

**ASSESSMENT OF MTBE DISCHARGE IMPACTS  
ON CALIFORNIA MARINE WATER QUALITY**

**Final Report**

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**By**

**Steven M. Bay and Jeffrey S. Brown**

**Southern California Coastal Water Research Project  
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## FOREWARD

The gasoline additive Methyl-*tert*-butyl ether (MTBE) is used extensively throughout the state of California to reduce exhaust emissions. Leaks of gasoline from underground storage tanks and watercraft exhaust emissions have resulted in the contamination of groundwater and lakes with MTBE. A number of sources of MTBE discharge to the marine environment have also been identified, such as refinery effluents, municipal wastewater, and watercraft, but the extent and significance of MTBE contamination of marine waters has not been investigated.

Recognizing the need to assess the impacts of MTBE on marine water quality, the State Water Resources Control Board initiated an investigation of the inputs, receiving water concentrations, and toxicity of MTBE in coastal waters. The project was initiated in June, 1999 and included a review of prior monitoring data, measurement of MTBE in effluents, streams and marine water, and also laboratory toxicity tests. This report presents the final results of all elements of the study. The results of the toxicity tests are presented in greater detail in a task report (Brown et al. 2000).

This report was prepared as partial fulfillment of agreement 8-168-250-0 with the State Water Resources Control Board. The total amount of this agreement is \$155,162.

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Sampling of northern California streams and bays was conducted by Moss Landing Marine Laboratories (San Jose State University Foundation). Measurements of MTBE and other volatile organics were conducted by Calscience Environmental Laboratories, Inc. (Garden Grove, CA).

## EXECUTIVE SUMMARY

Methyl-*tert*-butyl ether (MTBE) is a synthetic fuel additive that makes up about 11% of each gallon of gasoline in California. This volatile organic compound is highly soluble in water, binds weakly to soil, and does not readily biodegrade in the environment. These features, together with the widespread use of MTBE, have resulted in the contamination of ground water and surface water in California.

There is also potential for contamination of the coastal marine environment by MTBE. In addition to emissions from motorized watercraft, California's coastal waters receive discharges from multiple sources that may contain MTBE, including urban runoff, effluent from petroleum refineries, and treated municipal wastewater from publicly owned treatment works (POTWs). Limited data are available that describe the inputs, marine receiving water concentrations, and toxicity of MTBE. Consequently, we do not know the extent of MTBE contamination and likelihood for adverse effects on marine life.

This study was initiated by the State Water Resources Control Board (SWRCB) in order to examine the sources, fates, and effects of MTBE in the marine environment. The research was conducted by the Southern California Coastal Water Research Project (SCCWRP) and had three objectives: 1) to determine the relative importance of MTBE inputs from effluent and stream discharges; 2) to measure the occurrence and concentration of MTBE in coastal receiving waters; and 3) to determine whether MTBE contamination levels are toxic to marine life.

### Inputs

The input of MTBE from point source discharges was assessed using data obtained from a special study of MTBE concentrations in National Pollutant Discharge Elimination System (NPDES) discharges conducted by SWRCB in May-August, 1999. Water samples from 43 streams and rivers were analyzed during June-August, 1999 to determine the concentration of MTBE in dry weather discharges from urban areas.

MTBE was detected in the effluents of 49% of the sewage treatment plants (POTWs) and 100% of the refineries discharging to coastal waters. Combined, these point source discharges release approximately 228 kg/day of MTBE into the marine environment. Dry weather stream discharges constituted a minor input of MTBE. Only 12% of the streams sampled contained detectable (0.5 µg/L) concentrations of MTBE. Mass emission estimates indicated that dry weather stream flow accounts for less than 0.5% of the MTBE discharged to coastal waters in southern California. Stormwater inputs were not directly measured in this study, but preliminary estimates indicate that this source constitutes a relatively small input (approximately 5% of the southern California discharge from point sources).

Santa Monica Bay receives most (92%) of the input of MTBE from point sources, with the majority of this resulting 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.

## **Receiving Water**

Water samples from six waterbodies were analyzed to investigate the occurrence and concentration of MTBE in receiving water. Surface and bottom water samples were collected during June-July from 41 stations located in Humboldt Bay, San Francisco Bay, Santa Monica Bay, Los Angeles Harbor, Mission Bay, or San Diego Bay.

MTBE was detected in at least one sample from each study area. At most stations, surface water samples tended to have higher MTBE concentrations than bottom samples. The greatest frequency of detection (91%) and highest average MTBE concentration (5.2 µg/L) was measured at stations in marinas and areas used intensively for recreational boating. MTBE was only occasionally detected (25% of stations) in water samples taken from refinery or POTW discharge areas.

Surface water contamination by MTBE was most widespread in San Diego Bay and Mission Bay, areas with no refinery or POTW inputs. Mission Bay water samples contained the highest MTBE concentrations (up to 34 µg/L). The spatial pattern and concentration of MTBE in marine receiving waters was similar to the contamination that has been documented to result from watercraft use on California lakes.

## **Toxic Effects**

Laboratory experiments were conducted to measure the toxic response of four California species to MTBE exposures of seven days or less. The test organisms were a diverse group that included giant kelp (*Macrocystis pyrifera*), a mysid crustacean (*Holmesimysis costata*), an amphipod crustacean (*Grandidierella japonica*), and the purple sea urchin (*Strongylocentrotus purpuratus*).

The two species of crustaceans (an amphipod and a mysid) were most sensitive, showing 50% mortality at a MTBE concentration of approximately 150 mg/L. The threshold for toxic effects in the most sensitive species was 37 mg/L. Spores of the giant kelp were the least sensitive to MTBE.

None of the MTBE concentrations measured in receiving water were high enough to cause toxic effects. The highest concentration of MTBE measured in Mission Bay was less than 0.01% of the threshold effects level for the amphipod, the most sensitive California species tested. Even exposure to undiluted refinery effluent, containing the highest MTBE concentration measured during the study, would produce a dose that is only 4% of the acute effects value.

Receiving water MTBE concentrations were also far below chronic toxicity levels. Chronic toxicity tests were not conducted in this study, but others have calculated a preliminary MTBE water quality criterion of 18 mg/L for chronic effects from prior data. The receiving water MTBE concentration at the most contaminated site (Mission Bay) was only 0.2% of the preliminary criterion, a level calculated to be protective of chronic toxicity.

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## I. INTRODUCTION

Methyl-*tert*-butyl ether (MTBE) is a synthetic fuel additive that makes up about 11% of each gallon of gasoline in California. MTBE increases the oxygen content of gasoline, thereby making the fuel cleaner burning, and reducing exhaust emissions of carbon monoxide and benzene (a known human carcinogen). California started including MTBE in gasoline as part of an emission reductions policy in 1987.

MTBE has several chemical characteristics that result in a high potential to contaminate surface and ground water 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 features, together with the widespread use of MTBE, have resulted in the contamination of groundwater and surface water in California.

At least two public water supply systems have closed portions of their drinking water wells due to MTBE contamination since 1996, when mandatory monitoring went into effect. The South Tahoe Public Utilities Districts has closed seven of its 36 groundwater wells, while the City of Santa Monica lost 50 percent of its total water supply and has had to spend \$3.5 million purchasing replacement water. Groundwater contamination by MTBE is mostly due to leaking underground fuel tanks (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 from motorized boating activities (Reuter *et al.* 1998).

The coastal marine environment is also at risk of contamination by MTBE. In addition to emissions from motorized watercraft, California's coastal waters receive discharges from multiple sources that may 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 and relatively little is known about the concentrations and mass of MTBE discharged to California's coastal waters from these sources. While measurements of MTBE concentration have been made for some discharges, the data are limited and have not been used to assess the potential for contamination and toxic effects on marine life. Consequently, we do not know the extent of MTBE contamination and whether there are likely to be adverse effects on marine water quality in California.

To address concerns about impacts to marine life, the State Water Resources Control Board entered into an agreement with the Southern California Coastal Water Research Project (SCCWRP) to investigate MTBE impacts on marine water quality. An initial survey of existing monitoring and toxicity information indicated that insufficient data were available to describe the sources, fate, and effects of MTBE (summarized in Appendix). Field and laboratory studies were subsequently conducted to accomplish three objectives: 1) to determine the relative importance of MTBE inputs from effluent and stream discharges; 2) to measure the concentration and extent of MTBE contamination in coastal receiving waters; and 3) to determine whether MTBE

contamination levels are toxic to marine life. The results of these studies are presented in the following chapters of this report.

## II. INPUTS

### A. Introduction

Documenting the sources and relative mass emission of MTBE to the marine environment assists in determining the potential for adverse effects by identifying locations where exposure is likely to be greatest. The objective of this task was to assess the contribution of MTBE to the coastal environment resulting from both point source discharges (refineries and POTWs) and nonpoint sources (urban streams).

### B. Methods

#### Point source discharge data analysis

The input of MTBE from POTW and refinery discharges was estimated using data from a statewide special study of MTBE concentrations in National Pollutant Discharge Elimination System (NPDES) effluents conducted during May-September 1999. All NPDES facilities throughout the state discharging over 1 million gallons per day were instructed by the SWRCB to analyze four effluent samples for MTBE during the study period. The raw data from the survey were compiled and summarized for each region by the SWRCB (Bill Ray, pers. comm.) and provided to SCCWRP. These data were then sorted to retain only those values for facilities discharging into marine waters and were combined with 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 three geographic regions: Humboldt Bay, San Francisco Bay, and Southern California. The sampling sites were selected based on 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 6-27 streams discharging into each study site. At Humboldt Bay, six stations were selected for sampling based on recommendations of the North Coast Regional Water Quality Control Board (Figure 2.1). All of the Humboldt Bay stream samples were obtained from small streams that were less than 5 m wide and had earthen banks. The Jacoby Creek and Gannon Slough sites represent the greatest degree of urban influence from Arcata. Two stations on Martin Slough were sampled, these stations were located upstream and downstream of a golf course.

A total of 10 streams were sampled from the San Francisco Bay area (Figure 2.2). The stations that were selected represented a broad geographic distribution and had been previously used for flow measurements. Most of the streams drained watersheds dominated by residential and light industrial land uses, except for the most southerly

stations (Coyote Creek and Guadalupe River) which also reflected heavier industrial land uses. Calabasas Creek was a concrete channel; all of the other streams were unlined channels surrounded by riparian habitat.

In southern California, three streams discharging into Santa Monica Bay were sampled (Figure 2.3). Two of these, Ballona Creek and Santa Monica Canyon, were concrete channels draining areas dominated by residential land use, while the Malibu Creek watershed was mostly undeveloped. One stream (Switzer Creek) in San Diego Bay was sampled. This concrete channel drains residential and industrial areas and was sampled from a transportation yard. Other streams draining the San Diego Bay watershed could not be sampled because there was no flow present.

An additional 23 southern California streams were sampled in order to provide a more complete assessment of freshwater inputs of MTBE to coastal waters (Figure 2.3). These sites included the regions largest urban rivers (Los Angeles, San Gabriel, and Santa Ana Rivers), smaller concrete channels draining high-density residential areas (e.g., Talbert Channel, Coyote Creek), a tidally influenced channel adjacent to Los Angeles refineries (Dominguez Channel), and streams draining mostly undeveloped areas (e.g., Ventura River, Santa Margarita River).

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 contamination. The second tier of sampling consisted of repeated sampling at those sites found to contain MTBE in the first tier. Eight of the sites were revisited 2-5 times in July-August.

All sampling was done 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 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 was obtained from U.S. Army Corps of Engineers gauging stations or calculated using onsite measurements of surface velocity and stream cross sectional area.

### **Chemical Analysis**

The stream samples were analyzed for MTBE and BTEX (benzene, toluene, ethylbenzene, xylene) following USEPA SW-846 Method 8260B. This method uses purge-and-trap with quantitation by gas chromatograph/mass spectrometer.

Quality assurance procedures employed during sampling included the analysis of field (sampling equipment) blanks, and travel blanks. Laboratory quality control procedures included 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 five days after collection (maximum eight days). All blanks were below detection limit, and high recovery was obtained for the matrix spikes (102%) and low level standards (104%) (Table 2.1). Matrix spike duplicates and low level standards had low variability, indicating that the instrumental analysis procedure had high precision.

## **C. Results and Discussion**

### **Point sources**

Data were obtained for 68 POTWs, 6 petroleum refineries, and 10 other NPDES facilities discharging to California's marine environment. Half of these agencies detected MTBE in their discharge at least once during the survey period (Table 2.2). MTBE was most frequently detected in facilities located in the Los Angeles, Santa Ana, and San Francisco Bay Water Quality Control Board Regions (Figure 2.4). Between 60% and 100% of the facilities in these three regions detected MTBE in their effluent.

Statewide, large point sources discharged approximately 228 kg/day of MTBE to coastal waters (Table 2.2). Compared to the total mass of MTBE consumed on a daily basis in California, this value is relatively small (about 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.

Most of the mass of MTBE was discharged to two areas, Santa Monica Bay and San Francisco Bay. Over 98% of the MTBE entering coastal waters from refineries and POTWs is discharged into these two waterbodies, with Santa Monica Bay accounting for 92% (210 kg) of the total. MTBE was not detected in large point source discharges to Humboldt Bay or San Diego Bay.

Discharges from petroleum refineries contained the highest concentrations of MTBE. Effluent from the Chevron El Segundo refinery, which discharges into Santa Monica Bay, contained the highest mean concentration of MTBE of any discharge in this study (1877.5 µg/L). The daily mass emission from this facility was estimated to be 45.79 kg/day. The mass emission for all coastal refineries was approximately 52 kg/day.

The relatively high concentration of MTBE in refinery effluent is a result of its production in California as a gasoline additive. Much of the MTBE discharged from these facilities is probably a by product 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



Table 2.1. Quality control data for MTBE analysis in stream and receiving water samples.

QC batch number	Date	Method blank (µg/L)	MTBE spike recovery (%)	Matrix spike duplicate Relative percent difference	Field blank (µg/L)	Low level standard recovery (%)
1	6/10/99	< 0.5	97	6	< 0.5	101
2	6/10/99	< 0.5	91	6	<0.5	97
3	6/15/99	< 0.5	99	8	< 0.5	109
4	6/15/99	< 0.5	104	5	< 0.5	108
5	6/18/99	< 0.5	101	1	< 0.5	103
6	6/19/99	< 0.5	102	2	< 0.5	97
7	6/22/99	< 0.5	97	7	< 0.5	113
8	6/24/99	< 0.5	104	1	< 0.5	110
9	6/24/99	< 0.5	103	1	< 0.5	126
10	6/25/99	< 0.5	100	3	< 0.5	113
11	7/14/99	< 0.5	104	2	< 0.5	109
12	7/16/99	< 0.5	110	6	< 0.5	97
13	7/17/99	< 0.5	110	6	< 0.5	95
14	7/19/99	< 0.5	106	1	< 0.5	112
15	7/20/99	< 0.5	100	6	< 0.5	107
16	7/22/99	< 0.5	105	5	< 0.5	95
17	7/22/99	< 0.5	96	8	< 0.5	110
18	7/23/99	< 0.5	100	7	< 0.5	97
19	8/3/99	< 0.5	114	1	< 0.5	79
Mean		< 0.5	101.8	4.2	< 0.5	104.1

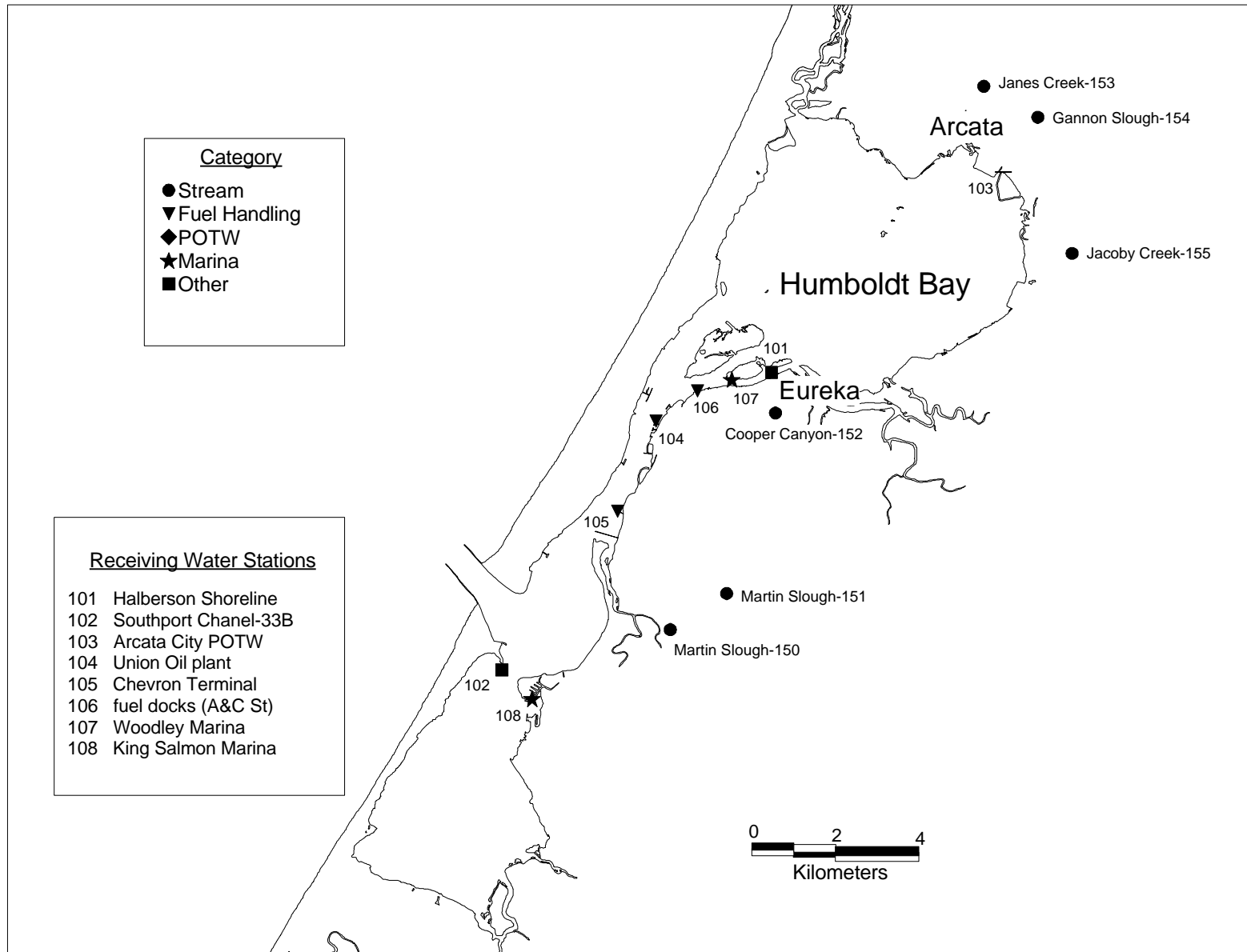


Figure 2.1 Humboldt Bay sampling locations for dry weather runoff and receiving water collected June to August 1999.

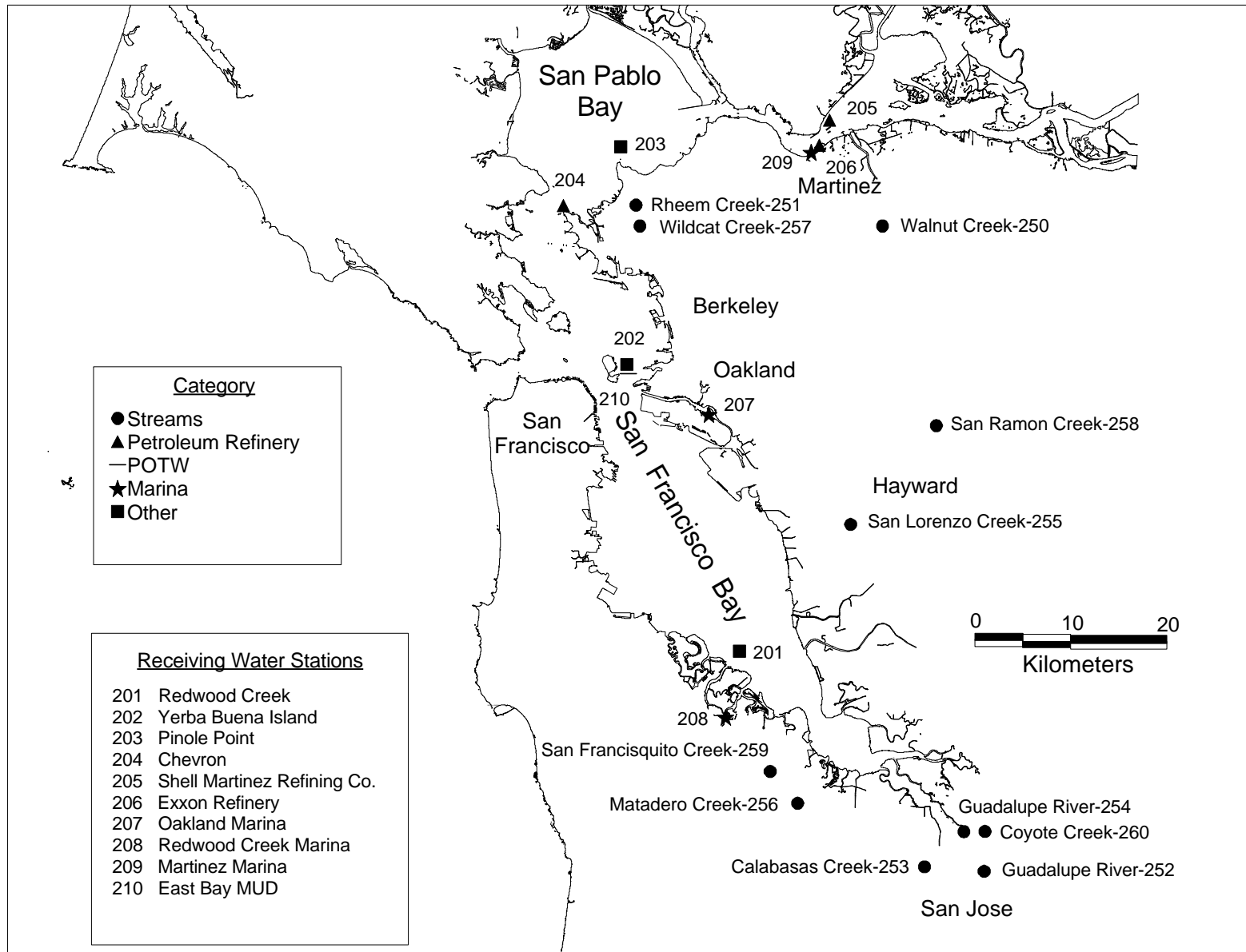


Figure 2.2 Sampling locations in San Francisco Bay for dry weather runoff and receiving water collected June to August 1999.

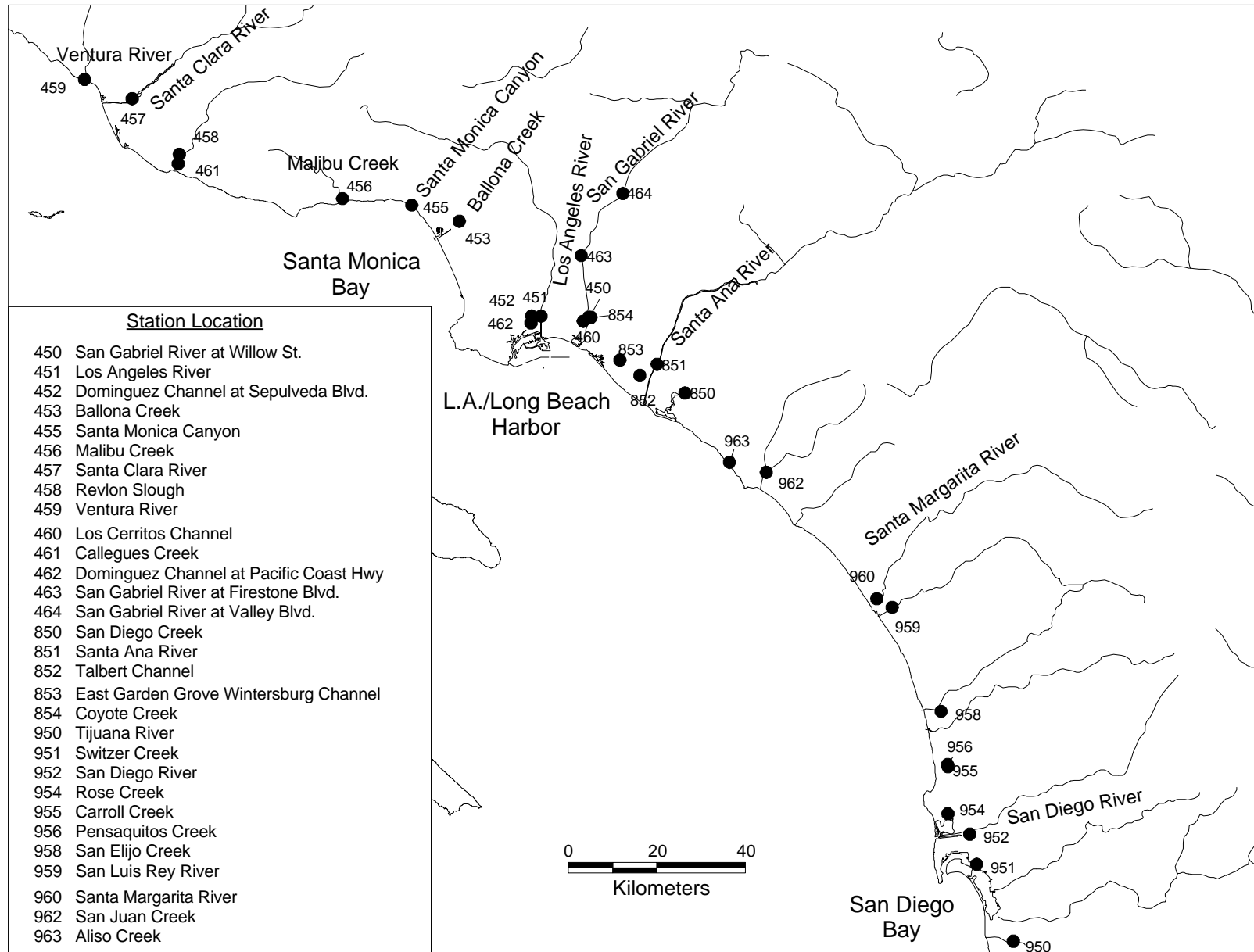


Figure 2.3 Southern California sampling locations for dry weather runoff collected June to August 1999.

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.

Although refinery effluents generally contained the highest concentrations, discharges from POTWs accounted for the greatest proportion (77%) of the daily mass emission of MTBE (Table 2.2). Approximately 50% of POTW discharges to the coastal environment contained detectable levels ( $> 0.5 \mu\text{g/L}$ ) of MTBE. Most notable of these inputs is the 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. In San Francisco Bay, POTW discharges released approximately 7 kg/day of MTBE, comparable to the emission calculated for refineries. The San Francisco Bay POTW discharges have lower average concentrations of MTBE compared to refineries, but the much greater discharge volume for POTWs results in approximately the same daily mass emission.

The major source of MTBE in JWPCP effluent is refinery waste, which is discharged into the municipal sewer system. The JWPCP facility processes refinery wastewater from nine refineries, five of which engage in MTBE generating activities (J. Stull, pers. comm.). The source of MTBE in other POTW effluents was not investigated. Several potential 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 waterbodies by Keller et al. (1998) found that MTBE was detected in 49% of the systems with 12% of the waterbodies reporting over  $14 \mu\text{g/L}$  in at least one sample.

### **Dry weather stream discharge**

A total of 74 surface water samples were collected from 43 stream locations during the field sampling program. MTBE was only detected in streams draining urban areas near San Francisco Bay and in Los Angeles County. Within these regions, MTBE was detected at low levels in about one third of the streams (Table 2.3).

The first tier of sampling detected MTBE in three streams discharging to San Francisco Bay: San Lorenzo Creek, Coyote Creek, and Guadalupe River (Figure 2.5). Follow up (tier two) sampling was conducted at these three sites. MTBE was found in all subsequent samples from Guadalupe River and Coyote Creek and in 1 subsequent sample from San Lorenzo Creek. MTBE concentrations were low in all samples, ranging from  $<0.5$  to  $1.1 \mu\text{g/L}$ . Overall, the 10 streams discharging into San Francisco Bay had a mean MTBE concentration of  $0.19 \mu\text{g/L}$  and discharged approximately 0.2 kg MTBE/day into the bay (Table 2.3). Concentrations below the reporting limit ( $0.5 \mu\text{g/L}$ ) were assigned a value of  $0 \mu\text{g/L}$  for all calculations.

Of the 27 streams and channels that were sampled in southern California, MTBE was detected at four sites, Ballona Creek, Dominguez Channel, San Gabriel River, and

Switzer Creek (Figure 2.6). The tier one sample from the San Gabriel River contained the highest concentration of MTBE of any stream measured in this study: 52.0 µg/L. This river receives discharge from POTWs as well as urban runoff. Two additional San Gabriel River stations upstream of the Willow Ave. sampling site were added during tier two in an attempt to locate the source of the high MTBE. 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 on 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 the five sampling events was 0.66 µg/L, with an estimated daily mass emission of 0.05 kg/day. MTBE was also detected in samples from Switzer Creek and the Dominguez Channel, discharging into San Diego Bay and Los Angeles Harbor, respectively. Both of these sites were tidally-influenced and the water samples contained >80% seawater. Data for these stations were not used in the analysis because the MTBE concentrations for these samples were similar to those in the adjacent bay/harbor and could not be ascribed to freshwater inputs to the channel.

### **Source comparison**

Because most of the dry weather stream discharges in southern California were sampled for MTBE, a mass emission estimate for the region can be made. This source category represents a minor input of MTBE to coastal waters. Nearly all of the estimated 0.89 kg/day discharged from streams during the study period was supplied by the San Gabriel River. This amount is trivial compared to emissions from point sources, representing less than 0.5% of the amount discharged from southern California POTWs and refineries (Figure 2.7).

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. Little data was located that described MTBE concentrations in stormwater runoff in California. Studies conducted in other states have detected MTBE in 40% of stormwater samples from cities with known MTBE use (USGS 1996). MTBE concentrations in stormwater with detectable MTBE ranged from 0.2 to 8.7 µg/L, with a median of 1.5 µg/L. These results are consistent with limited recent California stormwater data obtained, which reported MTBE concentrations ranging up to 6.5 µg/L (Appendix).

Although a confident estimate of the emission of MTBE in stormwater cannot be made for California 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 on the method used by Schiff (1997) to estimate the emission of other constituents in stormwater. A stormwater discharge volume of  $2.9 \times 10^{12}$  L was used, which represents the total annual runoff flow for southern California

gauged rivers in 1994-1995 (approximately 2x average rainfall). Emission of MTBE was calculated using both the 10<sup>th</sup> and 90<sup>th</sup> 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. 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 2.7).

The mass emission estimates presented in this report are based on a limited data set. The dry weather stream and point source survey data cover a relatively short time interval (about 3 months) and thus may not be representative of other time periods. Nonpoint source mass emission estimates were restricted to southern California because the analytical and flow data were most complete for this region. 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. We have attempted to provide a conservative estimate for southern California by using data for a range of concentrations and combining it with flow data from an above average rainfall year. Analysis of many stormwater samples from multiple locations and storms is needed to provide a more precise estimate of MTBE inputs from stormwater.

Table 2.2 Concentration and mass emission of MTBE in NPDES discharges to bays and coastal waters. Sampling was conducted May-August 1999. Concentrations below the reporting limit were assigned a value of 0 µg/L for all calculations. Reporting limits, which varied by facility, are indicated by “<”, where appropriate.

Discharge location/Category	Number of agencies with data	Percentage of agencies with detectable MTBE	MTBE (µg/L)		MTBE (kg/day)
			Mean	Range	Mass
<b>Coastal Areas Statewide</b>					
POTW	68	49	3.8	< 0.5 – 123.3	175.31
Refinery	6	100	395.6	34.3 – 1877.5	52.36
Other	10	30	2.6	< 0.5 – 13.0	0.11
<b>Humboldt Bay</b>					
POTW	2	0	0	< 0.5	0.00
<b>San Francisco Bay</b>					
POTW	37	57	2.2	< 0.5 – 37.0	6.98
Refinery	4	100	102.1	34.3 – 281.3	5.83
Other	2	50	0.2	< 0.5, 0.4	< 0.01
<b>Santa Monica Bay</b>					
POTW	2	100	63.6	3.9, 123.3	163.99
Refinery	1	100	1877.5	–	45.79
<b>San Diego Bay</b>					
Other	2	0	0	< 5, < 20	0.00



Table 2.3. MTBE concentrations measured in dry weather stream inputs to coastal waters of 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. Concentration means 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)		Mass
			Mean	Range	(kg/day)
Humboldt Bay	6	0	0	< 0.5	0.0
San Francisco Bay	10	30	0.2	< 0.5 – 0.9	0.24
Santa Monica Bay	3	33	0.2	< 0.5 – 0.7	0.05
San Diego Bay	0 <sup>a</sup>	-	-	-	-
Southern California <sup>c</sup>	25 <sup>a, b</sup>	8	0.5	< 0.5 - 11.5	0.89

<sup>a</sup> Does not reflect samples from Switzer Creek, which were > 80% seawater.

<sup>b</sup> Does not reflect samples from Dominguez Channel, which were > 80% seawater.

<sup>c</sup> Includes Santa Monica Bay data.

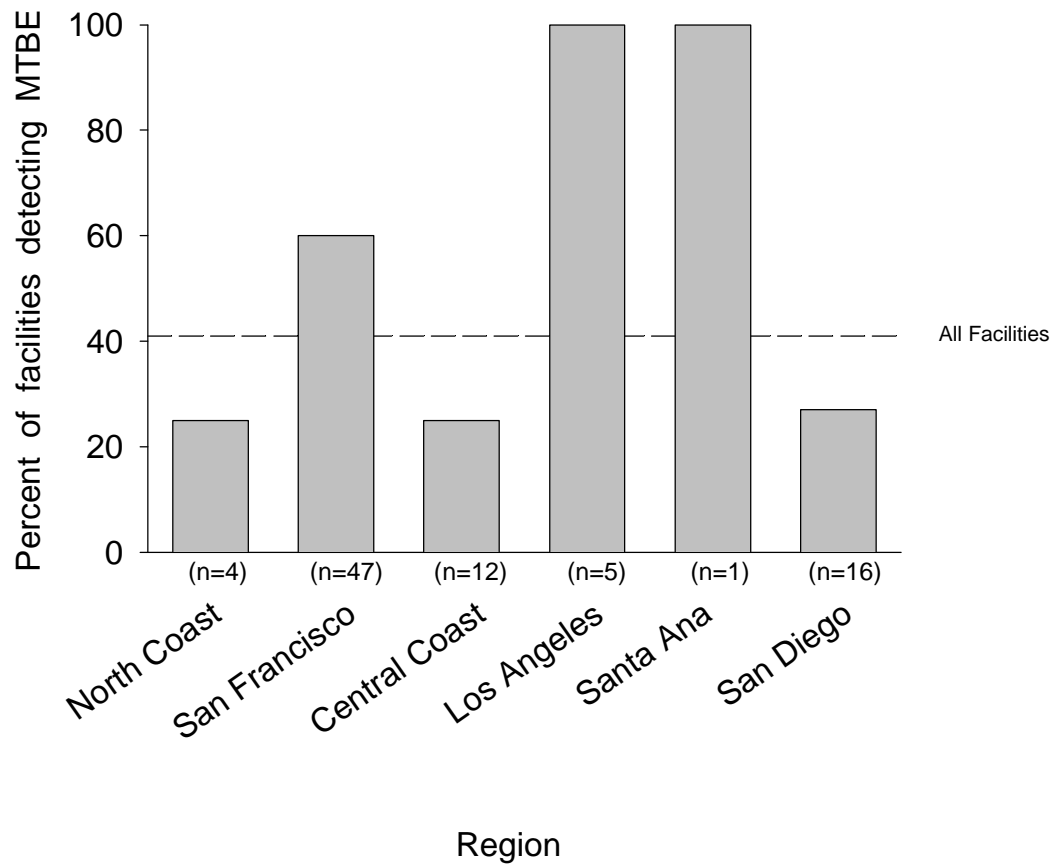


Figure 2.4 Occurrence of MTBE in NPDES discharges to coastal waters. Data are organized by Regional Water Quality Control Boards. Dashed line indicates statewide average of NPDES facilities that have detected MTBE in their effluent, and includes inland dischargers.

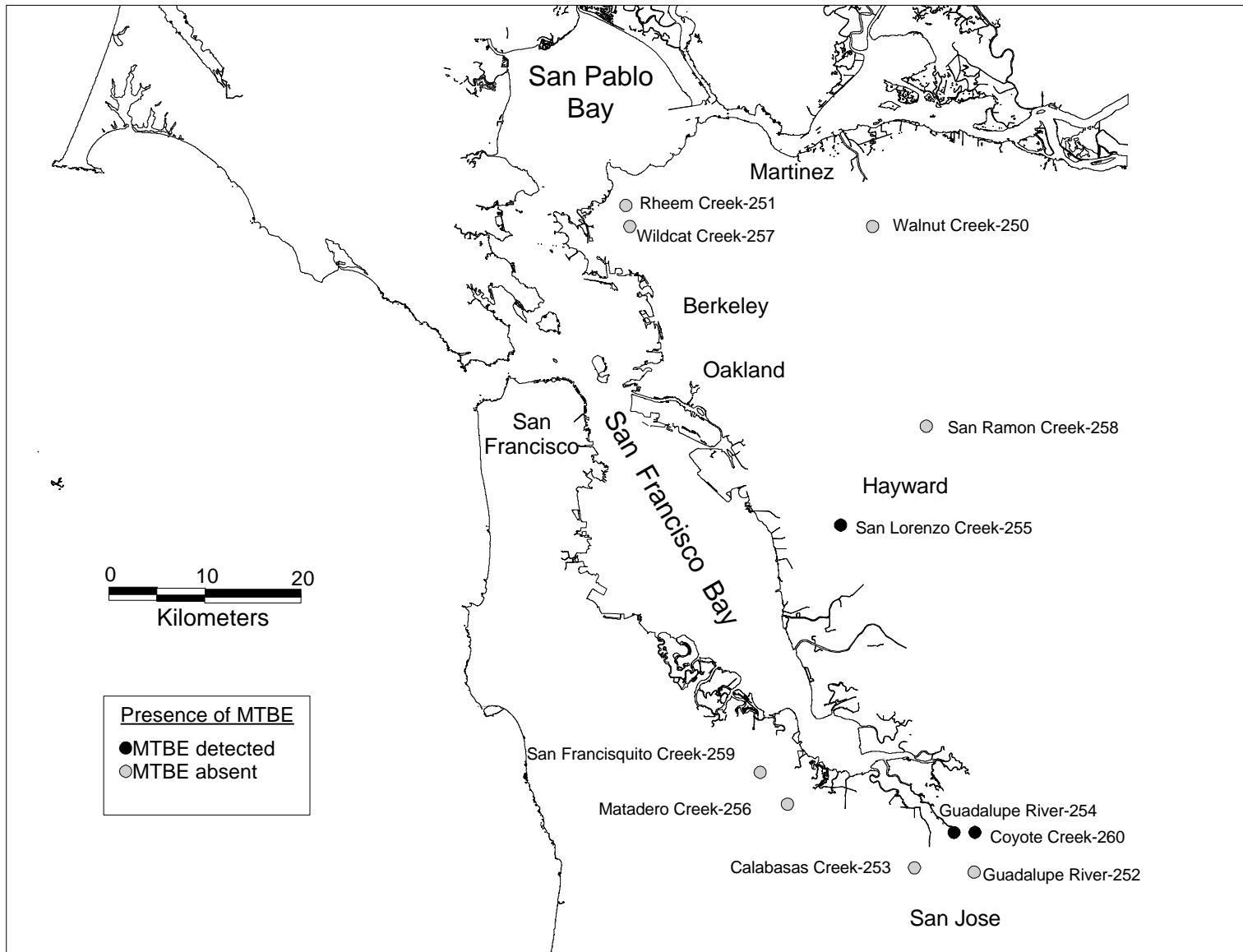


Figure 2.5 Presence of detected MTBE in streams discharging into San Francisco Bay.

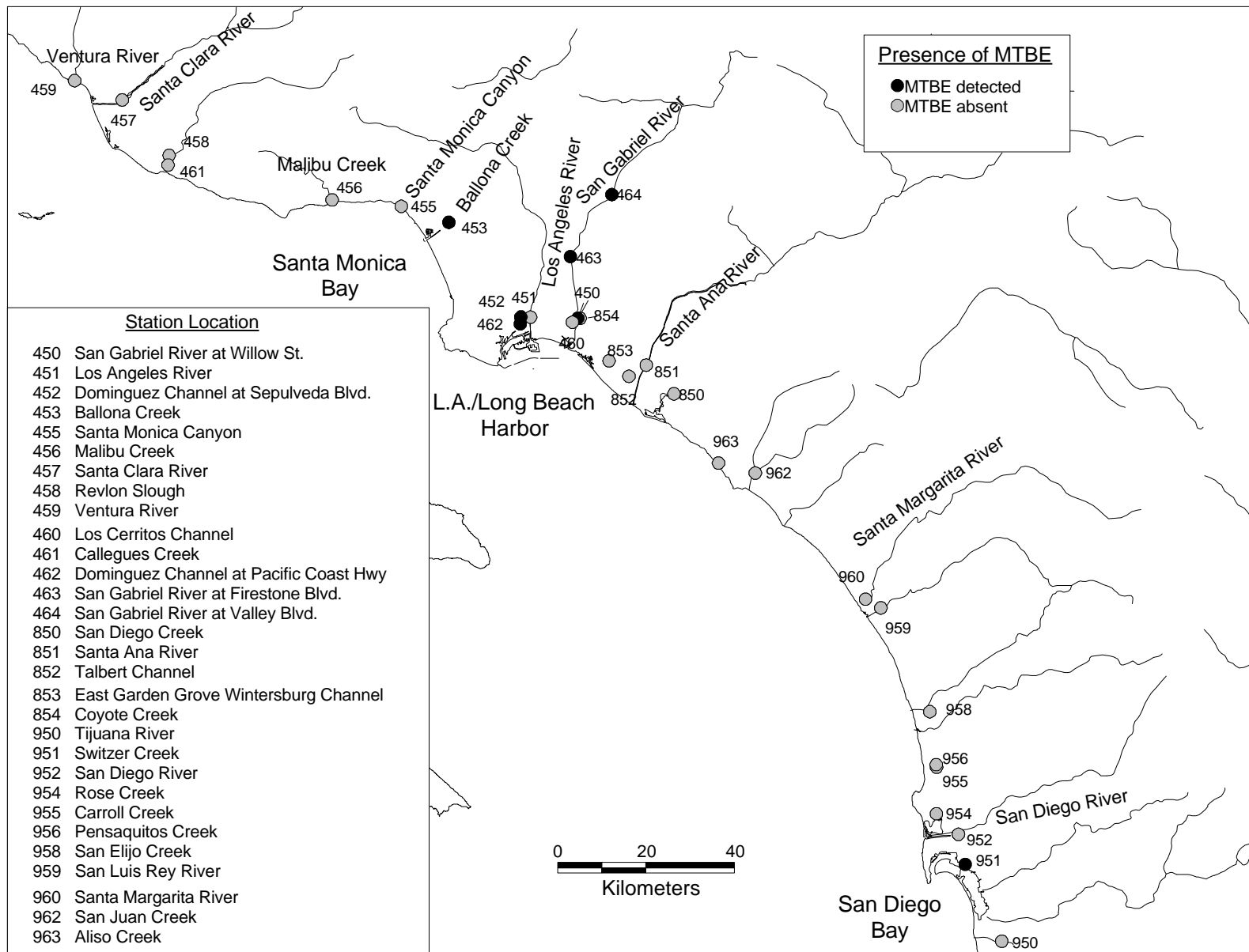


Figure 2.6 Presence of detectable MTBE in streams discharging into the southern California Bight.

## Southern California

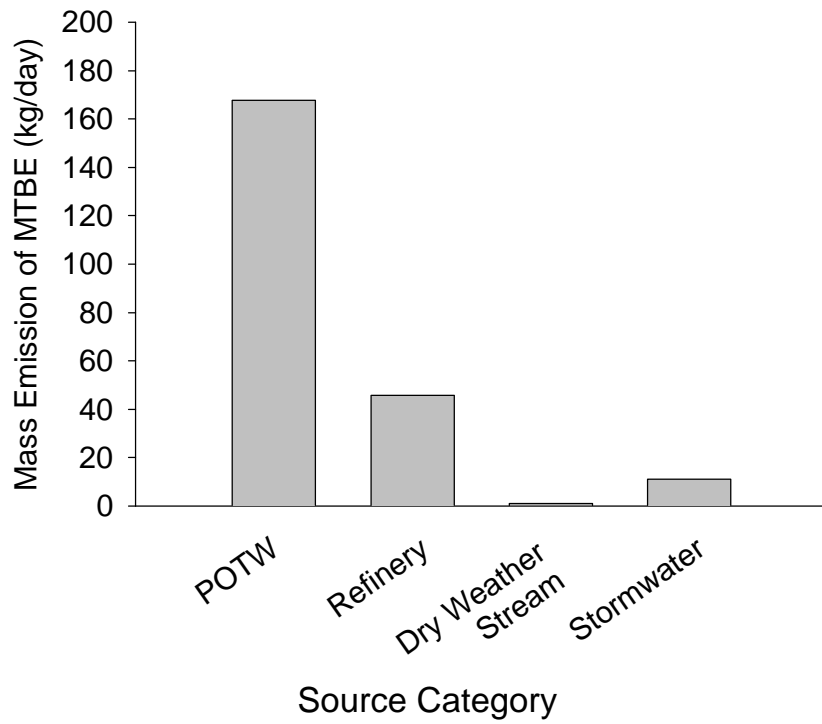


Figure 2.7. Comparison of total MTBE mass emissions from various inputs to the southern California marine environment.

### III. RECEIVING WATER

#### A. Introduction

The receiving water study represents the first coordinated effort to examine MTBE contamination in California's bays. The objective of this study was to measure the concentration and extent of MTBE contamination in coastal receiving waters. Receiving water concentrations reflect the fate of MTBE and help establish the significance of different input types. In addition, these data are valuable for estimating the toxic effects of MTBE for they describe the concentrations that marine life are exposed to.

#### B. Methods

##### Field sampling

Water column samples from Humboldt Bay, San Francisco Bay, 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 MTBE-containing discharges (refinery or POTW effluent) or uses with the potential to release MTBE (fuel handling or marina/recreational boating). Additional stations represented ambient conditions throughout each bay. The ambient stations, termed "other" in this study, represented either stations reflecting multiple uses or reference stations located distant from MTBE contamination sources. These stations often included locations used in previous monitoring programs. Station locations are provided in the Appendix.

A total of eight receiving water stations were sampled in Humboldt Bay (Figure 2.1). The stations represented three potential MTBE source categories: the Arcata POTW discharge (station 103); three sites associated with fuel handling (oil storage terminals stations 104, 105) and a fuel dock (106); and two sites within marinas (107 and 108). The remaining two sites represented ambient conditions.

Three receiving water stations in San Francisco Bay were located near the effluent discharges for the Shell Martinez (205), Exxon (206), and Chevron (204) refineries (Figure 2.2). One station was located near the East Bay MUD POTW discharge (210) and three stations were located within marinas (207-209). Three ambient stations were sampled. These stations were located at established regional monitoring stations in San Pablo Bay (203), near Yerba Buena Island in central San Francisco Bay (202), and near Redwood Creek (201) in the south bay.

Receiving water stations in Santa Monica Bay (Figure 3.1) were located at the discharges for two POTWs, the City of Los Angeles' Hyperion Treatment Plant (409) and the Los Angeles County Sanitation Districts' JWPCP treatment plant (402). Stations were also located at the Chevron El Segundo refinery discharge (406) and within two marinas,

Marina del Rey (408) and King Harbor (404). Ambient stations were located at similar depths to the POTW and refinery sites, as well as near the mouth of Ballona Creek (407). One station was located in the main channel of Los Angeles Harbor (401).

Sampling within San Diego Bay represented just one potential source category, marinas (902, 903) (Figure 3.2). There are no POTW discharges within the bay and no industrial discharges were identified as likely to contain MTBE. Additional stations within San Diego Bay included areas adjacent to boat anchorages (904, 907), areas expected to have relatively high commercial/recreational boat traffic [Chollas Creek (906), Sweetwater Channel (908), and outside the Chula Vista Harbor (910)], as well as three stations characteristic of ambient conditions (901, 905, 909). The sampling program in San Diego also included two stations within Mission Bay, located 5 km to the north (Figure 3.2). Samples from Mission Bay were obtained adjacent to boat docks, as were some samples from marinas in Humboldt Bay and San Francisco Bay.

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 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 preservative, and kept on ice. Temperature and conductivity/salinity were measured on the remaining sample.

Detection of thermoclines and effluent plumes was accomplished using a conductivity-temperature-depth (CTD) profiler. The CTD 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 sampling in Humboldt Bay and San Francisco Bay and also during the June sampling 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. Water quality sampling in Santa Monica Bay and San Diego Bay during July was conducted using a SBE 19 CTD. All CTDs were factory or laboratory calibrated just prior to use.

### **Chemical analysis**

Receiving water samples were analyzed for MTBE and BTEX compounds according to USEPA SE-846 method 8260B. The same field and lab QA/QC procedures used for stream sampling were employed during receiving water sampling. Both types of field

samples were analyzed concurrently, and the QA/QC results summarized in Table 2.1 apply to both stream and receiving water samples. All blanks were below detection limit, and high recovery was obtained for the matrix spikes and low level standards. Matrix spike duplicates and low level standards had low variability, indicating that the instrumental analysis procedures had high precision.

## **C. Results and Discussion**

### **Occurrence of MTBE in bays and harbors**

A total of 41 receiving water stations were sampled in 6 waterbodies. MTBE was detected at 56% of all stations, and in each of the waterbodies. Other volatile compounds present in gasoline (benzene, toluene, ethylbenzene, and xylenes) were only rarely detected, however. Although MTBE was detected in at least one sample from each of the study areas, the prevalence and concentration of MTBE varied for each location.

#### *Humboldt Bay*

MTBE was detected in only one out of 30 receiving water samples analyzed (Figure 3.3). Surface water collected in June from the King Salmon Marina contained 0.7 µg/L (just above the reporting limit of 0.5 µg/L). This sample also contained low concentrations of two other volatile organic compounds, toluene (1.6 µg/L) and xylenes (1.2 µg/L). These compounds are common components of gasoline and suggest that a recent fuel spill may have occurred at the site. Water quality data from King Salmon Marina (Figure 3.4), as well as at the other stations in Humboldt Bay, showed little change between the surface and bottom, indicating that the water column was well mixed.

Samples were also taken from a POTW discharge, near two facilities used for fuel storage, and near a fuel dock that was not located within a marina. MTBE was not detected at these locations or at any of the other stations within Humboldt Bay (Table 3.1).

#### *San Francisco Bay*

MTBE was detected with 75-100% frequency at 3 locations within San Francisco Bay (Figure 3.5). All three of these stations were located within marinas (Redwood Creek, Oakland, and Martinez). Average MTBE concentrations were similar in each marina, ranging from 0.9 to 1.6 µg/L. Sampling locations in the Oakland and Martinez marinas were located adjacent to fuel docks; but no fuel dock was present at the Redwood Creek Marina, the station containing the highest MTBE concentrations. No other volatile organics were detected at these sites.

MTBE was present in both surface and bottom samples at each marina, with the surface sample always containing the greater concentration (Figure 3.6). Temperature and



salinity did not vary with depth at the marina sites, indicating that there was no stratification of the water column.

Samples were also collected near refinery and POTW effluent discharges known to contain MTBE, but no MTBE or other volatile organics were detected (Table 3.1).

### *Santa Monica Bay*

MTBE was detected at 6 stations in Santa Monica Bay (Figure 3.7). The greatest frequency of detection was again 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  $\mu\text{g/L}$ , respectively. Similar to the patterns for marinas in San Francisco Bay, the two Santa Monica Bay marinas had higher concentrations of MTBE in surface water samples than samples collected near the bottom.

MTBE was also detected near the Chevron El Segundo refinery discharge during both the June and July sampling events. A thermocline was present in the offshore waters during both sampling cruises (Figure 3.8) 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  $\mu\text{g/L}$ ) 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 3.9). 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  $\mu\text{g/L}$ . A similar concentration of MTBE (0.5  $\mu\text{g/L}$ ) was measured in a single sample collected from a reference location (station 410) at a depth of 10 m (above the thermocline).

### *Los Angeles Harbor*

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

### *Mission Bay*

MTBE was also consistently detected in Mission Bay (Figure 3.10). 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 2 times higher in the July collection, when greater personal watercraft (i.e., jet ski) use in Mission Bay was observed. 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 3.10). Little difference in average concentration was evident between the marina and other sites (Table 3.1). The water column was well-mixed within the bay, as indicated by similar temperature and salinity values between surface and bottom water samples. MTBE concentrations were approximately 2 times greater at the surface at one half of the stations, the remaining stations showed little difference in concentration with depth.

A marked temporal pattern was also evident in the concentration data. Surface water MTBE concentrations in samples collected in July were approximately 2 times greater than the June samples.

### **Spatial patterns related to use category**

The results for each waterbody also show a similar pattern when summarized by station category. MTBE was present in most marina areas (91% of the stations), but was seldom detected near POTW and refinery effluent discharges (25%), and was never detected near fuel handling facilities (Figure 3.11). MTBE was frequently (58%) detected at stations representing ambient conditions within bays (“other” category), a result that was strongly influenced by the widespread occurrence of MTBE in San Diego Bay.

There was also a difference among the categories for the concentrations of MTBE found. Marina/recreational boating areas had the highest concentrations of MTBE in each study site (Figure 3.12). Among all marina stations, the average MTBE concentration (5.2 µg/L) was approximately 5-10 times greater than the concentration measured in other categories (refinery and other).

The patterns of MTBE detection by receiving water use category did not resemble the patterns described for MTBE inputs found in Section 2. The greatest frequency of detection and the highest concentrations of MTBE in receiving waters were found in areas with no large discharges containing MTBE (e.g., Marina del Rey, Mission Bay, San Diego Bay). In contrast, receiving water stations near large NPDES discharges had the lowest prevalence of MTBE, yet 49% of the POTWs and 100% of the refineries had detectable amounts of MTBE in their effluent. 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.

Few measurements of MTBE in the marine environment have been made previously. The limited prior data that are available are consistent with our results, however. Multiple stations within Mission Bay have been previously monitored for MTBE (EMCON 1999). MTBE was frequently detected in samples collected during the past three years. Samples analyzed in 1998 produced similar results to 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 in order to ascertain the influence of a power boat racing event (MEC 1999). Similar to our study, MTBE was present in every surface water sample collected from 8 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.

The operation of two-stroke boat engines is a likely source of MTBE to marine waters. Studies of boat engines have demonstrated that two stroke engines are relatively inefficient, discharging up to 30% of the fuel unburned 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.

Studies of California lakes have also frequently detected MTBE at concentrations comparable to those measured in marine waters. A seasonal study of Donner Lake detected MTBE in surface waters at concentrations up to 12 µg/L, with the highest concentrations coinciding with periods of peak watercraft use (Reuter et al. 1998). 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, pers. comm.).

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 discharge 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.

#### *Depth and temporal patterns*

MTBE concentration varied with depth at some stations. When a difference was present, the highest concentrations of MTBE were usually present near the surface. This finding indicates that surface water sampling at sites of interest is sufficient to characterize the maximum exposure likely to be experienced by marine organisms. An exception to this pattern was observed, however, near NPDES discharges. MTBE was only detected in a

few samples collected below the thermocline, which was consistent with the expected location of the effluent plume.

A second pattern was a tendency for samples collected in July 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).

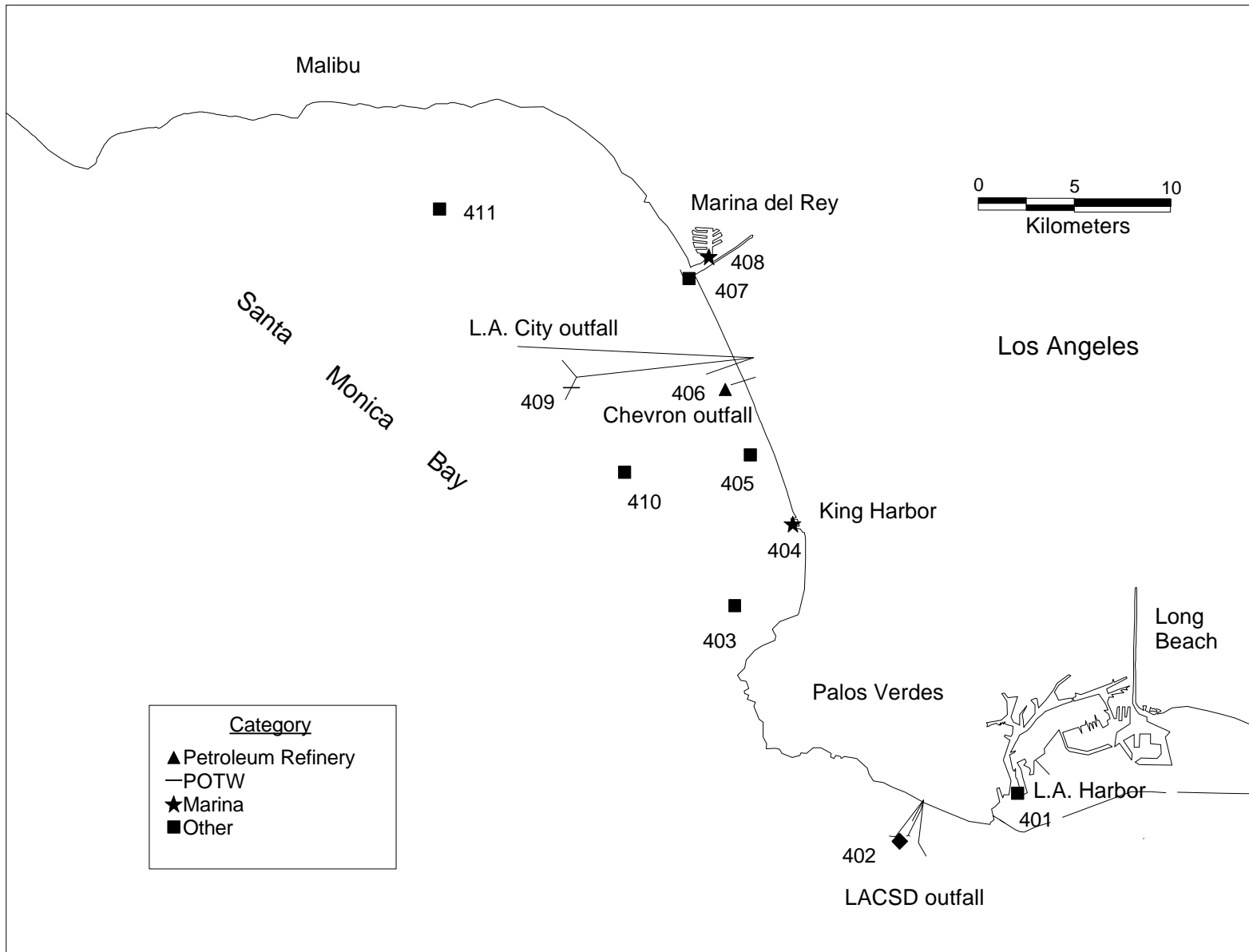


Figure 3.1 Santa Monica Bay sampling locations for receiving water collected June and July 1999.

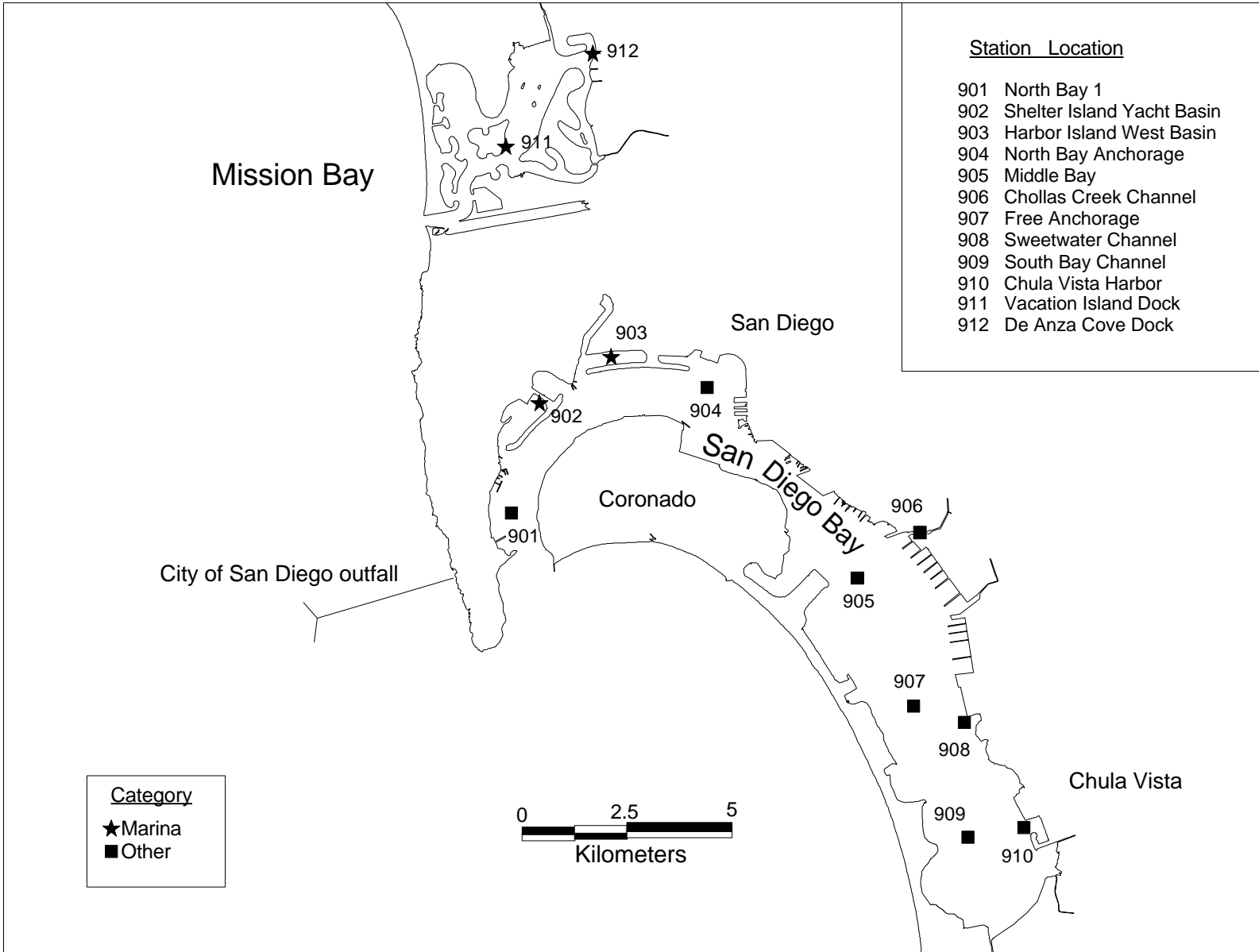


Figure 3.2 San Diego Bay sampling locations for receiving water collected June and July 1999.

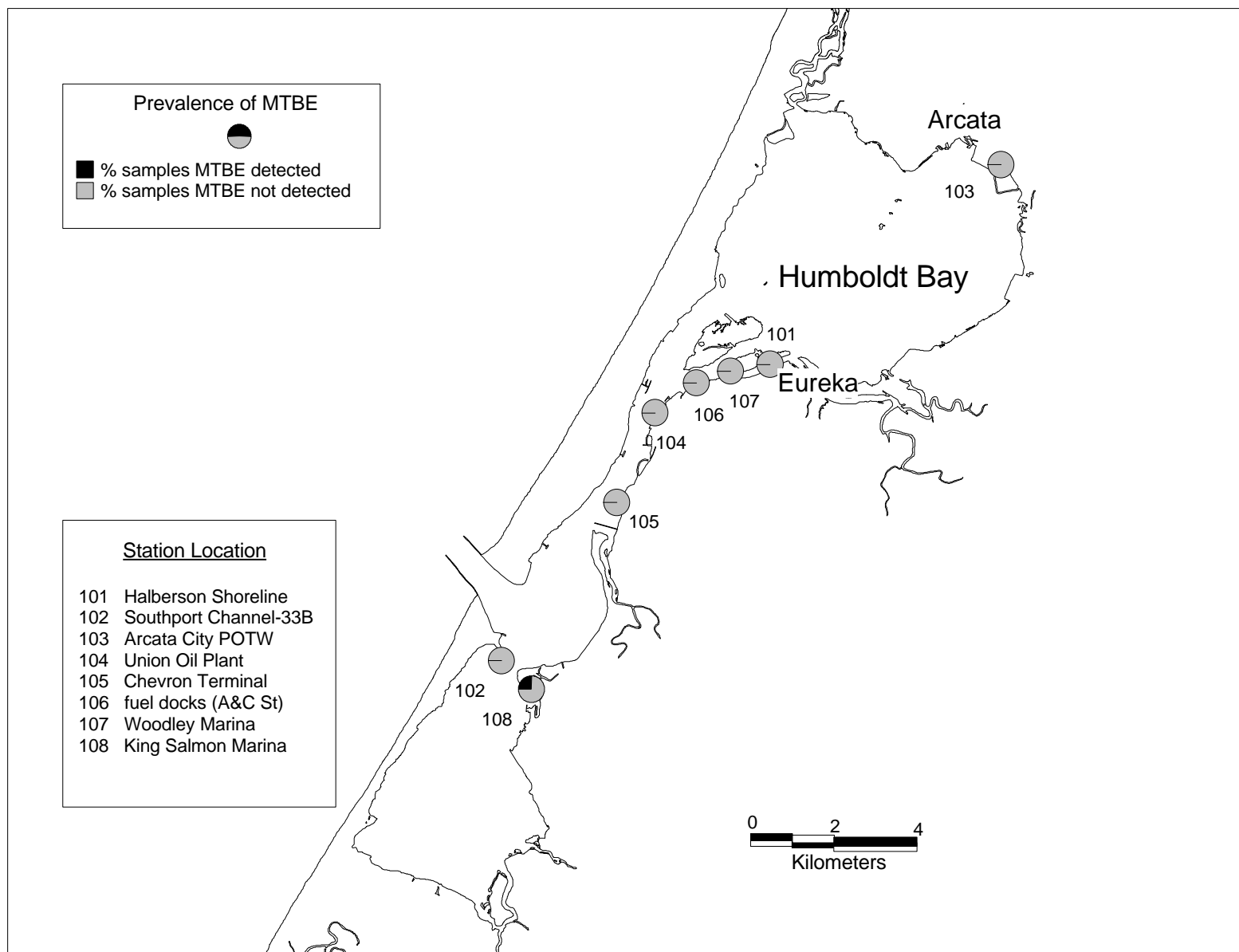


Figure 3.3 Occurrence of MTBE at Humboldt Bay receiving water stations.

### Humboldt Bay King Salmon Marina

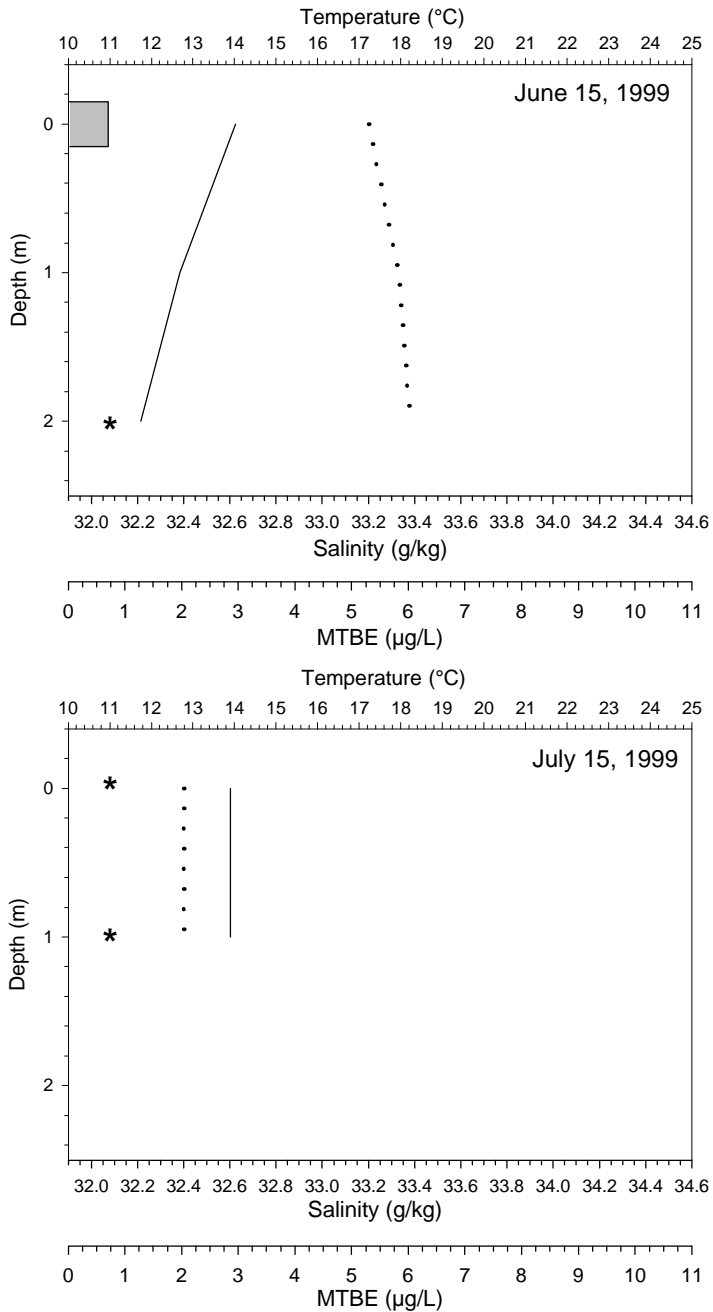
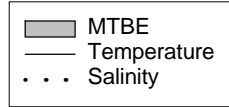


Figure 3.4 Distribution of MTBE with depth at King Salmon Marina (station 108), Humboldt Bay. Asterisks (\*) indicate sampled depths with MTBE below the detection limit (0.5 µg/L).



Table 3.1 Average MTBE concentrations in different receiving water use categories of California bays and harbors. Values are mean concentrations  $\pm$  standard deviations. Concentrations below the reporting limit (0.5  $\mu\text{g/L}$ ) were assigned a value of 0  $\mu\text{g/L}$ . Dash indicates samples not analyzed for the category. Stations in the “Other” category are not influenced by any single dominant potential source of MTBE.

Location	MTBE ( $\mu\text{g/L}$ )														
	Fuel handling			Refinery			POTW			Marina			Other		
Humboldt Bay	0	$\pm$	0	-			0			0.1	$\pm$	0.1	0	$\pm$	0
San Francisco Bay	-			0	$\pm$	0	0			1.3	$\pm$	0.3	0	$\pm$	0
Santa Monica Bay	-			1.4			< 0.1	$\pm$	0.1	3.5	$\pm$	3.3	0.2	$\pm$	0.5
Los Angeles Harbor	-			-			-			-			0.6		
Mission Bay	-			-			-			20.1	$\pm$	8.3	-		
San Diego Bay	-			-			-			2.9	$\pm$	0.2	1.8	$\pm$	0.5

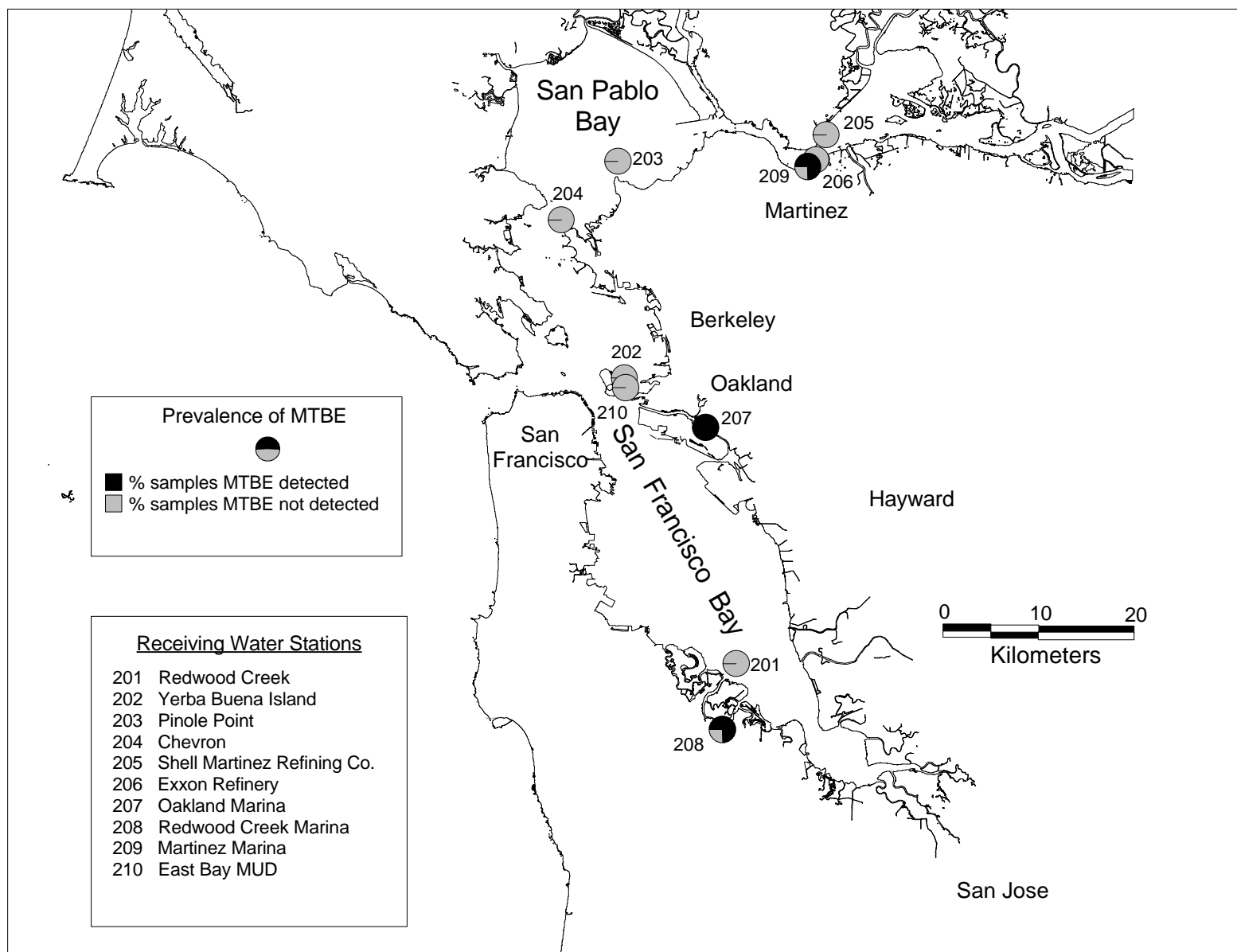


Figure 3.5 Occurrence of MTBE at San Francisco Bay receiving water stations.

### San Francisco Bay Oakland Marina

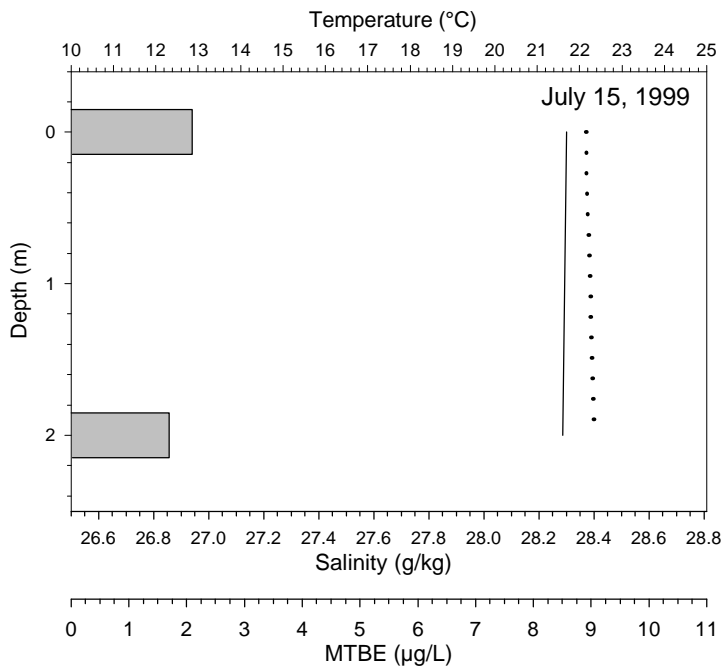
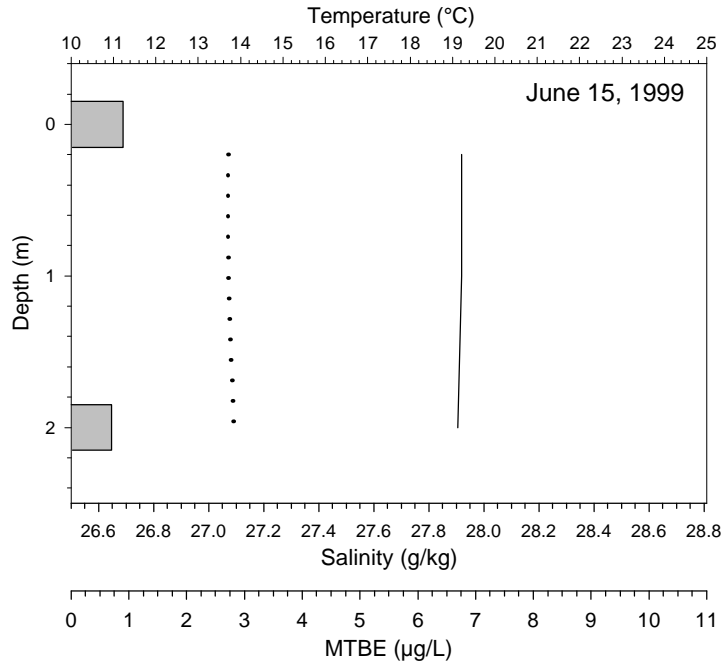
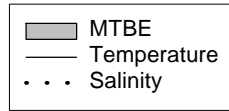


Figure 3.6 Distribution of MTBE with depth at Oakland Marina (station 207), San Francisco Bay.

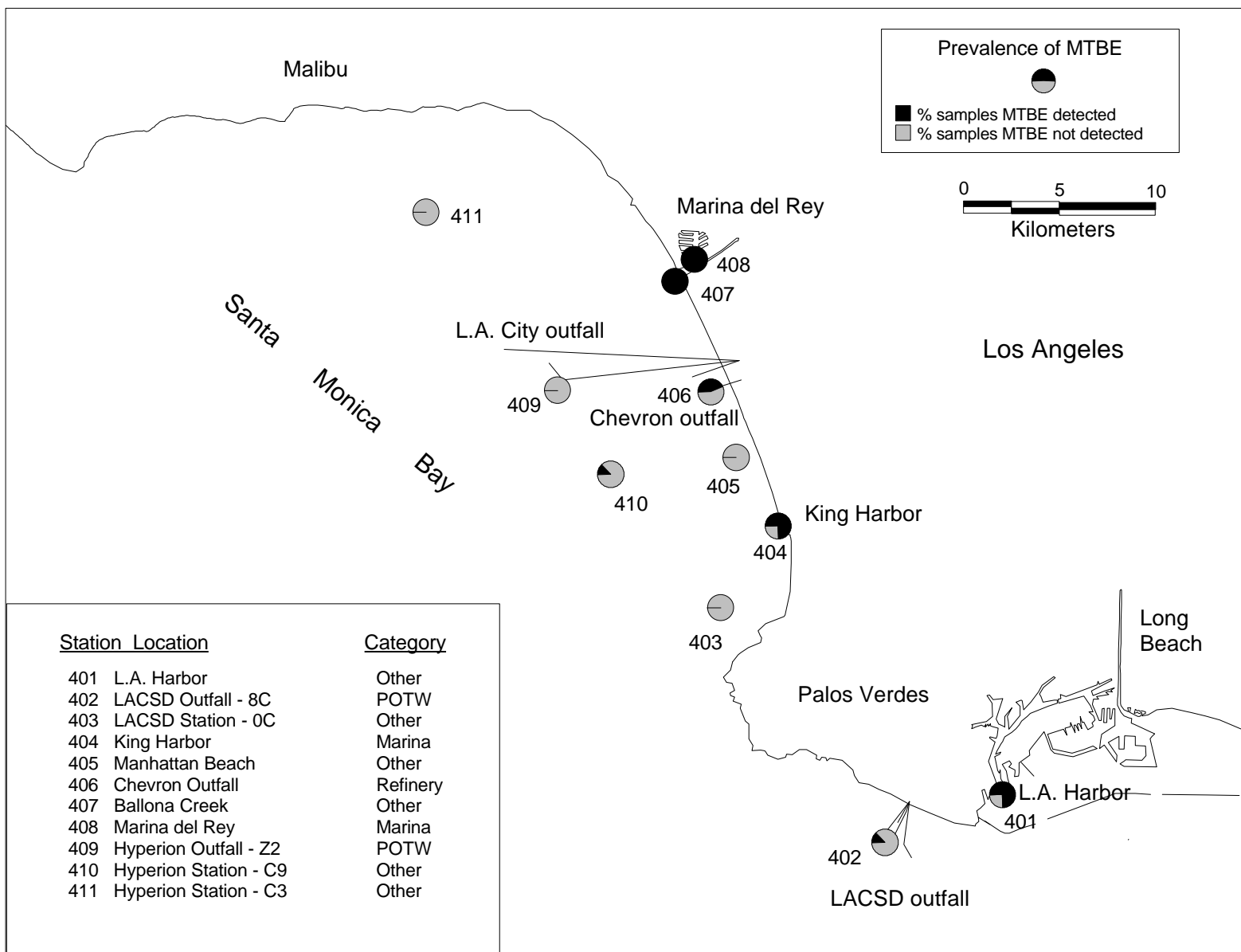


Figure 3.7 Occurrence of MTBE at Santa Monica Bay and Los Angeles Harbor receiving water stations.

### Santa Monica Bay Chevron Outfall

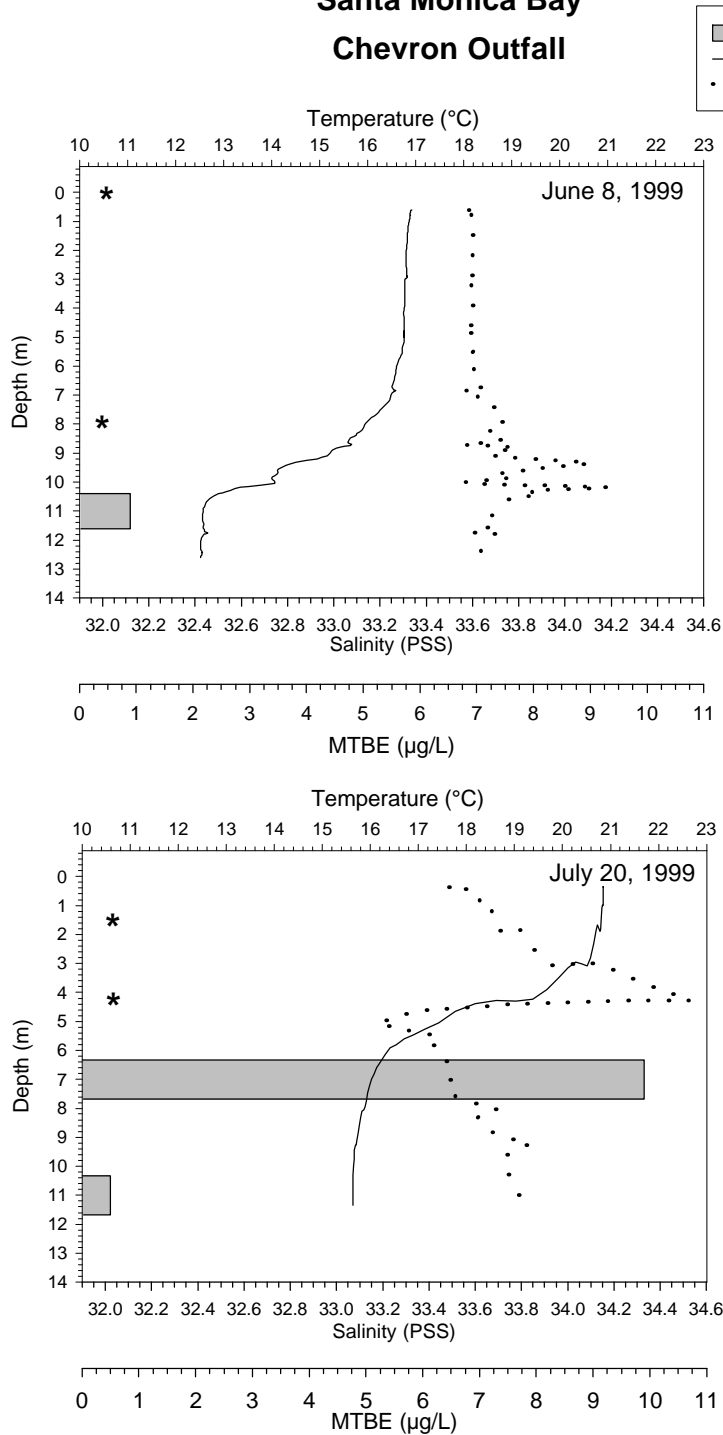


Figure 3.8 Distribution of MTBE with depth at the Chevron El Segundo Refinery outfall system (station 406), Santa Monica Bay. Asterisks (\*) indicate sampled depths with MTBE concentrations below the detection limit (0.5 µg/L).

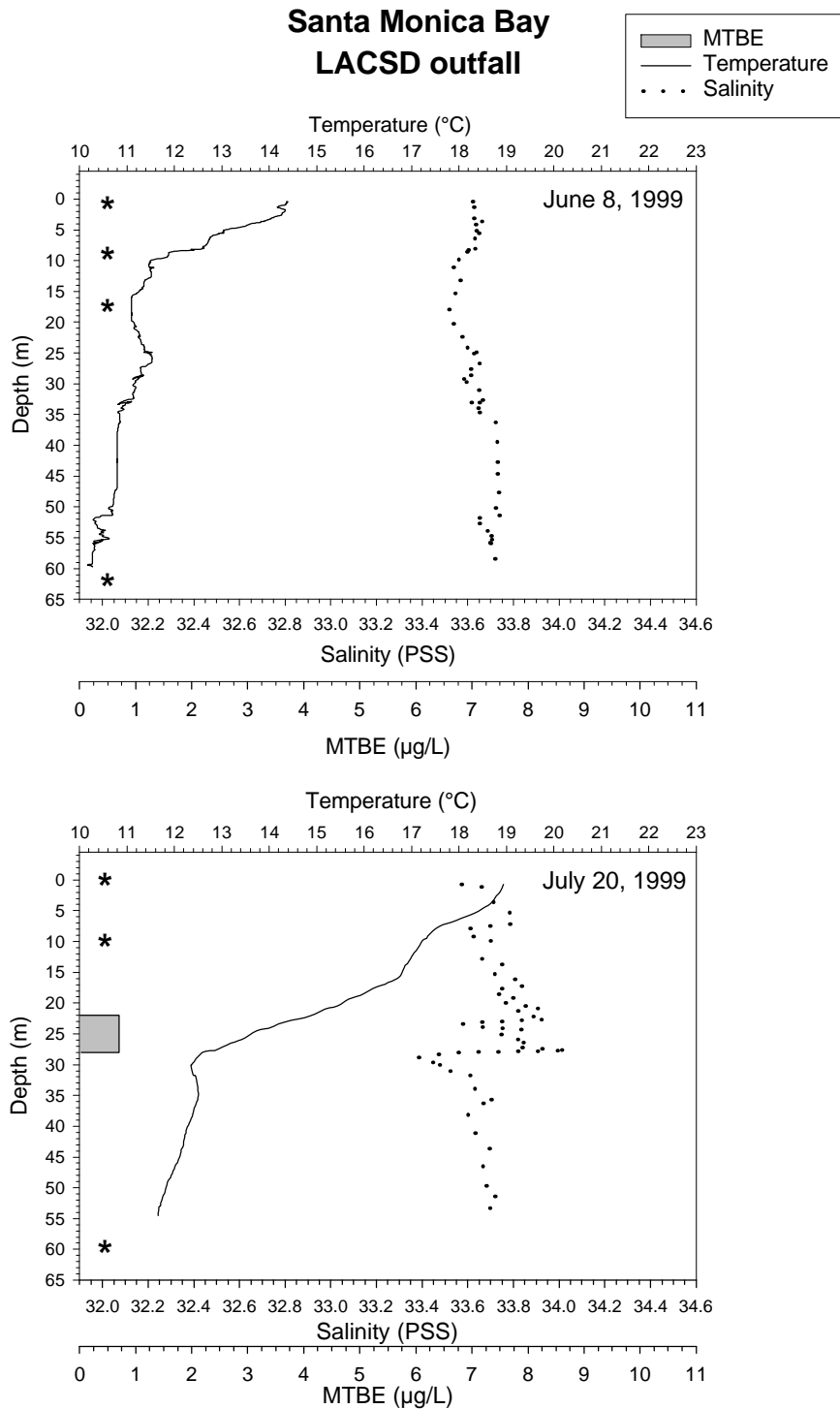


Figure 3.9 Distribution of MTBE with depth at the Los Angeles County Sanitation Districts JWPCP outfall system (station 402), Santa Monica Bay. Asterisks (\*) indicate sampled depths with MTBE concentrations below the detection limit (0.5 µg/L).

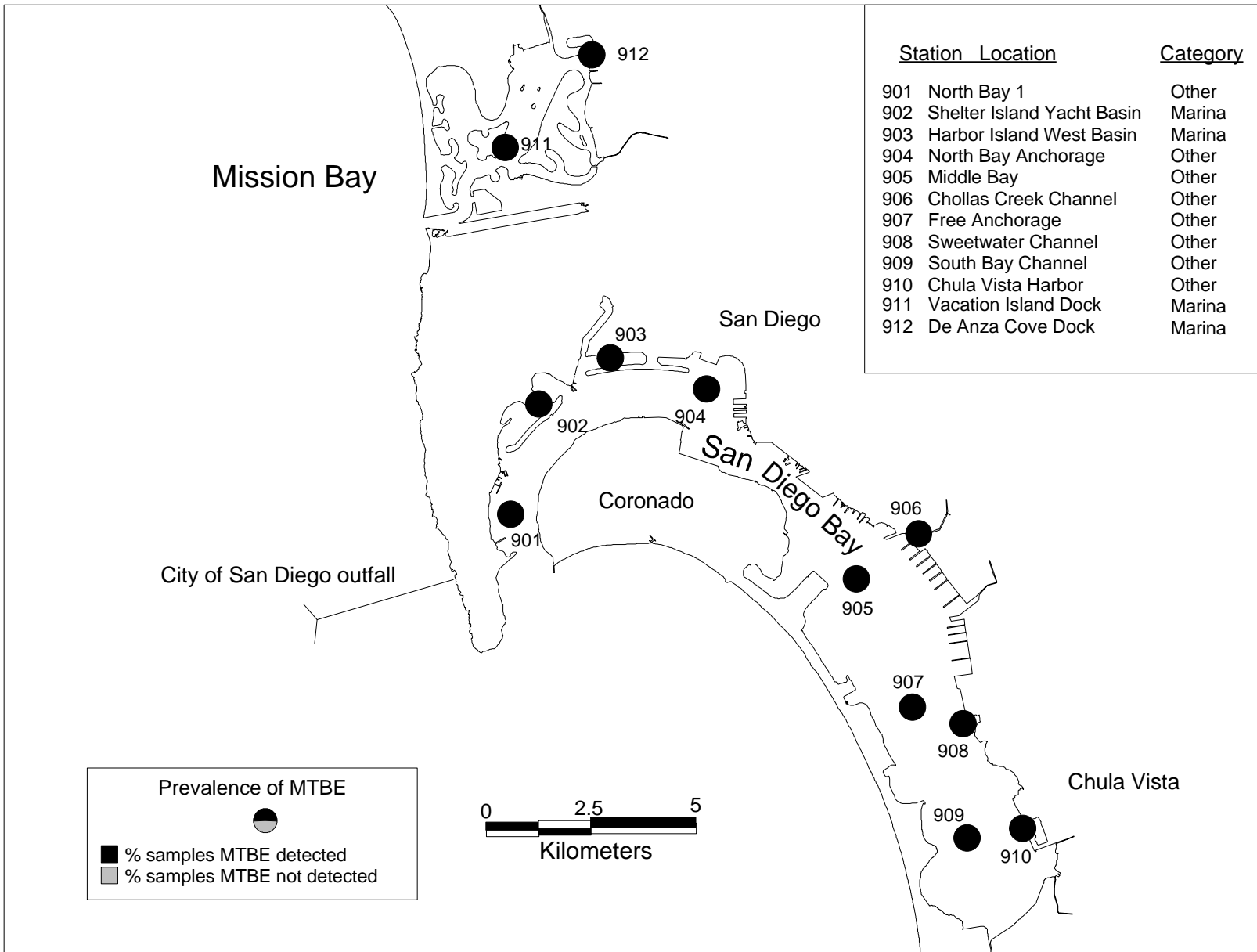


Figure 3.10 Occurrence of MTBE at Mission Bay and San Diego Bay receiving water stations.

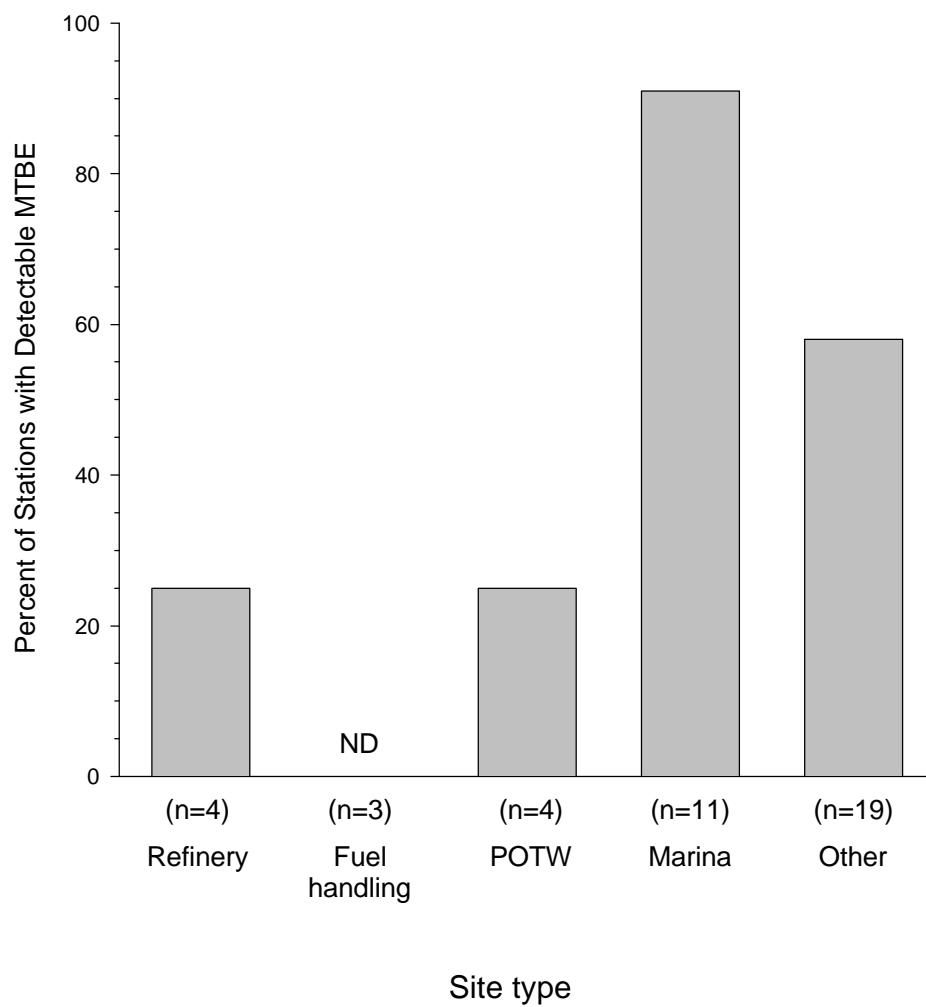


Figure 3.11 Statewide percentage of receiving water stations in the different site type categories that detected MTBE. Samples were collected from Humboldt Bay, San Francisco Bay, Santa Monica Bay, Los Angeles Harbor, Mission Bay, and San Diego Bay. Abbreviation: ND = not detected.



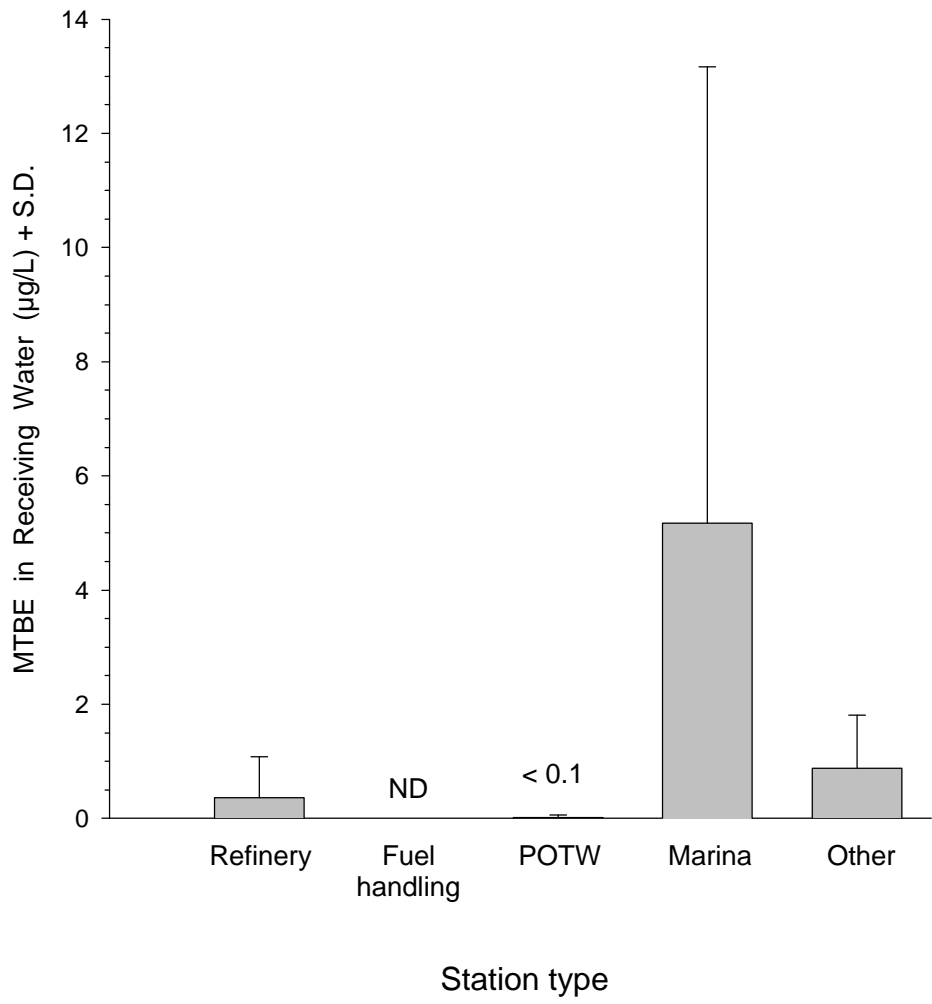


Figure 3.12 Statewide concentration of MTBE in the different receiving water station type categories. Samples were collected from Humboldt Bay, San Francisco Bay, Santa Monica Bay, Los Angeles Harbor, Mission Bay, and San Diego Bay. Values are the average concentration + standard deviation. Abbreviation: ND = not detected.

## IV. TOXICITY

### A. Introduction

The short-term toxicity of MTBE to four California marine organisms was measured in this study. The species used represent diverse taxonomic groups with commercial and recreational importance from habitats with high potential for exposure to MTBE. Three of the tests examined the sublethal effects of MTBE, including the purple sea urchin (*Strongylocentrotus purpuratus*) 3-day embryo development test, the giant kelp (*Macrocystis pyrifera*) 2-day germination and growth test, and the 7-day mysid (*Holmesimysis costata*) growth test. In addition, the effects of MTBE on the survival of a sediment-dwelling amphipod (*Grandidierella japonica*) were measured. The exposures were conducted under static conditions, with solution renewals in the mysid and amphipod tests. All tests were conducted in sealed containers to minimize the loss of MTBE. All test concentrations were verified by chemical measurement. The resulting effects data were compared with concentrations measured in the receiving water.

### B. Methods

#### Purple sea urchin embryo development test

Purple sea urchins (*Strongylocentrotus purpuratus*) were collected from a reference location at Point Dume, California. The sea urchins were maintained in a flow-through seawater culture system at 15°C and fed brown algae for more than one month before testing.

Sea urchins were spawned on the initial day of the MTBE experiment, and the resulting gametes were combined to produce embryos. The embryos were exposed to MTBE for 72 h following the methods of USEPA (1995). There were 25 eggs/mL test solution for each treatment. The experiment was a static non-renewal test conducted in 250 mL glass Boston bottles with screw top caps. Each container had 25 mL headspace. The test was conducted at 15°C, with a 16 h light/8 h dark photoperiod. Randomized placement of each test chamber was maintained throughout the test.

Nominal test concentrations were 0 (control), 200, 500, 1,000, 2,000, and 4,000 mg MTBE/L. Dilution seawater was obtained from 0.5 miles off Redondo Beach, California, and filtered to 0.4 µm. Four replicates of each concentration were tested. Water quality parameters (pH, dissolved oxygen, total ammonia, salinity) were measured at the beginning and end of the experiment. Temperature was monitored continuously. The test was terminated after 72 h by preserving the embryos with formalin. Embryo development was assessed by microscopic examination. At least 100 embryos from each container were examined. The test endpoint was the percentage of normally developed embryos.

A reference toxicant exposure with copper was conducted concurrently with the MTBE test.

### **Giant kelp germination and germ tube growth test**

Giant kelp (*Macrocystis pyrifera*) sporophylls were collected from kelp beds off Point Loma, California and transported to the lab on the initial day of the test.

The spores were released from the sporophylls following desiccation of the kelp blades. The spores were exposed to MTBE for 48 h following the methods of USEPA (1995). The experiment was a static non-renewal test conducted in 400 mL glass beakers sealed with Saran Wrap™. Each container had 50 mL headspace. The test was conducted at 15°C,  $50 \pm 10 \mu\text{E}/\text{m}^2/\text{s}$  illumination, with a 16 h light/8 h dark photoperiod. Randomized placement of each test chamber was maintained throughout the test.

Nominal test concentrations were 0 (control), 100, 200, 500, 1,000, 2,000, and 4,000 mg MTBE/L. Dilution seawater was obtained from 0.5 miles off Redondo Beach, California, and filtered to 0.4  $\mu\text{m}$ . There were five replicate beakers per treatment. Water quality parameters (pH, dissolved oxygen, total ammonia, salinity) were measured at the beginning and end of the experiment. Temperature was monitored continuously. The test was terminated after 48 h by preserving a subsample of the settled spores with glutaraldehyde. Germination and germ tube length were assessed by microscopic examination. The endpoints for the kelp test were the percentage of germinated spores, and germ tube growth.

A reference toxicant exposure with copper was conducted concurrently with the MTBE test.

### **Amphipod survival test**

Amphipods (*Grandidierella japonica*) were collected four days before testing from upper Newport Bay, California. Sediment from the site was partially screened in the field and returned to the laboratory. Holding bins were kept at 15°C and provided aeration and flowing seawater.

Test procedures followed methods recommended by ASTM (1996) for 96 h reference toxicant tests. On the day of MTBE test initiation, juvenile amphipods (2 to 4 mm length) were screened out of the holding sediment and placed into large petri dishes. Ten animals were then randomly distributed into each exposure container. The amphipods were exposed to MTBE for 96 h under static conditions with one renewal of solution at 48 h. The exposure was conducted in 250 mL glass Boston bottles with screw top caps. Each container had 25 mL of headspace. The test was conducted at 15°C, with a 16 h light/8 h dark photoperiod. Randomized placement of each test chamber was maintained throughout the test. Amphipods were not fed during the test.

Nominal test concentrations were 0 (control), 25, 50, 100, 200, and 400 mg MTBE/L. Dilution seawater was obtained from 0.5 miles off Redondo Beach, California, and filtered to 0.4 µm. Five replicates of each concentration were tested. Water quality parameters (pH, dissolved oxygen, total ammonia and salinity) were measured at the beginning and end of the exposure. Dissolved oxygen was also measured at the time of renewal. Temperature was monitored continuously.

After 96 h, the test solutions were poured through a screen to remove the animals. The number of live animals was then counted and percent survival calculated.

A reference toxicant exposure with cadmium was conducted concurrently with the MTBE test.

### **Mysid survival and growth test**

Adult mysids (*Holmesimysis costata*) were collected off Point Loma, California and transported to a local laboratory. Juvenile mysids released from adult females were collected and transported to SCCWRP.

Juvenile mysids were exposed to MTBE for 7 days following the methods of USEPA (1995). The experiment was conducted in 250 mL glass Boston bottles with screw top caps. Each container had 25 mL headspace. The exposure was conducted under static conditions, with two solution renewals, after 48 and 96 h. Each container had five animals per replicate, with five replicates per treatment. The test was conducted at 15°C with a 16 h light/8 h dark photoperiod. Randomized placement of each test chamber was maintained throughout the test. Each container received 40 *Artemia* nauplii per mysid each day of the exposure to feed the test organisms.

Nominal test concentrations were 0 (control), 25, 50, 100, 200, and 400 mg MTBE/L. Dilution seawater was obtained from 0.5 miles off Redondo Beach, California, and filtered to 0.4 µm. Water quality parameters (pH, dissolved oxygen, total ammonia, salinity) were measured at the beginning and end of the experiment. These parameters, excluding total ammonia, were also measured in the old solutions at the 48 and 96 h time points. Temperature was monitored continuously.

Survival was recorded at each water change, as well as at the end of the experiment. The surviving mysids were placed in tin weigh boats, desiccated at 60°C overnight, and then weighed. The endpoints for the mysid test were percent survival, and growth.

A reference toxicant exposure with zinc was conducted concurrently with the MTBE test.

### **MTBE spiking procedure**

All test solutions were prepared in gallon jars. The jars were filled with seawater to a volume that minimized headspace and were covered with Saran Wrap™. A magnetic stirrer was used to vigorously mix the seawater while neat MTBE (99.99% purity) was slowly added using a gas tight syringe. The jars were then sealed with an additional layer of Saran Wrap™ and mixed for five minutes. The solutions were then transferred to cubitainers for temporary storage (< 2 h) before addition to the exposure containers.

### **Verification of exposure concentrations**

The concentration of MTBE was verified by GC/MS for each concentration tested. Samples were collected for analysis at the start and end of each test, as well as at each water change. Both the new and old solutions from the water changes were analyzed in order to document temporal changes in exposure concentration. Each sample for analysis was a composite of equal volumes of solution from several replicate exposure containers. Water samples were placed in 40 mL VOA vials containing acid preservative and stored under refrigeration until analyzed. Samples were analyzed within five days of sampling, using EPA method 8260B.

Quality control procedures for the MTBE measurements included the analysis of method blanks, recovery surrogates, and matrix spike/matrix spike duplicates for each set of samples analyzed. These measurements were made on samples prepared by the analytical laboratory. In addition duplicate samples of water spiked to 5 or 500 mg/L at SCCWRP were analyzed in order to estimate variability associated with sampling, handling, and dilution of the samples.

Results of the analytical lab QC samples are shown in Table 4.1. All method blanks were below detection limits and high recovery (103%) of MTBE was obtained from spiked samples. Matrix spike duplicates had low variability, indicating that the instrumental analysis procedure had high precision. Measurements of duplicate samples spiked at SCCWRP showed somewhat higher variability (7-21%), as expected. The variability between duplicates was similar to that measured between water changes during the toxicity tests.

### **Data analysis**

The data were analyzed using Toxstat statistical analysis software (West and Gulley 1996). The assumptions of data normality and homogeneity of variance were tested using the Shapiro-Wilk's test and Bartlett's test, respectively (USEPA 1995). Both assumptions were met for all four species. For the kelp, amphipod, and mysid tests, we used Dunnett's test to identify treatments that were significantly different from the control ( $\alpha = 0.05$ ) for determination of the LOEC (Lowest Observed Effect Concentration) and NOEC (No Observed Effect Concentration). For the urchin test, we used t-tests with Bonferroni adjustment because there was unequal replication in the data.

The concentrations causing 50% mortalities in amphipods or mysids ( $LC_{50}$ ) were determined using probit analysis. The concentrations estimated to inhibit the development or growth by 25% and 50% of the control sea urchin, kelp or mysid values ( $IC_{25}$  and  $IC_{50}$  respectively) were determined by linear interpolation. All calculations used the measured MTBE concentrations.

## **C. Results and Discussion**

### **Toxicity test quality control**

Results of the chemical verification measurements indicated that the MTBE dosing method produced accurate and stable exposure concentrations. The average measured concentrations of samples collected at the beginning and end of the exposure period were generally greater than 80% of the nominal values for all tests (Figure 4.1). The MTBE concentrations remained relatively constant during each experiment, with concentrations declining only 2.6-14.8% during the tests. Water quality parameters remained within acceptable limits throughout each test, indicating that the use of sealed exposure containers did not cause a significant decrease in oxygen content or a build up of waste products during the test. All of the toxicity tests met the acceptability criteria for control performance and sensitivity to a standard reference toxicant.

### **Response of California species to MTBE**

There was a wide range in response to MTBE among the tests, as indicated by a greater than 10x difference in toxicity summary statistics among species (Table 4.2). The kelp growth and amphipod survival tests had the most sensitive initial responses to MTBE, with significant reductions in growth or survival first occurring (LOEC) at approximately 80 mg/L. In contrast, the mysid survival LOEC was twice this amount (180 mg/L), and the sea urchin development LOEC was more than 20 times higher (1,700 mg/L).

Statistics such as the LOEC and NOEC indicate the threshold effects concentration for each species, but can be misleading because they do not describe the magnitude of response occurring. Examination of the response over a concentration gradient for each species provides a more reliable measure of the overall sensitivity of each species (Figure 4.2). This dose-response relationship is often described using a measure of the median response for survival ( $LC_{50}$ ) or sublethal ( $IC_{50}$ ) effects (Table 4.2).

Both crustacean species (amphipod and mysid) showed a similar dose response pattern and had the greatest overall sensitivity to MTBE (Figure 4.2). Median effects on survival occurred at similar concentrations for the amphipod (155 mg/L) and mysid (141 mg/L) tests. No survival was observed for either species at a test concentration of 320 mg/L, while there was less than a 15% effect on kelp and sea urchins at a similar exposure concentration.

The mysid dose response plot suggests that survival effects were occurring at 40 mg/L MTBE (24% reduction in survival), but the response was not statistically significant. Amphipods and mysids surviving at intermediate test concentrations often displayed much reduced swimming activity, typical of a narcotic mode of toxicity observed in other MTBE toxicity tests (Drottar et al. 1998).

Mysid growth was not affected by MTBE. The weights of mysids surviving in the MTBE exposures were not significantly different from the controls. Consequently, NOEC and LOEC values could not be calculated. The median response (IC<sub>50</sub>) of 245 mg/L for mysid growth was derived by including data for the highest test concentration, which had no growth because there was no survival.

The high sensitivity of the kelp growth test to the initial effects of MTBE was a statistical effect of the high precision of the test. While statistically significant growth effects were measured at the two lowest MTBE concentrations, they were quite small in magnitude (6% reduction relative to the control) as shown in Figure 4.2. The overall sensitivity of the kelp test was lower than for the other tests, with a median inhibition concentration for germ tube growth of 2,236 mg/L, 14 times higher (less sensitive) than the amphipod LC<sub>50</sub> (155 mg/L). The kelp germination endpoint had the lowest overall sensitivity to MTBE, with less than a 25% reduction in germination at the highest concentration tested (3,250 mg/L).

Sea urchin embryos were intermediate in sensitivity compared to kelp and crustaceans, with an IC<sub>50</sub> of 1,341 mg/L. The dose response for this species was very steep; no inhibition of development was seen at 885 mg/L MTBE while the next higher exposure level (1,700 mg/L) produced 86% abnormal development.

### **Comparison to other species**

The effects of MTBE on the survival of California crustacean species was similar to that reported for other crustaceans (Figure 4.3). The LC<sub>50</sub> for mysids and amphipods in this study (155 and 141 mg/L, respectively) were similar (within a factor of two) to the values for the marine mysid *Americamysis (Mysidopsis) bahia* (mean = 127 mg/L), the grass shrimp *Palaemonetes pugio* (166 mg/L), and the blue crab *Callinectes sapidus* (306 mg/L), but at least four times lower than the LC<sub>50</sub> for the marine copepod *Nitocra spinipes* (> 1,000 mg/L) (Drottar et al. 1998, Mancini et al. 1999). Fish survival appears to be less sensitive to MTBE than crustacean survival. The LC<sub>50</sub> for California crustaceans were at least 4-16 times lower than values for four species of fish (*Menidia beryllina* LC<sub>50</sub> = 574 mg/L; *Gasterosteus aculeatus* LC<sub>50</sub> = 929 mg/L; *Alburnus alburnus* LC<sub>50</sub> > 1,000 mg/L; *Cyprinodon variegatus* LC<sub>50</sub>s = 1,358, and > 2,500 mg/L).

Three of the four sublethal endpoints measured in this study were less sensitive to MTBE than previous studies (Figure 4.4). The sea urchin development IC<sub>50</sub> (1,341 mg/L) was 2-9 times higher than the results of short-term (≤ 96 hr) tests using other marine species (*Crassostrea virginica* EC<sub>50</sub> = 150 mg/L; *A. bahia* EC<sub>50</sub> = 187 mg/L; *G. aculeatus* EC<sub>50</sub> = 297 mg/L; *C. variegatus* EC<sub>50</sub> = 663 mg/L) (Drottar et al. 1998, Mancini et al. 1999).

The kelp growth  $IC_{50}$  (2,236 mg/L) was 3-15 times higher than the values for these species. The mysid growth  $IC_{50}$  in this study (245 mg/L), however, was similar to the responses obtained for other species.

### **Potential for MTBE toxicity in receiving water**

Comparison of the toxicity and field sampling data produced by this study demonstrate that the concentrations of MTBE occurring in the marine environment are unlikely to pose a significant risk to marine fish and invertebrates. The highest concentration measured in marine waters, 34  $\mu\text{g/L}$  in Mission Bay, is less than 0.01% of the threshold effect level (NOEC) for amphipod survival, the most sensitive California species tested (Figure 4.5).

Data from this and other studies are being used by the MTBE Water Quality Criteria Work Group of the American Petroleum Institute to derive proposed acute and chronic water quality criteria for MTBE (Mancini et al. 1999). Development of the proposed criteria is still in progress, but preliminary calculations yield acute and chronic values for marine life of 53 mg/L and 18 mg/L, respectively. The proposed criteria will be submitted to USEPA for review.

Using the preliminary acute criterion as an estimate of the concentration protective of a diverse group of animals also indicates that MTBE concentrations in receiving water and undiluted effluent are below levels that cause toxicity to marine life. Concentration in Mission Bay were less than 0.05% of the acute criterion. Undiluted effluent from the Chevron El Segundo refinery, which contained the highest MTBE concentrations of any NPDES facility (1,878  $\mu\text{g/L}$ ), contained 4% of the acute effects value (Figure 4.5). Undiluted POTW effluents, with lower MTBE concentrations, contained 0.2% of the acute effects criterion.

While our experiments did not examine chronic exposure effects, concentrations in receiving waters are below levels that caused toxic effects in other studies. The only life cycle test conducted with a marine species reported an  $EC_{50} = 44$  mg/L for effects on survival and growth of *A. bahia* (Drottar et al. 1998). Chronic MTBE effects on freshwater species yield similar values (Mancini et al. 1999), with  $IC_{20}$  values of 42 mg/L for the water flea (*Daphnia magna*) and 289 mg/L for the minnow (*Pimephales promelas*). The highest concentration of MTBE measured in Mission Bay (34  $\mu\text{g/L}$ ) is far below these effect levels and only 0.2% of the proposed chronic effects criterion of 18 mg/L. A large margin of safety is also present for MTBE discharges from point sources. For example, exposure to undiluted effluent from the Chevron El Segundo refinery contained MTBE concentrations that were 10% of the chronic effects value (Figure 4.5). Concentrations in undiluted POTW effluents were less than 1% of the chronic effects criterion.

Impacts to the sediment-dwelling (benthic) organisms were indirectly investigated in the present study. One of the test species, the amphipod *G. japonica*, lives in the sediments of coastal bays and harbors, such as Los Angeles Harbor and San Diego Bay. This



species was found to have a similar sensitivity to MTBE as other crustaceans (Figure 4.3). Contaminated sediments and prey organisms are common routes of pollutant exposure for many organisms; these routes are not expected to be a significant route of exposure for MTBE as this compound does not have a tendency to bind onto sediments or bioaccumulate in tissues (Squillace et al. 1997). The available data indicates that the principal exposure of benthic organisms to MTBE is from the water, which is below levels known to cause toxicity in marine life.

MTBE is not the only compound discharged from motorized watercraft with the potential to cause aquatic life toxicity. Other compounds contained in engine exhaust have been identified as a cause of surface water toxicity in lakes. Increased mortality and reduced reproduction in zooplankton, and reduced growth in larval fish were associated with PAH (polycyclic aromatic hydrocarbon) contamination from boat exhaust in surface waters from Lake Tahoe (Oris et al. 1998). The threshold for toxic effects estimated for PAHs ranged from 3.4 ng/L for zooplankton reproduction to 9.0 ng/L for larval fish growth. In contrast, the no-effect concentration of MTBE to *A. bahia* observed by Drott et al. (1998) was 3-8 million times higher (26 mg MTBE/L). These data suggest that there are compounds in watercraft exhaust with a greater potential than MTBE to cause adverse effects on marine life at environmentally realistic concentrations.

Table 4.1 MTBE analysis quality control data for toxicity test samples.

<b>Analysis Date</b>	<b>Method Blank (µg/L)</b>	<b>MTBE Spike Recovery (%)</b>	<b>Matrix Spike Duplicate Relative Percent Difference</b>
9/15/99	< 0.50	100	2
9/17/99	< 0.50	99	7
9/17/99	< 0.50	104	0
9/20/99	< 0.50	99	0
9/20/99	< 0.50	100	2
9/22/99	< 0.50	118	2
Mean	< 0.50	103.3	2.2

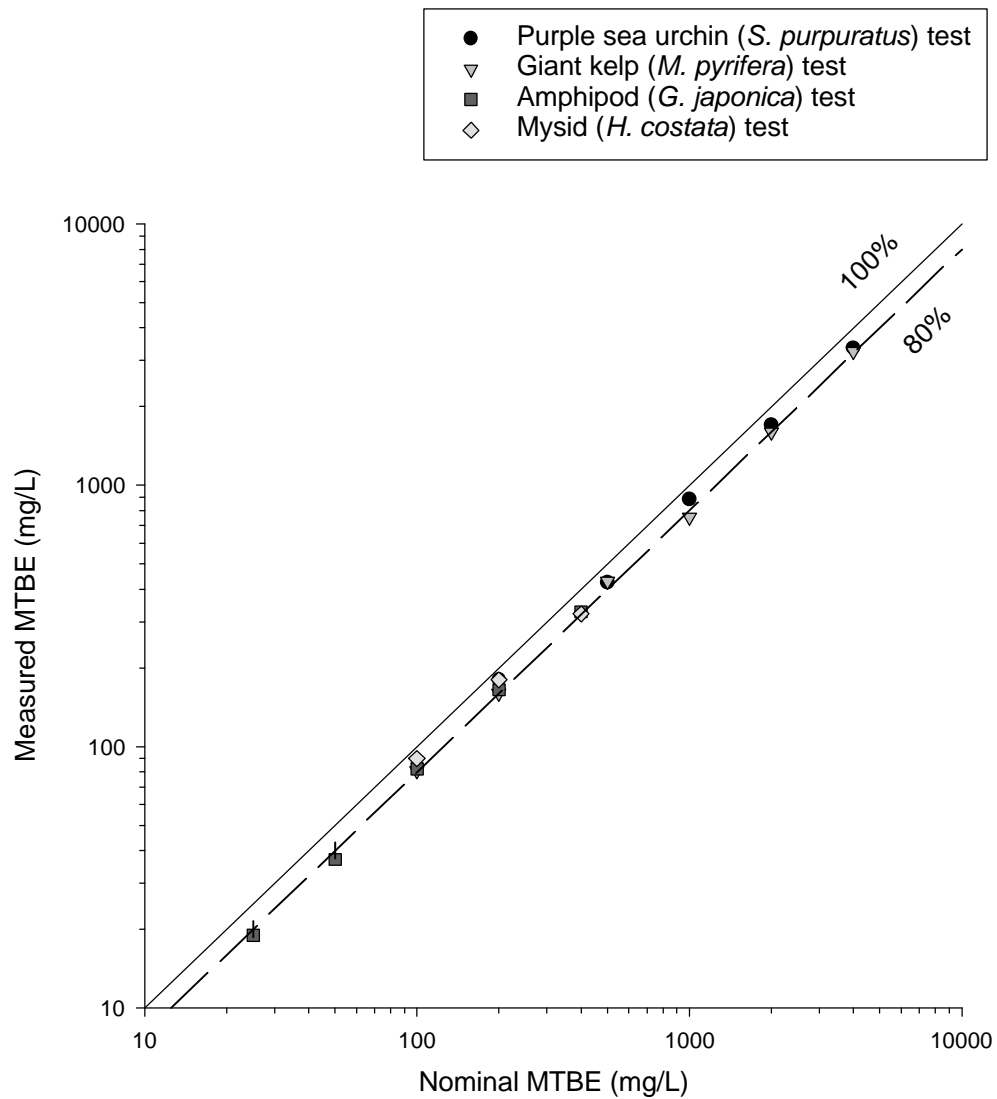


Figure 4.1 Correspondence between nominal and measured MTBE concentrations in toxicity tests. Reference lines indicate 100 and 80% of nominal values.

Table 4.2 Summary of MTBE toxicity results for California marine species. Abbreviations: NOEC = No effect concentration; LOEC = lowest effective concentration; LC<sub>50</sub> = concentration lethal to half the organisms; IC = concentration that inhibits the growth or development by a proportion of the control.

	Days	MTBE (mg/L)				
		NOEC	LOEC	LC <sub>50</sub>	IC <sub>25</sub>	IC <sub>50</sub>
Sea urchin ( <i>S. purpuratus</i> ) development	3	885	1,700		1,093	1,341
Kelp ( <i>M. pyrifera</i> ) % germination	2	430	755		> 3,250	> 3,250
growth	2	< 81 <sup>a</sup>	81		616	2,236
Amphipod ( <i>G. japonica</i> ) survival	4	37	82	155		
Mysid ( <i>H. costata</i> ) survival	7	90	180	141		
growth	7	≥ 90 <sup>b</sup>	> 90 <sup>b</sup>		206	245

<sup>a</sup> Response at all MTBE test concentrations were significantly different from control.

<sup>b</sup> Higher concentrations were tested, but the data were not used for analysis of the growth endpoint due to significantly reduced survival, as directed by USEPA 1995.

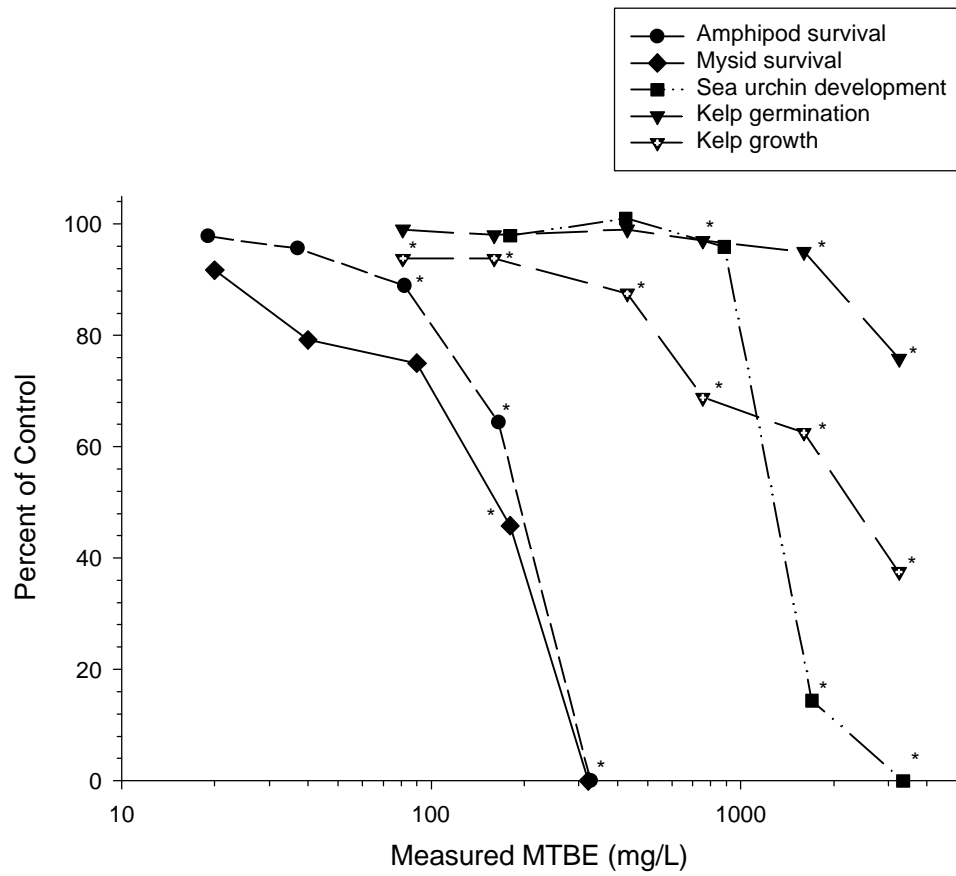


Figure 4.2 Response of marine species to MTBE exposure. Values are the mean of the treatment replicates, normalized to the control response. The asterisks (\*) indicate concentrations that are significantly different from the control.

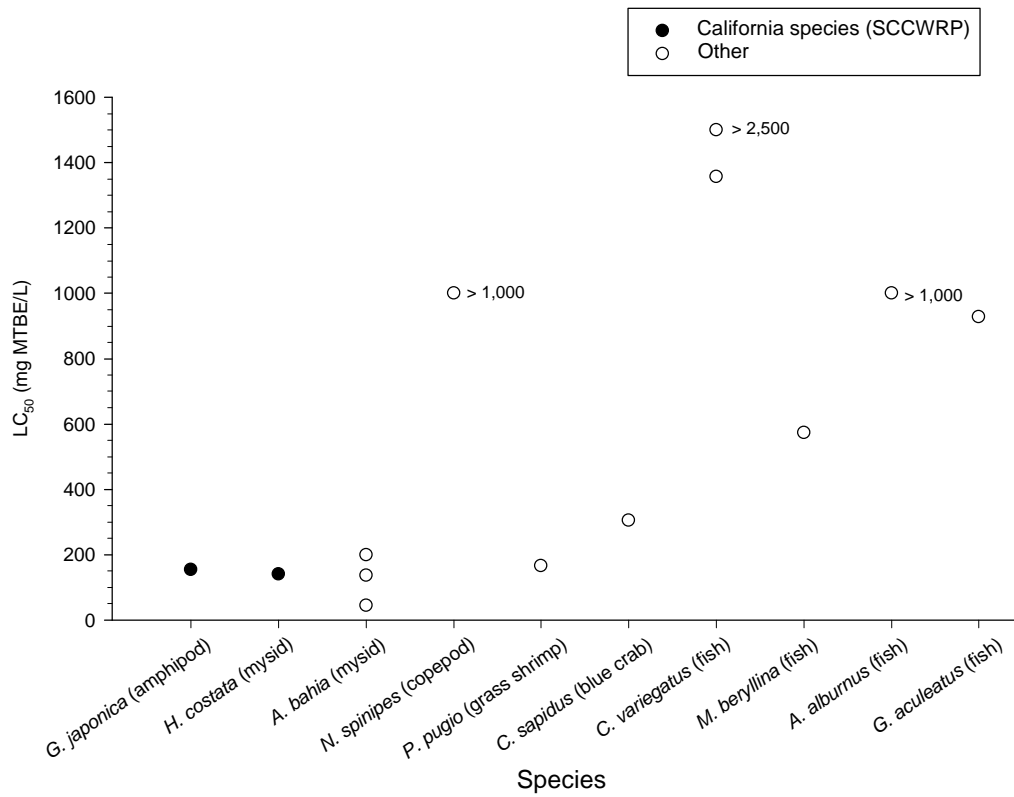


Figure 4.3 Effects of MTBE on survival of marine species. Closed symbols indicate SCCWRP data.

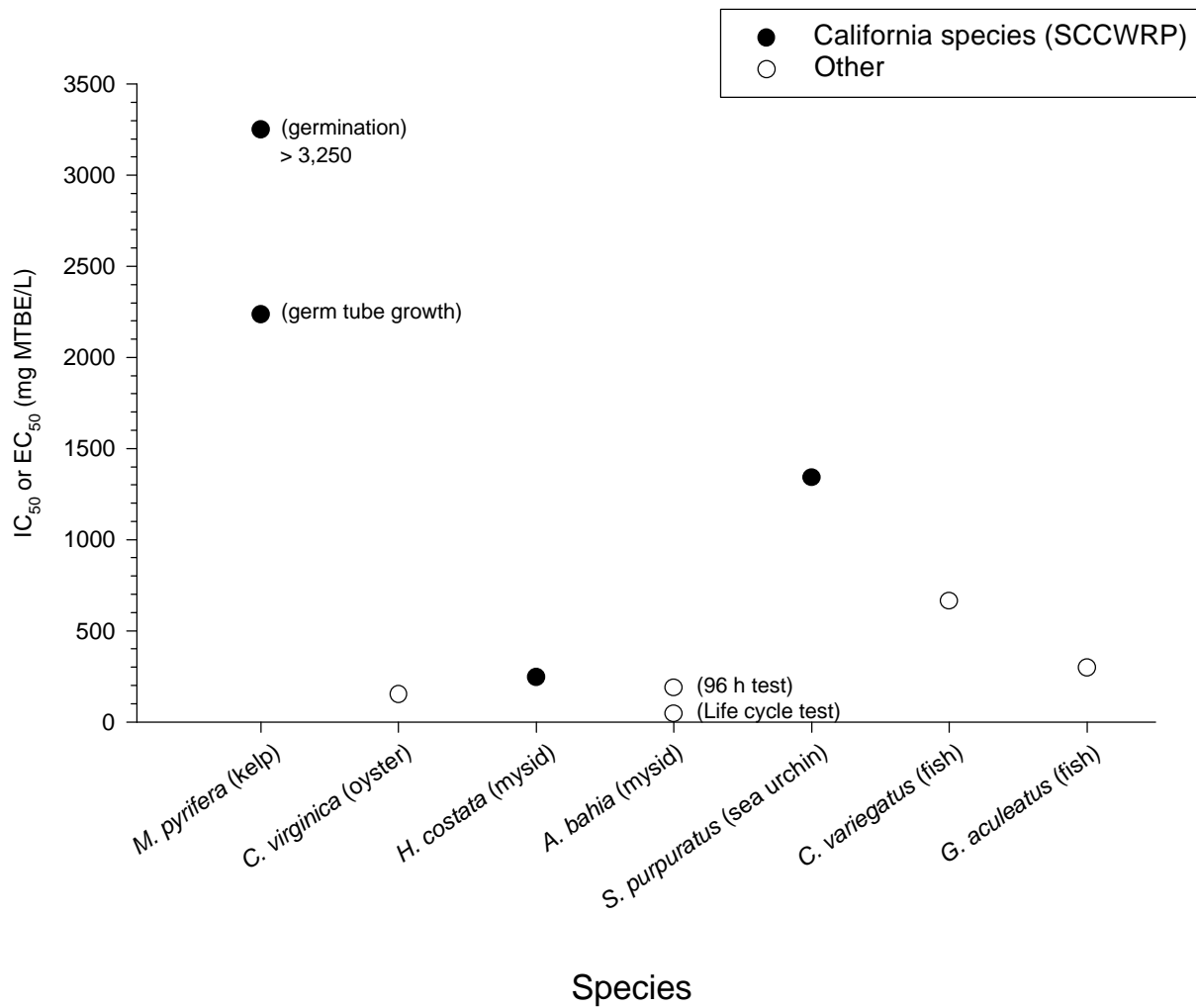


Figure 4.4 Sublethal effects of MTBE on marine species. All tests are short-term exposures ( $\leq 7$  days) except where noted.

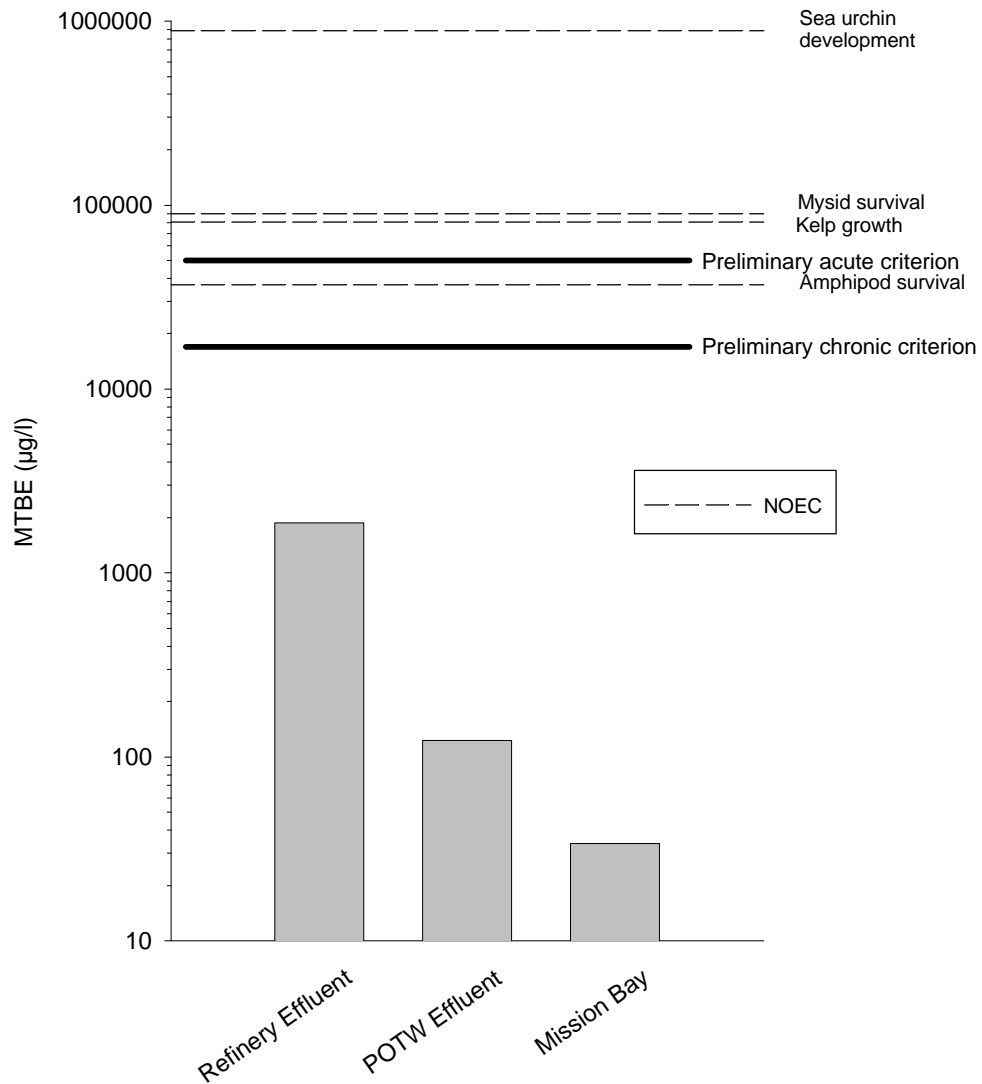


Figure 4.5 Comparison of environmental MTBE concentration and effect levels. The highest concentrations for NPDES discharge categories and receiving water are shown. Dashed lines indicate NOEC for California species. Solid lines indicate preliminary water quality criteria from Mancini et al. (1999).



## V. CONCLUSIONS

This study has provided the first integrated look at the contamination and potential for effects of MTBE in the marine environment. Three primary conclusions are evident from the data:

- **Discharges containing refinery wastewater represent the largest input of MTBE to the marine environment.**

Approximately 228 kg/day of MTBE enters coastal waters from discharges of refinery or POTW effluents. Summertime inputs of MTBE from urban runoff are much smaller. For southern California, dry weather runoff contributes less than 0.5% of the mass of MTBE discharged in effluents. Preliminary estimates of the amount contributed by stormwater discharge to southern California are also small, accounting for approximately 5% of the amount discharged by point sources.

Santa Monica Bay receives most (approximately 92%) of the MTBE discharged in effluents to California's coastal environment. More MTBE enters coastal waters from POTW effluents than from refinery outfalls. The situation is the result of refineries in Los Angeles County discharging their wastewater to the municipal sewer system, rather than directly to the ocean.

- **Receiving water contamination is most prevalent in areas of high watercraft use, and less so in areas receiving POTW or refinery discharge.**

MTBE contamination was most prevalent (detected at 91% of stations) and most concentrated in marinas and other areas characterized by relatively high watercraft use and low water circulation. Refinery and POTW effluent discharge did not usually produce detectable concentrations of MTBE in the water column. MTBE was detected at low concentrations at 25% of the stations near effluent discharges and there was no evidence of bay-wide MTBE contamination related to these outfalls.

Surface water contamination by MTBE was most widespread in San Diego Bay and Mission Bay, areas with no refinery or POTW inputs. The spatial pattern and concentration of MTBE in marine receiving waters is similar to the contamination that has been documented to result from watercraft use on California lakes.

- **Marine receiving water MTBE concentrations pose little risk of toxicity to fish and invertebrates.**

MTBE is toxic to marine life, with adverse effects on California species occurring at concentrations above 37 mg/L. The results of our toxicity tests are consistent with those of other studies that indicate a receiving water concentration of 18 mg/L is protective of

chronic effects on marine life. None of the receiving water samples measured in this study contained toxic concentrations of MTBE. The highest MTBE concentrations measured in receiving water were less than 0.5% of the proposed chronic effects guideline, providing a wide margin of safety for marine life.

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# **Appendix**

## **Compilation and Analysis of Existing Monitoring Data**

## Compilation and Analysis of Existing Monitoring Data

### Introduction

A summarization and analysis of recent MTBE monitoring data was conducted to evaluate the adequacy of existing monitoring programs to describe the inputs of MTBE into selected waterbodies. Additional data for NPDES discharges has been generated during a subsequent SWRCB survey conducted in May-August 1999.

### Methods

Data describing MTBE input and receiving water concentrations for Humboldt Bay, San Francisco Bay, Santa Monica Bay, San Diego Bay, and additional southern California coastal waters were compiled. Two approaches were used to locate recent data (1997-spring 1999). First, facilities with discharges to the study areas (e.g., POTWs, petroleum refineries, and stormwater management agencies), and agencies familiar with monitoring or research programs in the area (e.g. U.S. Geological Survey) were contacted for information. These interviews were useful in identifying agencies that have analyzed their discharge for MTBE, and estimated its mass emission when detected. Second, the USEPA Toxic Release Inventory (TRI, [www.epa.gov/enviro/html/tris](http://www.epa.gov/enviro/html/tris)) was queried. This database lists the types and amounts of chemicals that were released to the environment from industrial discharges. The database also indicates the media that each contaminant was released to (e.g., air, water), including the name of the stream or body of water. Because the most recent information in the TRI is from 1997, we relied upon the database only when information was not available through the telephone interviews. Averages were calculated for each agency using a value of 0 µg/L for samples with nondetectable MTBE concentrations. The daily mass emission for each discharge was calculated by multiplying the daily flow by the average concentration.

### Results

Our search for recent monitoring data located MTBE analysis results for 14 discharges or locations within Humboldt Bay, San Francisco Bay, or Santa Monica Bay. Table 1 summarizes the most recent data for each study site; additional data for prior years is listed by facility in Table 2. The information described below represents data available for 1997-April 1999.

#### Humboldt Bay

Discharges from POTWs, urban runoff, and groundwater pumping represent potential input sources of MTBE to Humboldt Bay. Prior to May, 1999 neither of the two POTWs discharging to the bay had analyzed their effluents for MTBE. Stormwater from one industrial site (a fuel depot) has been monitored for MTBE for three years, where it has not been detected since 1998. Monitoring of groundwater discharge from a single location has been conducted for several years and has occasionally detected MTBE, with a mean concentration of 0.26 µg/L for the

most recent sampling year. Flow data for the groundwater discharge were not available, so mass emission estimates could not be calculated.

One receiving water site, near the groundwater discharge to Humboldt Bay has also been analyzed for MTBE. The most recent samples had detectable amounts of the compound, with a mean concentration of 0.28 µg/L MTBE for 1998. Because the samples were collected at only one receiving water location, this value may not represent conditions throughout the bay.

### **San Francisco Bay**

San Francisco Bay receives inputs from over 30 POTWs and 7 major industrial facilities (including five petroleum refineries), in addition to urban runoff. MTBE analysis information was obtained from two POTWs, four refineries, and one stormwater agency (Table 1).

MTBE was detected in effluent from both POTWs. These facilities represent two of the five largest discharges to the Bay and account for approximately 25% of the total volume of municipal wastewater discharged. Concentrations ranged from 3.9 to 21.0 µg/L MTBE. The mass emission of MTBE for each facility was estimated by multiplying the average concentration measured for the most recent sampling period times the annual flow. This calculation yielded an annual mass emission of 6.31 kg/day for the two facilities.

Each of the four petroleum refineries had measurable quantities of MTBE in their discharge. Information for three of the facilities came from the TRI query, which lists mass emissions, but not concentrations or flow volumes. Therefore the range in MTBE concentrations among the facilities was not available. Using the most recent mass emission data available (1998 or 1997) yielded a combined mass emission of 56.44 kg/day MTBE for the four refineries.

MTBE was measured in stormwater runoff from one location, Castro Valley Creek in Alameda County. Three out of five storm events during the 1997/98 winter season had detectable amounts, ranging from 1.1 to 3.3 µg/L. Flow volumes were not available, precluding mass emission estimates.

The number of organizations that analyzed their effluent for MTBE represent only a portion of the facilities likely to be discharging the compound to San Francisco Bay. Over half the POTW effluent and runoff discharged to the Bay is not analyzed for MTBE. Because the data are limited, a comparison of the relative input from POTWs, refineries, and stormwater is not possible.

Receiving water data was located for only one location in the study area, Suisun Bay. A single sample from this site did not contain a detectable level (< 2.5 µg/L) of MTBE.

### **Santa Monica Bay**

The Santa Monica Bay study area included the region extending from Point Dume to the north to Point Fermin on the Palos Verdes Peninsula. Potential sources of MTBE discharge within

this area include two POTWs, one refinery, and urban runoff. Information was obtained for both POTWs, and the refinery. Urban runoff, however, has not been analyzed for MTBE. Similarly, no information regarding receiving water concentrations of MTBE in Santa Monica Bay was located.

Routine monitoring data show that MTBE is present in refinery effluent discharged into Santa Monica Bay. The concentration for the most recent sampling period was 610 µg/L, representing a mass emission of 15.34 kg/day. The data from previous years show approximately a 10-fold variation in concentration due to variation in wastewater composition, indicating that mass emission of MTBE is variable throughout the year.

The effluents of both POTWs have been analyzed infrequently for MTBE. Concentrations varied greatly between facilities (4.1-220 µg/L MTBE). Effluent concentrations from the Los Angeles County Sanitation Districts' JWPCP facility were comparable to those from refineries in California, reflecting the presence of refinery wastewater in the treatment plant's influent. The combined mass emission of MTBE from these POTWs was estimated to be 287.67 kg/day, nearly 20 times the emission from refinery discharge.

### **San Diego Bay**

No data were located describing MTBE concentrations in discharges to San Diego Bay. There are no POTWs or petroleum refinery discharges to San Diego Bay, and no other industrial inputs of MTBE to the bay were identified in the TRI database. Stormwater runoff entering San Diego Bay has not been analyzed for MTBE.

MTBE data were also not located for San Diego Bay receiving waters. However, it has been detected in the receiving waters of Mission Bay, 5 km north of San Diego Bay. Concentrations in Mission Bay ranged from 6.3 to 18.7 µg/L MTBE in 1998, with a mean of 11.2 µg/L. Like San Diego Bay, Mission Bay does not receive discharges from POTWs or industrial sources, but does receive inputs from urban runoff and year-round recreational boating activity.

### **Other southern California inputs**

Ten additional POTWs in southern California with ocean discharges were contacted, representing most of the additional municipal wastewater inputs to the region. Two stormwater monitoring agencies were also contacted, as well as the port districts for Los Angeles and Long Beach Harbors and a refinery in Wilmington.

Of the agencies contacted, only one stormwater agency (Ventura County Flood Control Department) has analyzed samples for MTBE. No MTBE was detected in their stormwater samples.



## **Summary**

Examination of the monitoring data available prior to May, 1999 shows that insufficient information is available to characterize the mass emission and receiving water concentration of MTBE for California's bays and coastal waters. While refinery discharges have been routinely monitored for MTBE for several years, only fragmentary data is available for POTW discharges, stormwater, and other inputs.

Review of the existing data indicate that POTWs represent a significant source of MTBE to the marine environment. In San Francisco Bay, two POTW discharges accounted for approximately 10% of the known emission of MTBE into the bay. Discharge from the JWPCP outfall system in Santa Monica Bay appears to represent over 90% of the MTBE input to this area.

Table 1. Summary of existing MTBE monitoring data. The most recent data obtained for 1997-99 from NPDES agency reports and from the Toxic Release Inventory (queried August 1999) are shown. Abbreviations: na = not available; nd = not detected.

Sample location/Category	Number of sites with data	MTBE	
		Concentration range (µg/L)	Estimated mass (kg/day)
<b>Humboldt Bay</b>			
Stormwater	1	nd	-
Groundwater Discharge	1	0.26	na
Receiving Water	1	0.28	-
<b>San Francisco Bay</b>			
POTW Effluent	2	3.9-21.0	6.31
Stormwater	1	2.2	na
Refinery Effluent	4	na	56.44
Receiving Water	1	nd	
<b>Santa Monica Bay</b>			
POTW Effluent	2	4.1-220	287.67
Refinery Effluent	1	610	15.34
<b>San Diego Bay</b>			
	0	-	-

Table 2. Existing MTBE discharge and receiving water data. Abbreviations: TRI = Toxic Release Inventory queried August 1999; na = data not available; nd = not detected.

<b>Sample type / Agency</b>	<b>Period covered</b>	<b>N</b>	<b>Concentration (µg/L)</b>	<b>Estimated mass (kg/day) discharged to water</b>	<b>Information source</b>
<b>Humboldt Bay</b>					
<u>Stormwater</u>					
Chevron Marine Terminal, Eureka	1/99 – 3/99	3	nd	nd	RWQCB 1
	1998	1	nd – 6.5	na	
	1997	5	10 – 6,300	na	
<u>Groundwater</u>					
Pepsi-Cola, Eureka	1998	1	1.1 – 1.4	na	RWQCB 1
	1997	8	nd - 1.6	na	
	1996	2	nd	nd	
<u>Receiving Water</u>					
Pepsi-Cola, Eureka	1998	5	nd – 1.4	-	RWQCB 1
	1997	1	nd	-	
<b>San Francisco Bay</b>					
<u>POTW</u>					
East Bay MUD	1/99	1	3.9	1.03	RWQCB 2
	1998	4	3.1 – 7.5	1.37	
	1997	4	2.9 – 12	1.92	
	1996	5	3 – 39	4.38	

<b>Sample type / Agency</b>	<b>Period covered</b>	<b>N</b>	<b>Concentration (µg/L)</b>	<b>Estimated mass (kg/day) discharged to water</b>	<b>Information source</b>
City & Co. of San Francisco Southeast outfall	10/98	?	21	5.29	RWQCB 2
	12/96	?	4.3	1.10	
<u>Stormwater</u>					
Alameda County Clean Water Program, Castro Valley Creek	10/97 – 2/98	5	nd – 3.3	na	RWQCB 2
<u>Petroleum</u>					
Chevron Richmond Refinery	1997		na	27.40	TRI
	1996		na	28.50	
Exxon Benicia Refinery	1997		na	0.55	TRI
Shell Martinez Refinery	1997		na	26.03	TRI
Tosco Rodeo Refinery	1998		210	2.47	RWQCB 2
	1997		2,950	39.18	
	1996		1,250	13.97	
<u>Receiving Water</u>					
Central Contra Costa S.D. Suisun Bay	1999	2	<2.5	nd	RWQCB 2
<b>Santa Monica Bay</b>					
<u>POTW</u>					
Los Angeles County Sanitation Districts; Joint Water Pollution Control Plant	7/98, 9/98	2	220	282.19	Agency

<b>Sample type / Agency</b>	<b>Period covered</b>	<b>N</b>	<b>Concentration (µg/L)</b>	<b>Estimated mass (kg/day) discharged to water</b>	<b>Information source</b>
City of Los Angeles Hyperion Wastewater Treatment Plant	10/98, 1/99	2	3.2, 4.1	4.38, 5.48	Agency
<u>Petroleum</u>					
Chevron El Segundo Refinery	2/99	1	610	15.34	Agency
	1998	3	130 – 1,100	20.0	
	11/97	1	400	11.78	
<b>San Diego Bay</b>					
No Data Located	-		-	-	-
<b>Other Southern California Inputs and Receiving Waters</b>					
<u>Stormwater</u>					
Ventura County FCD	1997 - 98		nd	nd	Agency
<u>Receiving Water</u>					
City of San Diego Mission Bay	1998	4	6.3 – 18.7	-	EMCON 1999
	1996	1	<1.4 – 58.6	-	
		1			

**State Water Resources Control Board NPDES Survey**

Results of State Water Resources Control Board survey for NPDES discharge to the marine environment. Concentrations below the reporting limit were assigned a value of 0 µg/L for all calculations. Abbreviations: P = POTW; R = refinery; O = other; C. Bay = Carmel Bay; H. Bay = Humboldt Bay; Mis. Bay = Mission Bay; Mon. Bay = Monterey Bay; Mor. Bay = Morro Bay; S.D. Bay = San Diego Bay; S.F. Bay = San Francisco Bay; S.M. Bay = Santa Monica Bay.

NPDES Permit Agency	Category	Discharge site	Number of sampling events	MTBE (µg/L)		MTBE (kg/day)
				Mean	Range	Mass
<b>North Coast Region</b>						
Arcata	P	H. Bay	4	< 0.5	< 0.5	0.00
Crescent City	P	Ocean	4	0.66	< 0.05 - 1.5	< 0.01
Eureka	P	H. Bay	4	< 0.5	< 0.5	0.00
Fort Bragg	P	Ocean	4	< 0.5	< 0.5	0.00
<b>San Francisco Bay Region</b>						
Benicia, City of	P	S.F. Bay	5	1.04	< 0.5 - 3.5	0.01
Burlingame, City of	P	S.F. Bay	5	8.04	6.2 – 10.0	0.11
Central Contra Costa Sanitary District	P	S.F. Bay	5	6.08	2.4 - 16.6	1.01
Central Marin Sanitation Agency	P	S.F. Bay	5	1.18	0.9 - 1.5	0.04
Delta Diablo Sanitation District	P	S.F. Bay	5	< 1	< 1	0.00
Dublin San Ramon Services District	P	S.F. Bay	5	2.64	1.5 – 4.0	0.09
East Bay Municipal Utility District	P	S.F. Bay	5	4.32	3.35 - 6.55	1.14
Fairfield-Suisun Sewer District	P	S.F. Bay	5	0.44	< 0.5 - 0.6	0.02
Hayward, City of	P	S.F. Bay	5	0.56	< 0.5 - 1.03	0.03
Las Gallinas Valley Sanitary District of Marin County	P	S.F. Bay	6	< 0.5	< 0.5	0.00
Livermore, City of	P	S.F. Bay	5	1.68	1.3 - 2.3	0.03
Millbrae, City of	P	S.F. Bay	6	1.22	< 0.5 - 3.8	0.01
Mt. View Sanitation District	P	S.F. Bay	4	< 0.5	< 0.5	0.00
Novato Sanitary District - Ignacio Plant	P	S.F. Bay	5	< 0.5	< 0.5	0.00
Novato Sanitary District - Novato Plant	P	S.F. Bay	5	2.48	1.1 - 4.2	0.04
Oro Loma Sanitary District	P	S.F. Bay	5	1.74	0.7 - 3.6	0.10
Palo Alto, City of	P	S.F. Bay	5	1.19	< 0.5 - 2.22	0.11
Petaluma, City of	P	S.F. Bay	6	< 0.5	< 0.5	0.00
Pinole, City of	P	S.F. Bay	5	< 0.5	< 0.5	0.00
Richmond, City of	P	S.F. Bay	3	< 5	< 5	0.00
Rodeo Sanitary District	P	S.F. Bay	7	< 0.5	< 0.5 - < 1	< 0.01

NPDES Permit Agency	Category	Discharge site	Number of sampling events	MTBE ( $\mu\text{g/L}$ )		MTBE (kg/day)
				Mean	Range	Mass
San Francisco International Airport - Water Quality Control Plant	P	S.F. Bay	5	< 0.5	< 0.5	< 0.01
San Francisco, City and County - Southeast Treatment Plant	P	S.F. Bay	5	2.67	1.46 - 6.34	0.67
San Francisco, City and County - Treasure Island Treatment Plant	P	S.F. Bay	5	< 0.5	< 0.5	0.00
San Jose / Santa Clara WPCP	P	S.F. Bay	5	0.99	< 0.5 - 2.86	0.38
San Leandro, City of	P	S.F. Bay	5	3.12	1.86 - 4.69	0.06
San Mateo, City of	P	S.F. Bay	5	1.08	0.77 - 1.65	0.00
Sanitary District No. 5 of Marin County	P	S.F. Bay	5	< 0.5	< 0.5	0.00
Sausalito-Marín City Sanitary District	P	S.F. Bay	4	< 0.5	< 0.5	0.00
Sewerage Agency of Southern Marin	P	S.F. Bay	4	< 0.5	< 0.5	0.00
Sonoma Valley County Sanitation District	P	S.F. Bay	3	< 0.5	< 0.5 - < 1	0.00
South Bayside System Authority	P	S.F. Bay	5	37.01	1.26 - 57.5	2.66
South San Francisco, City of	P	S.F. Bay	5	2	1.0 - 3.0	0.07
Sunnyvale, City of	P	S.F. Bay	4	< 0.5	< 0.5	0.00
Union Sanitary District	P	S.F. Bay	4	2.96	< 1 - 9.55	0.33
Vallejo Sanitation and Flood Control District	P	S.F. Bay	5	0.58	< 0.5 - 0.8	0.03
West County Wastewater District	P	S.F. Bay	3	< 5	< 5	0.00
Chevron Richmond Refinery	R	S.F. Bay	5	38.34	20.5 - 71.5	0.65
Equilon Enterprises LLC - Shell	R	S.F. Bay	5	281.26	30.3 - 554	4.52
Exxon Company USA	R	S.F. Bay	5	54.6	31.6 - 81.9	0.41
Tosco Refining Company - San Francisco Area Refinery at Rodeo	R	S.F. Bay	5	34.31	0.5 - 154	0.25
California and Hawaiian Sugar	O	S.F. Bay	5	< 0.5	< 0.5	0.00
San Francisco International Airport - Industrial Wastewater Treatment Plant	O	S.F. Bay	5	0.38	< 0.5 - 1	< 0.01
North San Mateo County Sanitation District	P	Ocean	5	10.19	4.6 - 29.7	0.25
Pacifica, City of	P	Ocean	5	0.36	< 0.5 - 1.2	< 0.01
San Francisco, City and County - Ocean Side Treatment Plant	P	Ocean	5	< 0.5	< 0.5	0.00
Sewer Authority Mid-Coastside	P	Ocean	3	< 0.5	< 1 - < 2	0.00



NPDES Permit Agency	Category	Discharge site	Number of sampling events	MTBE ( $\mu\text{g/L}$ )		MTBE (kg/day)
				Mean	Range	Mass
<b>Central Coast Region</b>						
Morro Bay WWTP	P	Mor. Bay	4	12.42	9.7 - 15	0.26
Santa Barbara	P	Ocean	4	2.2	1.7 - 3.1	0.00
Carmel Area	P	C. Bay	4	< 0.5	< 0.5	0.00
Goleta SD	P	Ocean	4	< 5	< 5	0.00
Scotts Valley	P	Mon. Bay	4	< 2	< 2	0.00
Monterey Regional	P		4	< 5	< 5	0.00
Carpinteria	P	Ocean	3	< 5	< 5	0.00
Montecito Sanitary District	P	Ocean	4	< 5	< 5	0.00
Pismo Beach WWTP	P	Ocean	6	< 5	< 5	0.00
Watsonville	P	Mon. Bay	4	< 1	< 1	0.00
Santa Cruz WWTP	P	Mon. Bay	4	0.14	< 0.5 – 0.58	< 0.01
Chevron Gaviota	O	Ocean	4	< 5	< 5	0.00
<b>Los Angeles Region</b>						
L.A. City Hyperion	P	S.M. Bay	4	3.88	3.1 - 4.34	5.40
Chevron	R	S.M. Bay	4	1877.50	630 - 4,000	45.79
LACSD JWPCP	P	S.M. Bay	3	123.33	110 – 130	158.71
LA City Terminal Island	P	Ocean	4	15.30	3.28 - 25.5	0.96
Equilon	R	Ocean	6	87.83	< 1 - 210	0.74
<b>Santa Ana Region</b>						
OCSA	P	Ocean	5	2.06	1.2 - 2.9	1.81
<b>San Diego Region</b>						
Point Loma WWTP	P	Ocean	5	1.45	1.2 - 2.8	0.96
San Diego, ITP	P	Ocean	4	0.28	< 1 - 1.1	0.03
Encina WA	P	Ocean	5	< 5	< 5	0.00
Aliso WMA	P	Ocean	4	< 5	< 5	0.00
Fallbrook PUD	P	Ocean	4	< 20	< 5 - < 20	0.00
San Elijo JPA	P	Ocean	4	< 5	< 5	0.00
San Diego G&E, Beach Cities	O	Ocean	4	12.5	< 20 - 50	< 0.01
San Diego G&E, Metro	O	S.D. Bay	4	< 20	< 20	0.00
San Diego G&E, North Coast	O	Ocean	4	< 20	< 20	0.00
San Diego G&E, Orange County	O	Ocean	4	< 20	< 20	0.00
SeaWorld	O	Mis. Bay	6	13	3 - 22.8	0.11
San Diego Unified Port District	O	S.D. Bay	4	< 5	< 0.5 - < 5	0.00

NPDES Permit Agency	Category	Discharge site	Number of sampling events	MTBE ( $\mu\text{g/L}$ )		MTBE (kg/day)
				Mean	Range	Mass
UCSD	O	Ocean	2	< 2	< 2	0.00
Oceanside	P	Ocean	4	< 20	< 5 - < 20	0.00
Escondido	P	Ocean	4	< 10	< 10	0.00

## **Field Sampling Locations**

Location information for dry weather runoff and receiving water stations sampled between June and August 1999.

<b>Station</b>	<b>Location</b>	<b>Sample type</b>	<b>Depth (m)</b>	<b>Latitude (°)</b>	<b>Latitude (Min)</b>	<b>Longitude (°)</b>	<b>Longitude (Min)</b>	<b>Sampling site</b>
101	Halberson Shoreline	receiving	4	40	48.56100	124	9.23800	Humboldt Bay
102	Southport Channel-33B	receiving	7	40	44.55800	124	13.61000	Humboldt Bay
103	Arcata City POTW	receiving <sup>a</sup>	0	40	51.28400	124	5.43300	Humboldt Bay
104	Union Oil plant	receiving	3	40	47.86600	124	11.17000	Humboldt Bay
105	Chevron Terminal	receiving	6	40	46.67900	124	11.76000	Humboldt Bay
106	fuel docks (A&C St)	receiving	6	40	48.27900	124	10.48700	Humboldt Bay
107	Woodley Marina	receiving	5	40	48.45000	124	9.91100	Humboldt Bay
108	King Salmon Marina	receiving	2	40	44.20600	124	13.07700	Humboldt Bay
150	Martin Slough 1	stream		40	45.17400	124	10.77300	Humboldt Bay
151	Martin Slough 2	stream		40	45.67400	124	9.83800	Humboldt Bay
152	Cooper Canyon	stream		40	48.03700	124	9.14100	Humboldt Bay
153	Janes Creek	stream		40	52.38200	124	5.82800	Humboldt Bay
154	Gannon Slough	stream		40	52.01300	124	4.88300	Humboldt Bay
155	Jacoby Creek	stream		40	50.26900	124	4.19900	Humboldt Bay
201	Redwood Creek	receiving	11	37	33.55000	122	12.55000	S.F. Bay
202	Yerba Buena Island	receiving	7	37	49.45000	122	21.00500	S.F. Bay
203	Pinole Point	receiving	6	38	1.63300	122	21.83300	S.F. Bay
204	Chevron, northern California	receiving	16	37	58.25000	122	25.78300	S.F. Bay
205	Shell Martinez Refining Co.	receiving	8	38	1.98300	122	7.70000	S.F. Bay
206	Exxon refinery	receiving	7	38	3.40000	122	7.00500	S.F. Bay
207	Oakland Marina	receiving	2	37	46.78300	122	15.11700	S.F. Bay
208	Redwood Creek Marina	receiving	3	37	29.83300	122	13.41700	S.F. Bay
209	Martinez Marina	receiving	2	38	1.58300	122	8.25000	S.F. Bay
210	East Bay MUD	receiving	11	37	48.91600	122	20.88300	S.F. Bay
250	Walnut Creek	stream		37	57.53300	122	3.06700	S.F. Bay

<b>Station</b>	<b>Location</b>	<b>Sample type</b>	<b>Depth (m)</b>	<b>Latitude (°)</b>	<b>Latitude (Min)</b>	<b>Longitude (°)</b>	<b>Longitude (Min)</b>	<b>Sampling site</b>
251	Rheem Creek	stream		37	58.38300	122	20.63300	S.F. Bay
252	Guadalupe River I	stream		37	21.51700	121	54.91700	S.F. Bay
253	Calabasas Creek	stream		37	21.70000	121	59.13300	S.F. Bay
254	Guadalupe River II	stream		37	23.71700	121	56.40000	S.F. Bay
255	San Lorenzo Creek	stream		37	40.78300	122	4.86700	S.F. Bay
256	Matadero Creek	stream		37	25.10000	122	8.18300	S.F. Bay
257	Wildcat Creek	stream		37	57.21700	122	20.31700	S.F. Bay
258	San Ramon Creek	stream		37	46.41700	121	58.95000	S.F. Bay
259	San Francisquito Creek	stream		37	26.85000	122	10.16700	S.F. Bay
260	Coyote Creek, northern California	stream		37	23.75000	121	54.91700	S.F. Bay
401	L.A. Harbor	receiving	14	33	43.30833	118	16.20000	L. A. Harbor
402	LACSD Outfall - 8C	receiving	60	33	41.91000	118	20.14000	S. M. Bay
403	LACSD Control - 0C	receiving	6	33	48.43000	118	25.83000	S. M. Bay
404	King Harbor	receiving	7	33	50.75000	118	23.93000	S. M. Bay
405	Manhattan Beach	receiving	13	33	52.65624	118	25.38877	S. M. Bay
406	Chevron Outfall	receiving	11	33	54.48333	118	26.28333	S. M. Bay
407	Ballona Creek	receiving	4	33	57.56833	118	27.56500	S. M. Bay
408	Marina del Rey	receiving	4	33	58.19500	118	26.91667	S. M. Bay
409	Hyperion Outfall - Z2	receiving	60	33	54.45000	118	31.46667	S. M. Bay
410	Hyperion Station C9	receiving	60	33	52.11667	118	29.61667	S. M. Bay
411	Hyperion Station C3	receiving	61	33	59.38333	118	36.03333	S. M. Bay
450	San Gabriel River Willow	stream		33	48.21500	118	12.31100	So. Cal. Bight
451	L. A. River	stream		33	48.34500	118	24.16900	So. Cal. Bight
452	Dominguez Channel Sepulveda	stream		33	48.36500	118	41.10000	L. A. Harbor
453	Ballona Creek	stream		33	59.80200	118	31.06600	S. M. Bay
455	Santa Monica Canyon	stream		34	1.73700	118	6.22000	S. M. Bay
456	Malibu Creek	stream		34	2.52000	118	11.57100	S. M. Bay

<b>Station</b>	<b>Location</b>	<b>Sample type</b>	<b>Depth (m)</b>	<b>Latitude (°)</b>	<b>Latitude (Min)</b>	<b>Longitude (°)</b>	<b>Longitude (Min)</b>	<b>Sampling site</b>
457	Santa Clara River	stream		34	14.58400	119	4.75300	So. Cal. Bight
458	Revlon Slough	stream		34	7.88400	119	18.47600	So. Cal. Bight
459	Ventura River	stream		34	16.91500	119	4.91500	So. Cal. Bight
460	Cerritos Channel	stream		33	47.73500	118	5.10900	So. Cal. Bight
461	Calleges Creek	stream		34	6.72800	119	5.44400	So. Cal. Bight
462	Dominguez Channel at PCH	stream		33	47.51600	118	23.68100	L. A. Harbor
463	San Gabriel River Firestone	stream		33	55.66400	118	0.48700	So. Cal. Bight
464	San Gabriel River Valley	stream		34	3.14900	118	13.78700	So. Cal. Bight
850	San Diego Creek	stream		33	39.07900	117	55.51600	So. Cal. Bight
851	Santa Ana River	stream		33	42.54300	117	58.01700	So. Cal. Bight
852	Talbert Channel	stream		33	41.19900	117	0.90100	So. Cal. Bight
	Winterberg Channel East Garden							
853	Grove at Edwards	stream		33	43.05800	118	14.36900	So. Cal. Bight
854	Coyote Creek	stream		33	48.20200	118	3.89600	So. Cal. Bight
901	North Bay 1	receiving	10	32	41.67333	117	14.04500	San Diego Bay
902	Shelter Island Yacht Basin	receiving	5	32	43.08833	117	13.56667	San Diego Bay
903	Harbor Island West Basin	receiving	4	32	43.65667	117	12.45333	San Diego Bay
904	North Bay Anchorage	receiving	10	32	43.21667	117	11.00000	San Diego Bay
905	Middle Bay	receiving	4	32	40.70333	117	8.80000	San Diego Bay
906	Chollas Creek Channel	receiving	6	32	41.26333	117	7.82500	San Diego Bay
907	Free Anchorage	receiving	4	32	39.02500	117	8.00000	San Diego Bay
908	Sweetwater Channel	receiving	12	32	38.79500	117	7.23667	San Diego Bay
909	South Bay Channel	receiving	3	32	37.31500	117	7.23167	San Diego Bay
910	Chula Vista Harbor	receiving	6	32	37.41833	117	6.37500	San Diego Bay
911	Vacation Is. Dock	receiving	2	32	46.41000	117	13.96500	Mission Bay
912	De Anza Cove Dock	receiving	2	32	47.57600	117	12.59900	Mission Bay
950	Tijuana River	stream		32	32.94800	117	9.20100	So. Cal. Bight

<b>Station</b>	<b>Location</b>	<b>Sample type</b>	<b>Depth (m)</b>	<b>Latitude (°)</b>	<b>Latitude (Min)</b>	<b>Longitude (°)</b>	<b>Longitude (Min)</b>	<b>Sampling site</b>
951	Switzer Creek	stream		32	42.22400	117	10.20200	So. Cal. Bight
952	San Diego River	stream		32	45.85800	117	13.39100	So. Cal. Bight
954	Rose Creek	stream		32	48.32700	117	13.37300	So. Cal. Bight
955	Carroll Creek	stream		32	53.97700	117	13.41900	So. Cal. Bight
956	Pensaquitos Creek	stream		32	54.26900	117	51.48600	So. Cal. Bight
958	San Elijo Creek	stream		33	0.66700	117	21.46700	So. Cal. Bight
959	San Luis Rey River	stream		33	13.21300	117	39.68300	So. Cal. Bight
960	Santa Margarita River	stream		33	14.27100	117	10.77300	So. Cal. Bight
962	San Juan Creek	stream		33	29.51600	117	45.02300	So. Cal. Bight
963	Aliso Creek	stream		33	30.72000	117	6.50700	So. Cal. Bight

<sup>a</sup> Sample collected from outfall pipe.

## **MTBE Concentrations in Dry Weather Runoff**



MTBE concentrations measured in dry weather runoff inputs to coastal waters of 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 mass calculations. The mass estimate represents the average for all samples collected, except where noted.

Station Number	Sample Location	Collection Date	MTBE (µg/L)	MTBE (kg/day)
				Mass
<b>Humboldt Bay</b>				
153	Janes Creek	6/16/99	< 0.5	0.00
154	Gannon Slough	6/16/99	< 0.5	0.00
155	Jacoby Creek	6/16/99	< 0.5	0.00
152	Cooper Canyon	6/16/99	< 0.5	0.00
150	Martin Slough site 2	6/16/99	< 0.5	0.00
151	Martin Slough site 1	6/16/99	< 0.5	0.00
<b>San Francisco Bay</b>				
251	Rheem Creek	6/22/99	< 0.5	0.00
257	Wildcat Creek	6/22/99	< 0.5	0.00
250	Walnut Creek	6/22/99	< 0.5	0.00
258	San Ramon Creek	6/22/99	< 0.5	0.00
255	San Lorenzo Creek	6/22/99	0.7	< 0.01
		7/13/99	0.5	
		7/14/99	< 0.5	
		8/4/99	< 0.5	
		8/5/99	< 0.5	
260	Coyote Creek	7/14/99	0.8	0.05
		8/4/99	0.7	
		8/5/99	0.7	
252	Guadalupe River site I	6/22/99	< 0.5	0.00
254	Guadalupe River site II	6/22/99	1.0	0.19
		7/13/99	0.8	
		7/14/99	0.7	
		8/4/99	1.0	
253	Calabastas Creek	6/22/99	< 0.5	0.00
		8/5/99	1.1	
256	Matadero Creek	6/22/99	< 0.5	0.00

Station Number	Sample Location	Collection Date	MTBE (µg/L)	MTBE (kg/day)
				Mass
259	San Francisquito Creek	6/22/99	< 0.5	0.00
<b>L.A. Region</b>				
459	Ventura River	6/9/99	< 0.5	0.00
457	Santa Clara River	6/9/99	< 0.5	0.00
458	Revlon Slough	6/9/99	< 0.5	0.00
461	Callegues Creek	6/9/99	< 0.5	0.00
456	Malibu Creek	6/9/99	< 0.5	0.00
455	Santa Monica Canyon	6/11/99	< 0.5	0.00
453	Ballona Creek	6/11/99	0.6	0.05
		7/12/99	< 0.5	
		7/13/99	< 0.5	
		8/3/99	1.4	
		8/4/99	1.3	
452	Dominguez Channel at Sepulveda bridge	6/9/99	1.2 <sup>a</sup>	
462	Dominguez Channel at Pacific Coast Highway	7/12/99	2.1 <sup>a</sup>	
		7/13/99	1.4 <sup>a</sup>	
451	Los Angeles River	6/11/99	< 0.5	0.00
		7/12/99	< 0.5	
		7/13/99	< 0.5	
460	Los Cerritos Channel	6/11/99	< 0.5	0.00
464	San Gabriel River south of Valley Blvd.	7/12/99	0.6	0.07
		7/13/99	0.6	
463	San Gabriel River at Firestone Blvd.	7/12/99	3.7	< 0.01
		7/13/99	1.1	
		8/3/99	1.3	
		8/4/99	6.9	
450	San Gabriel River at Willow Street	6/11/99	52.0	0.84 <sup>b</sup>
		7/12/99	2.1	
		7/13/99	1.3	

Station Number	Sample Location	Collection Date	MTBE (µg/L)	MTBE (kg/day)
				Mass
		8/3/99	0.85	
		8/4/99	1.4	
<b>Santa Ana Region</b>				
854	Coyote Creek	6/11/99	< 0.5	0.00
853	East Garden Grove Wintersburg Channel	6/18/99	< 0.5	0.00
852	Talbert Channel	6/18/99	< 0.5	0.00
851	Santa Ana River	6/18/99	< 0.5	0.00
850	San Diego Creek	6/17/99	< 0.5	0.00
<b>San Diego Region</b>				
963	Aliso Creek	6/17/99	< 0.5	0.00
962	San Juan Creek	6/17/99	< 0.5	0.00
960	Santa Margarita River	7/14/99	< 0.5	0.00
959	San Luis Rey River	6/17/99	< 0.5	0.00
958	San Elijo Creek	6/17/99	< 0.5	0.00
956	Pensaquitos Creek	6/16/99	< 0.5	0.00
955	Carroll Creek	6/16/99	< 0.5	0.00
954	Rose Creek	6/16/99	< 0.5	0.00
952	San Diego River	6/16/99	< 0.5	0.00
951	Switzer Creek	6/16/99	1.5 <sup>a</sup>	
			3.4 <sup>a</sup>	
			2.8 <sup>a</sup>	
950	Tijuana River	6/16/99	< 0.5	0.00

<sup>a</sup> Sample was 80-100% seawater.

<sup>b</sup> Median value

## **MTBE Concentrations in Receiving Waters**

MTBE concentrations measured in California receiving water samples. Only locations with detectable amounts of MTBE are shown. A value of 0 µg/L was used for concentrations below the reporting limit (0.5 µg/L) for all calculations. Abbreviations: M = marina; P = Publicly Owned Treatment Works; R = refinery; O = other.

Station Number	Sample Location	Category	Collection Date	Number of Depths Sampled	MTBE (µg/L)	
					Mean	Range
<b>Humboldt Bay</b>						
108	King Salmon Marina	M	6/15/99	2	0.35	<0.5, 0.7
			7/15/99	2	< 0.5	< 0.5
<b>San Francisco Bay</b>						
207	Oakland Marina	M	6/21/99	2	0.8	0.7, 0.9
			7/13/99	2	1.9	1.7, 2.1
201	Redwood Creek Marina	M	6/21/99	2	1.8	1.2, 2.4
			7/14/99	2	1.35	< 0.5, 2.7
209	Martinez Marina	M	6/21/99	2	1.1	0.7, 1.5
			7/13/99	2	0.75	< 0.5, 1.5
<b>Santa Monica Bay</b>						
402	PV-8C	P	6/8/99	4	< 0.5	< 0.5
			7/20/99	4	0.18	< 0.5 - 0.7
404	King Harbor	M	6/8/99	2	1.2	< 0.5, 2.4
			7/20/99	2	1.1	0.9, 1.3
408	Marina del Rey	M	6/8/99	2	3.9	1.9, 5.9
			7/20/99	2	7.7	6.9, 8.5
406	Chevron Outfall	R	6/8/99	3	0.3	< 0.5 - 0.9
			7/20/99	4	2.6	< 0.5 - 9.9
407	Ballona Creek	O	6/8/99	2	1.55	0.7, 2.4

Station Number	Sample Location	Category	Collection Date	Number of Depths Sampled	MTBE ( $\mu\text{g/L}$ )	
					Mean	Range
			7/20/99	2	0.65	0.6, 0.7
410	Hyperion-C9	O	6/8/99	4	< 0.5	< 0.5
			7/20/99	4	0.12	< 0.5 – 0.5
<b>Los Angeles Harbor</b>						
401	Main Channel	O	6/8/99	2	0.3	< 0.5, 0.6
			7/20/99	2	1.0	1.0
<b>Mission Bay</b>						
911	Vacation Island Dock	M	6/10/99	1	7.4	-
			7/21/99	1	21.0	-
912	De Anza Cove Dock	M	6/10/99	1	18.0	-
			7/21/99	1	34.0	-
<b>San Diego Bay</b>						
902	Shelter Island Yacht Basin	M	6/10/99	2	2.0	1.3, 2.7
			7/21/99	2	3.5	2.1, 4.9
903	Harbor Island West Basin	M	6/10/99	2	2.35	1.9, 2.8
			7/21/99	2	3.6	2.8, 4.4
901	North Bay 1	O	6/10/99	2	1.5	1.2, 1.8
			7/21/99	2	4.05	0.7, 7.4
904	North Bay Anchorage	O	6/10/99	2	1.45	1.4, 1.5
			7/21/99	2	2.25	1.6, 2.9

Station Number	Sample Location	Category	Collection Date	Number of Depths Sampled	MTBE ( $\mu\text{g/L}$ )	
					Mean	Range
905	Mid Bay	O	6/10/99	2	1.1	1.0, 1.2
			7/21/99	2	2.6	2.5, 2.7
906	Chollas Creek Channel	O	6/10/99	2	1.25	1.2, 1.3
			7/21/99	2	2.6	2.6
907	Free Anchorage	O	6/10/99	2	1.1	1.1
			7/21/99	2	1.6	1.6
908	Sweetwater Channel	O	6/10/99	2	1.05	1.0, 1.1
			7/21/99	2	2.0	1.8, 2.2
909	South Bay Channel	O	6/10/99	2	0.8	0.8
			7/21/99	2	1.85	1.1, 2.6
910	Chula Vista Harbor	O	6/10/99	2	1.35	1.0, 1.7
			7/21/99	2	2.95	1.8, 4.1

## **Toxicity Test Results**



Results of the sea urchin embryo (*Strongylocentrotus purpuratus*) 72 h development test conducted 9/14/99.

Measured concentration		% Normally developed	Mean	Standard deviation	Number counted
0 mg/L	MTBE	98	97	0.8	4
0 mg/L	MTBE	97			
0 mg/L	MTBE	97			
0 mg/L	MTBE	96			
180 mg/l	MTBE	94	95	2.2	4
180 mg/l	MTBE	96			
180 mg/l	MTBE	92			
180 mg/l	MTBE	97			
425 mg/l	MTBE	99	98	2.2	4
425 mg/l	MTBE	100			
425 mg/l	MTBE	99			
425 mg/l	MTBE	95			
885 mg/l	MTBE	92	93	2.6	3
885 mg/l	MTBE	96			
885 mg/l	MTBE	91			
1,700 mg/l	MTBE	18	14	4.2	4
1,700 mg/l	MTBE	9			
1,700 mg/l	MTBE	16			
1,700 mg/l	MTBE	11			
3,350 mg/l	MTBE	0	0	0.5	4
3,350 mg/l	MTBE	1			
3,350 mg/l	MTBE	0			
3,350 mg/l	MTBE	0			

Results of the germination endpoint for the giant kelp (*Macrocystis pyrifera*) 48 h test conducted 9/18/99.

Measured concentration		% Germinated	Mean	Standard deviation	Number counted
0 mg/l	MTBE	100	99	1.3	5
0 mg/l	MTBE	100			
0 mg/l	MTBE	99			
0 mg/l	MTBE	100			
0 mg/l	MTBE	97			
81 mg/l	MTBE	98	98	1.8	5
81 mg/l	MTBE	96			
81 mg/l	MTBE	99			
81 mg/l	MTBE	96			
81 mg/l	MTBE	100			
160 mg/l	MTBE	99	97	1.5	5
160 mg/l	MTBE	98			
160 mg/l	MTBE	95			
160 mg/l	MTBE	98			
160 mg/l	MTBE	97			
430 mg/l	MTBE	98	98	0.5	5
430 mg/l	MTBE	98			
430 mg/l	MTBE	97			
430 mg/l	MTBE	97			
430 mg/l	MTBE	98			
755 mg/l	MTBE	92	96	2.3	5
755 mg/l	MTBE	98			
755 mg/l	MTBE	96			
755 mg/l	MTBE	97			
755 mg/l	MTBE	97			
1,600 mg/l	MTBE	93	94	2.9	5
1,600 mg/l	MTBE	95			
1,600 mg/l	MTBE	94			
1,600 mg/l	MTBE	98			
1,600 mg/l	MTBE	90			
3,250 mg/l	MTBE	70	75	5.5	5
3,250 mg/l	MTBE	76			
3,250 mg/l	MTBE	69			
3,250 mg/l	MTBE	80			
3,250 mg/l	MTBE	81			

Results of the germ tube growth endpoint for the giant kelp (*Macrocystis pyrifera*) 48 h test conducted 9/18/99.

Measured concentration		Germ Tube Length (µm)	Mean	Standard deviation	Number counted
0 mg/l	MTBE	15.9	16	0.9	5
0 mg/l	MTBE	15.1			
0 mg/l	MTBE	17.1			
0 mg/l	MTBE	17.1			
0 mg/l	MTBE	16.5			
81 mg/l	MTBE	16.2	15	0.5	5
81 mg/l	MTBE	15.4			
81 mg/l	MTBE	14.8			
81 mg/l	MTBE	15			
81 mg/l	MTBE	15.1			
160 mg/l	MTBE	15.7	15	1.0	5
160 mg/l	MTBE	16.2			
160 mg/l	MTBE	13.6			
160 mg/l	MTBE	15.1			
160 mg/l	MTBE	15.1			
430 mg/l	MTBE	13.9	14	0.4	5
430 mg/l	MTBE	13.9			
430 mg/l	MTBE	13.6			
430 mg/l	MTBE	13.3			
430 mg/l	MTBE	13			
755 mg/l	MTBE	10.4	11	0.7	5
755 mg/l	MTBE	11			
755 mg/l	MTBE	12.2			
755 mg/l	MTBE	11.9			
755 mg/l	MTBE	11			
1,600 mg/l	MTBE	9.9	10	0.6	5
1,600 mg/l	MTBE	10.4			
1,600 mg/l	MTBE	9.3			
1,600 mg/l	MTBE	9.3			
1,600 mg/l	MTBE	9			
3,250 mg/l	MTBE	6.1	6	0.2	5
3,250 mg/l	MTBE	5.8			
3,250 mg/l	MTBE	6.1			
3,250 mg/l	MTBE	5.8			
3,250 mg/l	MTBE	5.8			

Results of the amphipod (*Grandidierella japonica*) 96 h survival test conducted 9/13/99.

<b>Measured concentration</b>	<b>%Survival</b>	<b>Mean</b>	<b>Standard deviation</b>	<b>Number counted</b>
0 mg/L MTBE	100	90	10.0	5
0 mg/L MTBE	80			
0 mg/L MTBE	100			
0 mg/L MTBE	80			
0 mg/L MTBE	90			
19 mg/L MTBE	90	88	4.5	5
19 mg/L MTBE	90			
19 mg/L MTBE	90			
19 mg/L MTBE	80			
19 mg/L MTBE	90			
37 mg/L MTBE	90	86	5.5	5
37 mg/L MTBE	90			
37 mg/L MTBE	80			
37 mg/L MTBE	90			
37 mg/L MTBE	80			
82 mg/L MTBE	70	80	10.0	5
82 mg/L MTBE	70			
82 mg/L MTBE	90			
82 mg/L MTBE	80			
82 mg/L MTBE	90			
165 mg/L MTBE	70	58	8.4	5
165 mg/L MTBE	60			
165 mg/L MTBE	60			
165 mg/L MTBE	50			
165 mg/L MTBE	50			
328 mg/L MTBE	0	0	0.0	5
328 mg/L MTBE	0			
328 mg/L MTBE	0			
328 mg/L MTBE	0			
328 mg/L MTBE	0			

Results of mysid (*Holmesimysis costata*) survival 7 day test conducted 9/15/99.

<b>Measured concentration</b>		<b>% Survival</b>	<b>Mean</b>	<b>Standard deviation</b>	<b>Number counted</b>
0 mg/l	MTBE	100	96	8.9	5
0 mg/l	MTBE	100			
0 mg/l	MTBE	100			
0 mg/l	MTBE	80			
0 mg/l	MTBE	100			
20 mg/l	MTBE	100	88	11.0	5
20 mg/l	MTBE	80			
20 mg/l	MTBE	80			
20 mg/l	MTBE	100			
20 mg/l	MTBE	80			
40 mg/l	MTBE	100	76	32.9	5
40 mg/l	MTBE	80			
40 mg/l	MTBE	80			
40 mg/l	MTBE	100			
40 mg/l	MTBE	20			
90 mg/l	MTBE	80	72	30.3	5
90 mg/l	MTBE	20			
90 mg/l	MTBE	80			
90 mg/l	MTBE	100			
90 mg/l	MTBE	80			
180 mg/l	MTBE	40	44	21.9	5
180 mg/l	MTBE	40			
180 mg/l	MTBE	20			
180 mg/l	MTBE	80			
180 mg/l	MTBE	40			
322 mg/l	MTBE	0	0	0.0	5
322 mg/l	MTBE	0			
322 mg/l	MTBE	0			
322 mg/l	MTBE	0			
322 mg/l	MTBE	0			

Results of mysid (*Holmesimysis costata*) 7 day growth test conducted 9/15/99.  
 Abbreviation: NM = Not measured; all test organisms had died.

Measured concentration		Weight per Mysid (mg)	Mean	Standard deviation	Number counted
0 mg/l	MTBE	0.2626	0.2723	0.0244	5
0 mg/l	MTBE	0.2444			
0 mg/l	MTBE	0.2591			
0 mg/l	MTBE	0.2928			
0 mg/l	MTBE	0.3024			
20 mg/l	MTBE	0.2729	0.3004	0.0297	5
20 mg/l	MTBE	0.3007			
20 mg/l	MTBE	0.2684			
20 mg/l	MTBE	0.3305			
20 mg/l	MTBE	0.3296			
40 mg/l	MTBE	0.3134	0.3156	0.0690	5
40 mg/l	MTBE	0.296			
40 mg/l	MTBE	0.2248			
40 mg/l	MTBE	0.3267			
40 mg/l	MTBE	0.417			
90 mg/l	MTBE	0.421	0.2787	0.0973	5
90 mg/l	MTBE	0.1524			
90 mg/l	MTBE	0.2414			
90 mg/l	MTBE	0.2847			
90 mg/l	MTBE	0.2938			
180 mg/l	MTBE	0.2367	0.2729	0.0473	5
180 mg/l	MTBE	0.266			
180 mg/l	MTBE	0.3515			
180 mg/l	MTBE	0.2354			
180 mg/l	MTBE	0.275			
322 mg/l	MTBE	NM	NM	NM	0
322 mg/l	MTBE	NM			
322 mg/l	MTBE	NM			
322 mg/l	MTBE	NM			
322 mg/l	MTBE	NM			