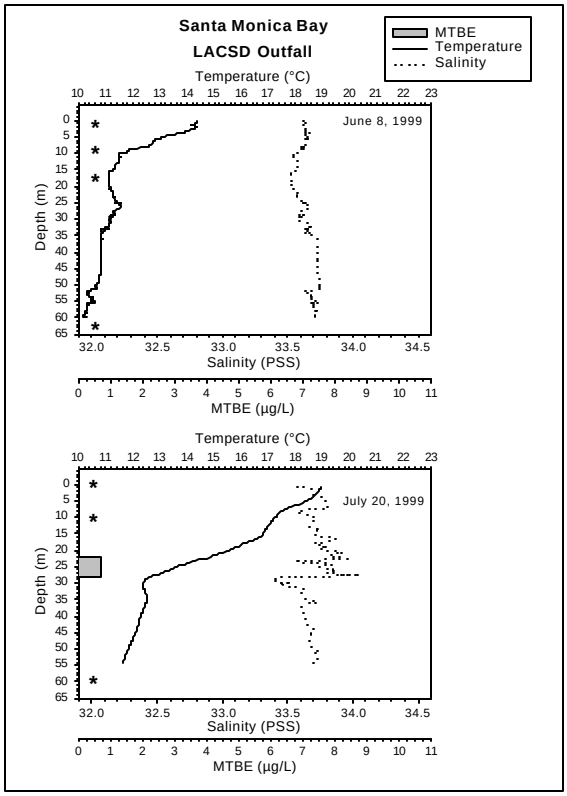


FIGURE 6. Distribution of MTBE with depth at the Los Angeles County Sanitation Districts JWPCP outfall system (Station 402), Santa Monica Bay. Asterisks (*) indicate sampled depths with MTBE concentrations below the detection limit (0.5 µg/L).



tion with depth. A marked temporal pattern was also evident in the concentration data. Surface water MTBE concentrations in samples collected in July were approximately two times greater than those in the June samples.

DISCUSSION

Point Sources

The relatively high concentration of MTBE in refinery effluent is a result of its use in California as a gasoline additive. Much of the MTBE discharged from the facilities in this study is probably a byproduct of the reprocessing of contaminated or "out of spec" products from the refinery (Oswalt 1997). The volume and type of waste processed by refineries varies greatly over time, resulting in order-of-magnitude variations in MTBE discharge (W. Ishimoto, pers. comm.). Consequently, the mass emissions calculated from the SWRCB survey may not be representative of refinery discharges at other times. For this reason, mass emissions were calculated on a daily, instead of an annual basis.

The major source of MTBE in JWPCP effluent is refinery waste, which is discharged to the municipal sewer system. The JWPCP facility processes refinery wastewater from nine refineries (J. Stull, personal communication). The source of MTBE in other POTW effluents was not investigated. Several sources are possible, including refinery discharges, urban runoff inputs to sewer systems, infiltration from contaminated groundwater, and inputs due to trace quantities in drinking water supplies. MTBE has been detected in a number of drinking water systems in California. An assessment of MTBE analysis data for 105 California water bodies by Keller *et al.* (1998) found that MTBE was detected in 49% of the systems, with 12% of the water bodies reporting over 14 µg/L in at least one sample.

Compared to the total mass of MTBE consumed on a daily basis in California, the amount contained in POTW and refinery discharge is relatively small (approximately 0.002%). More MTBE is released to the atmosphere each day through exhaust and evaporation (39,009 kg/day) than is discharged from NPDES facilities (Oswalt 1997).

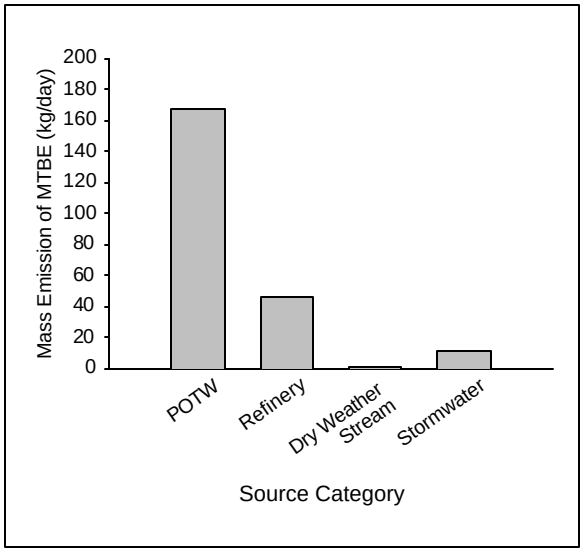
Stream Discharge

Streams represent a minor input of MTBE to coastal waters. The amount discharged by streams (0.89 kg/day) is trivial compared to emissions from point sources, representing less than 0.5% of the amount discharged from southern California POTWs and refineries (Figure 7).

Stormwater represents a potentially significant, yet poorly documented source of MTBE to the marine environment. No measurements of stormwater MTBE concentrations were made for this study because sampling was limited to the dry season. Studies conducted in other states have detected MTBE in 40% of stormwater samples from cities with known MTBE use (USGS 1996). The MTBE concentrations in stormwater with detectable levels ranged from 0.2 to 8.7 µg/L, with a median of 1.5 µg/L. These results are consistent with recent limited California stormwater data, which reported MTBE concentrations ranging up to 6.5 µg/L (Bay and Brown 1999).

Although a confident estimate of the emission of MTBE in stormwater cannot be made without additional data, a very rough estimate of the emission for southern California stormwater was made in order to compare the potential importance of this source. The calculation was based upon the method used by Schiff (1997) to estimate the emission of other constituents in stormwater. A stormwater discharge volume of 2.9×10^{12} L was used, which represents the total annual runoff flow for southern California gauged rivers in 1994-1995 (approximately two times the average rainfall). The emission of MTBE was calculated using both the 10^{th} and 90^{th} percentile concentrations in dry-weather stream samples in order to represent the range likely to occur in stormwater. These concentrations were 0.25 µg/L (one-half of the reporting limit) and 1.4 µg/L, respectively. Multiplication of the estimated volume times the concentration range gives an annual mass emission estimate of between 725 and 4,060 kg/yr. Expressed on a daily basis for comparison with the other MTBE emission estimates, stormwater represents a maximum input of 11 kg/day. This amount is relatively small, representing approximately 5% of the input from point sources in southern California (Figure 7).

FIGURE 7. Comparison of total MTBE mass emissions from various inputs to the southern California marine environment.



The mass emission estimates presented in this report are based upon a limited data set. The dry-weather stream and point source survey data cover a relatively short time interval (approximately 3 months), and thus may not be representative of other time periods. The greatest uncertainty is associated with the mass emission estimate for stormwater, since large assumptions were made regarding concentration and flow rate. Mass emission of MTBE from stormwater is expected to vary substantially between years as a result of rainfall variations alone. To obtain a conservative estimate for southern California, we used data for a range of concentrations combined with flow data from an above-average rainfall year. The analysis of many stormwater samples from multiple locations and storms is needed to provide a more precise estimate of MTBE inputs from stormwater.

MTBE in Receiving Waters

Similar to the results for southern California, MTBE was prevalent in northern California marinas (Bay and Brown 2000). Low levels were found in most (80%) marina stations in Humboldt and San Francisco bays, with concentrations ranging from < 0.5–1.9 µg/L. In addition, MTBE concentrations were consistently higher in samples collected near the surface. However, unlike southern California receiving waters, MTBE was not detected near refinery or POTW discharges in San Francisco Bay.

Few studies of the presence of MTBE in the marine environment had been conducted prior to Bay and Brown (2000). However, the limited data available prior to this period proved to be consistent with our results. MTBE was frequently detected in samples taken from multiple stations within Mission Bay over a three-year period (EMCON 1999). Samples analyzed in 1998 produced results similar to those of this study, with concentrations ranging from 6.3 to 18.7 µg/L. Subsequent to our study, MTBE was measured in Mission Bay on multiple occasions in September 1999 during sampling to ascertain the influence of a power boat racing event (MEC 1999). Similar to the results of our study, MTBE was present in every surface water sample collected from eight stations throughout Mission Bay. Concentrations in the MEC study were highest (up to 21.1

µg/L) near De Anza Cove, the location of the highest MTBE concentrations in samples collected by SCCWRP.

Studies of California lakes also frequently have detected MTBE at concentrations comparable to those measured in marine waters. A seasonal study of Donner Lake (Reuter *et al.* 1998) detected MTBE in surface waters at concentrations up to 12 µg/L, with the highest concentrations coinciding with periods of peak watercraft use. Concentrations of MTBE in nearshore areas of Lake Tahoe were found to range up to 47 µg/L in areas of known boat use (Allen *et al.* 1998). Recent monitoring in Lake Sonoma has detected MTBE at concentrations of 2-9 µg/L (P. Otis, perssonal communication).

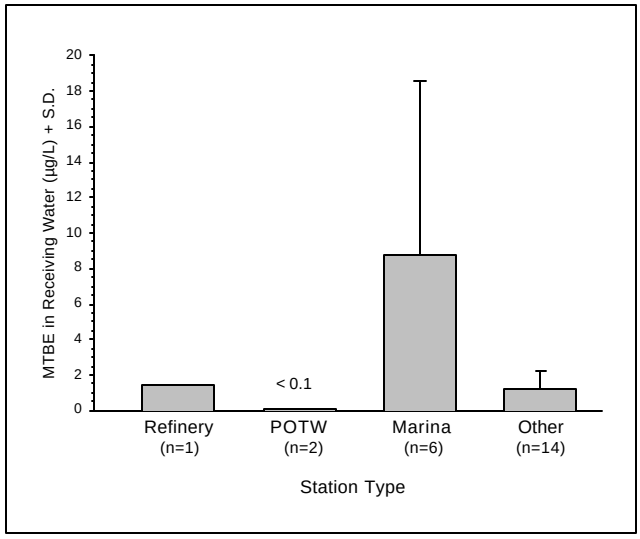
Influence of Receiving Water Uses

The spatial patterns of MTBE detection by receiving water use category did not resemble the patterns described for MTBE inputs from effluents or urban runoff. The highest concentrations of MTBE in receiving waters were found in marinas, locations without large discharges containing MTBE (Figure 8). MTBE contamination was present in all marina areas and was frequently (79%) detected at reference/mixed-use stations within bays ("Other" category), a result that was strongly influenced by the widespread occurrence of MTBE in San Diego Bay. MTBE was consistently detected near the Chevron El Segundo Refinery discharge, but at lower concentrations than in marinas. MTBE was detected near POTW discharges less frequently. If refinery or POTW discharges were the major source of the MTBE detected in receiving water, then MTBE concentrations would be expected to be highest at stations located closest to these discharges.

Because of its widespread use in gasoline, MTBE has sources of discharge to the marine environment other than effluents. The operation of two-stroke boat engines is one likely cause of MTBE contamination in marine waters. Studies of boat engines have demonstrated that two-stroke engines are relatively inefficient, discharging up to 30% of the unburned fuel into the environment (ARB 1999). Two-cycle engines were estimated to contribute over 90% of the MTBE load to Lake Tahoe (Allen *et al.* 1998). The same engines are used to power outboard motor boats and personal watercraft (jet skis) used on marine waters. This study found that samples collected in July tended to have higher concentrations than samples collected in June. Increased recreational boating activity prompted by summer tourism and warmer weather may be responsible for this pattern. Studies at Donner Lake and Lake Tahoe have found that boating activity was the principal source of MTBE contamination (Reuter *et al.* 1998, Allen *et al.* 1998).

Fuel spills are another potential source of the MTBE detected in marina areas during this study. The relative significance of spilled fuel and watercraft exhaust is difficult to determine using chemical analysis, since both types of discharges contain unburned fuel and would be expected to contain similar concentrations of BTEX compounds. Fuel spills or leaks from fuel docks do not appear to be the principal source of MTBE, since surface water samples collected near fuel docks did not contain markedly higher MTBE concentrations relative to marina stations located away from fuel handling facilities.

FIGURE 8. Concentration of MTBE in the different receiving water station categories in southern California. Samples were collected from Santa Monica Bay, Los Angeles Harbor, Mission Bay, and San Diego Bay. Values are the average concentration + standard deviation.



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