

Sampling for Tributyltin (TBT) in Lake Tahoe Keys Marina, Lake Tahoe
and Shelter Island Yacht Basin
San Diego Bay, California

August 1991

INTRODUCTION

Tributyltin (TBT) has been found in high enough concentrations in coastal areas of California to pose a threat to marine life. A survey of ten marinas in six California lakes conducted during the summer of 1987 also revealed high concentrations of TBT in a ~~number of marinas in Lake Tahoe~~. The results of more extensive monitoring in September, 1987, indicated that an unacceptable hazard to aquatic life exists in Tahoe Keys Marina. Observed concentrations of TBT in the Tahoe Keys Marina exceeded chronic values (0.03 to 0.10 ug/L) and approached lethal levels (0.30 to 4.0 ug/L) for fish and invertebrates. Tissue residues in Lake Tahoe indicated fish in the main body of the lake were also exposed to TBT.

State legislation enacted at the end of 1988 restricted the use of TBT-based paints on boats shorter than 85 feet, thus eliminating the release of TBT in many freshwater harbors and greatly reducing the release in saltwater harbors. The state Department of Fish and Game and Department of Pesticide Regulation plan to continue jointly monitoring Tahoe Keys Marina and Shelter Island Yacht Basin (San Diego Bay) for several years to determine the effectiveness of the new regulations in lowering TBT residues in fresh and saltwater environments. Shelter Island Yacht Basin was chosen as the site for saltwater monitoring because of its extensive history of environmental monitoring of TBT.

Long-term monitoring of Tahoe Keys Marina and Shelter Island Yacht Basin began in summer 1988. At Tahoe Keys Marina, the concentration of TBT in water decreased while concentrations in sediment and tissue remained unchanged from 1987 (Harrington 1991). Results of the 1989 and 1990 monitoring indicated that residues in water, sediment and tissue were constant and much lower than in 1987 and 1988 at both Lake Tahoe and San Diego.

The alternative biocide for use in antifouling paints is copper, which is also highly toxic to fish and aquatic invertebrates. Copper concentrations in Californian marinas may increase as TBT concentrations decrease and therefore, will be monitored starting in 1991.

OBJECTIVE

The objectives of this monitoring program are to determine (a) whether changes in concentrations of TBT and the degradation product, dibutyltin (DBT), will occur over time in water, sediment and biological tissue and (b) whether concentrations of copper will increase as a result of restricted TBT use.

PERSONNEL

This study will be conducted jointly by the Department of Fish and Game's (CDFG) Pesticide Investigations Unit, and the Department of Pesticide Regulation (CDPR) Environmental Hazards Assessment Program, under the overall supervision of Brian Finlayson (CDFG) and Kean Goh (CDPR). Other key personnel are listed below:

Project Leaders - Jim Harrington (CDFG), Pam Wofford (CDPR)

Field Sampling - Russ Stein and Jesse Leyva (CDPR)

Chemical Analyses - CDFG, Water Pollution Control Laboratory

Madeline Ames will be the primary contact person for other agencies and the public. All questions should be directed to her at (916) 324-8916.

STUDY DESIGN

Monitoring Locations

Sampling for the freshwater environmental will occur at Tahoe Keys Marina, Lake Tahoe (Figure 1) and for the saltwater environment at the Shelter Island Yacht Basin, San Diego Bay. The Shelter Island Yacht Basin and three sites in Tahoe Keys Marina will be monitored.

1991 Schedule

Sampling at Lake Tahoe will be conducted on September 17-19, 1991. Sampling at San Diego Bay will be conducted on November 19-21, 1991. Mussels will be transplanted from Bodega Bay, California, to Shelter Island Yacht Basin on August 16, 1991, to allow for three months bioaccumulation of TBT.

Collection

Water - At Lake Tahoe and San Diego Bay, six replicate samples for TBT and DBT analyses will be collected in one-liter polycarbonate bottles at mid-depth. Samples will be cooled on wet ice, then frozen on dry ice, and kept at a temperature of 0°C or less until analyzed. Samples for copper analysis will also be collected at mid-depth in 100-mL Nalgene^R linear polyethylene (LPE) bottles. Sample water for copper analysis will be filtered through a Gelman^R 25-mm plastic fiber filter (porosity of 0.45µm). Samples will be placed in 25-ml LPE bottles, preserved

LAKE TAHOE

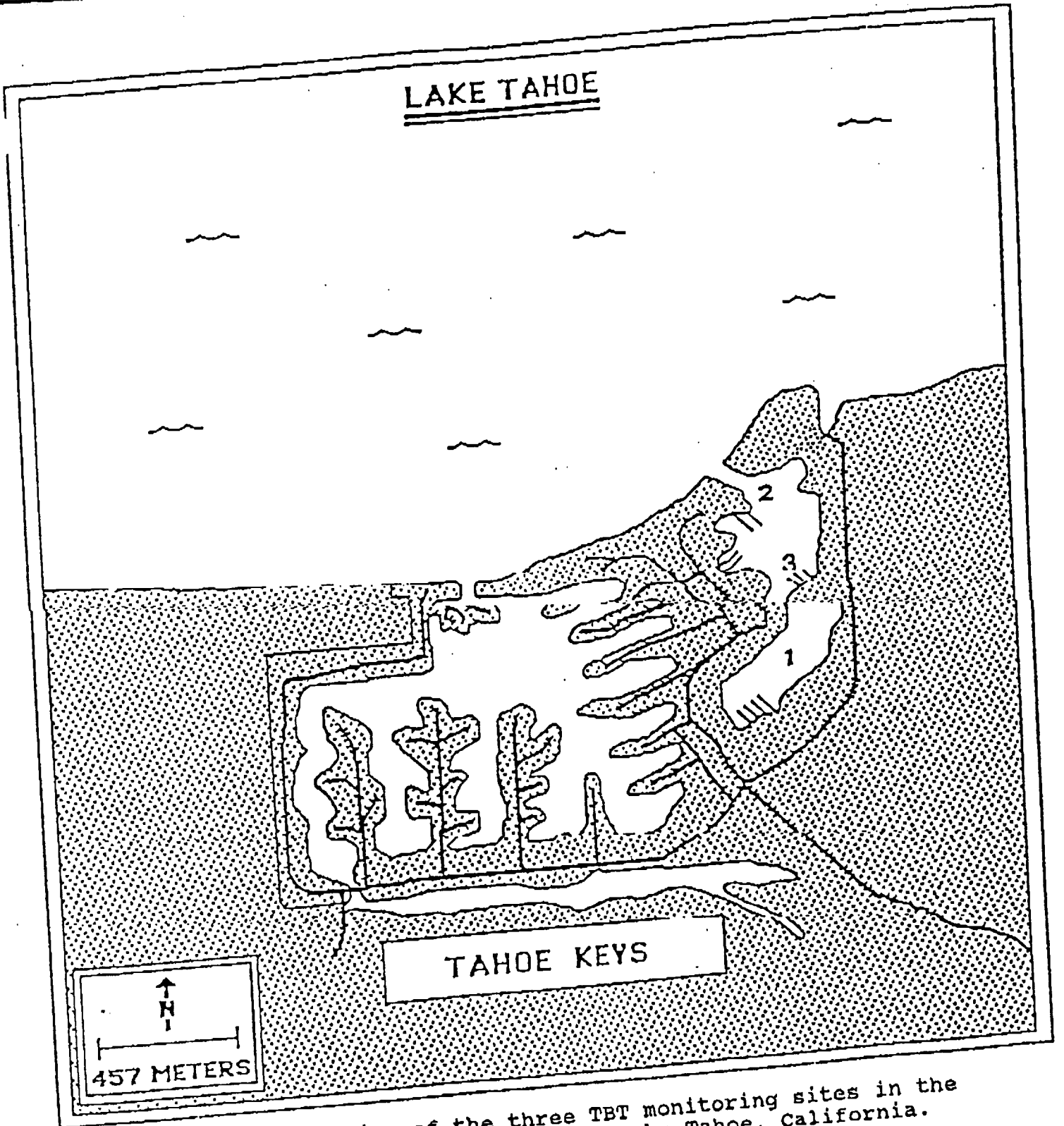


Figure 1. Location of the three TBT monitoring sites in the Tahoe Keys marina area, Lake Tahoe, California.

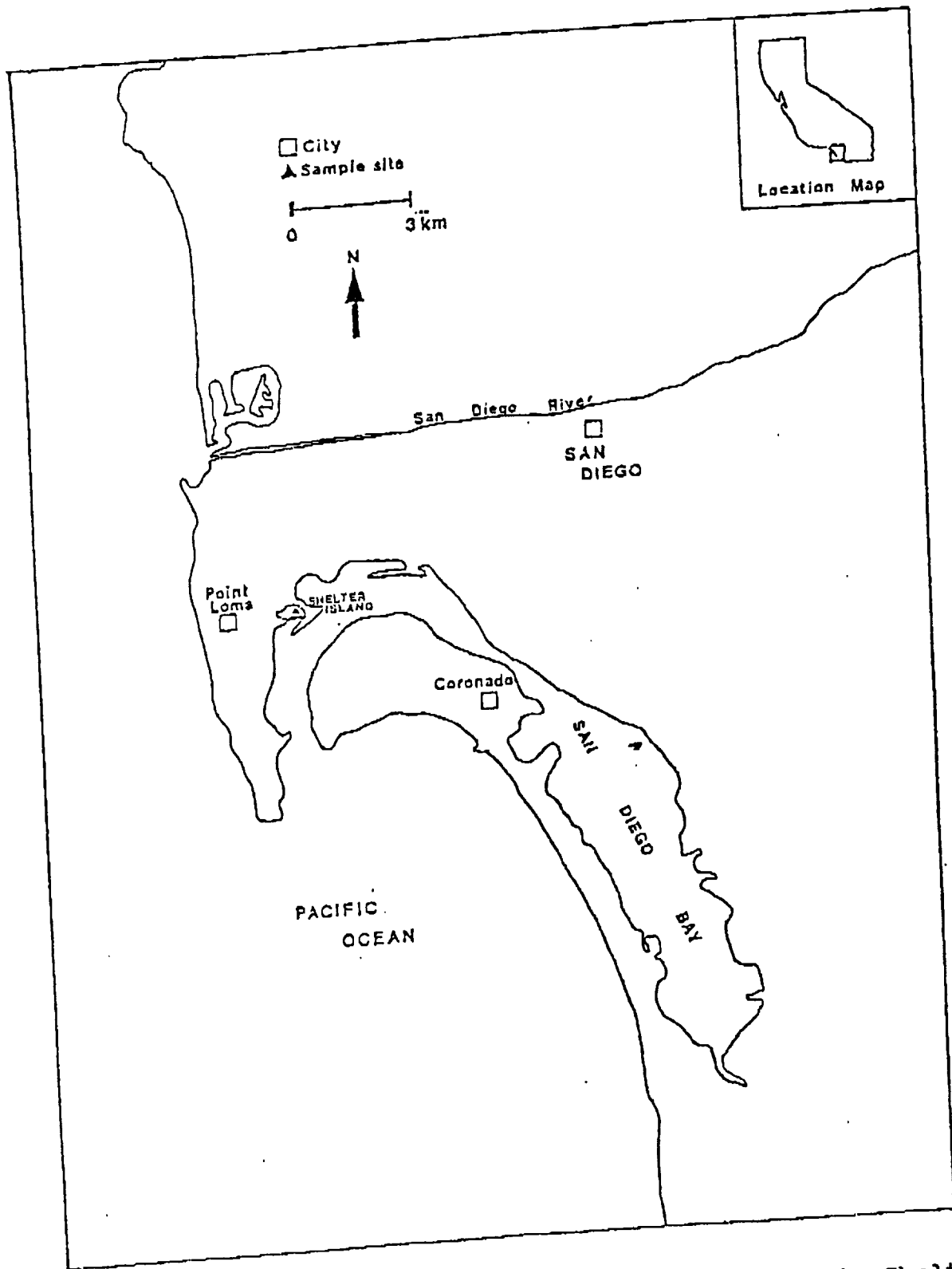


Figure 2. Location of tributyltin monitoring site in Shelter Island Yacht Harbor, San Diego Bay.

with 0.5 ml Ultrex^R grade HNO₃, and delivered to the CDFG laboratory for analysis.

Sediment - A stainless steel coring device will be used to obtain eight sediment samples for TBT, DBT, and copper analyses from three sites at Lake Tahoe and one site at San Diego Bay. The upper 10 cm of each core will be removed from the coring device and placed in polycarbonate jars. Sediment samples will be cooled on wet ice, then frozen on dry ice, and kept at a temperature of 0°C or less until analyses.

Biota - At Lake Tahoe, fish will be collected in the marina area using gill nets set on the bottom substrate. Twenty-four fish of the same species will be taken from gill nets to produce eight composite samples containing three fish each. Fillets from both sides of each fish will be removed and homogenized for analyses. The target species will be tui chub (*Gila bicolor*), or alternatively, Tahoe sucker (*Catostomus tahoemis*). Fish will be wrapped in aluminum foil, put in airtight plastic bags, placed on dry ice and kept at a temperature of 0°C or less until analyses.

Approximately 1000 mussels (*Mytilus californianus*) will be collected from Bodega Bay, California, and divided into 25 groups of 40 individuals. One group will be retained as a control and the other 24 groups will be divided into two sets of twelve groups. The mussel groups will be put into nylon bait bags,

transported to San Diego Bay, and suspended on weighted lines from two docks in the area of Shelter Island Boat Harbor. Ninety-days following the transplant, eight samples of mussels will be randomly chosen from the 12 groups collected from one set. Two sets will be used in case of vandalism. Mussels will be wrapped in aluminum foil, placed on dry ice and kept at 0°C or less until analysis. The entire body of the mussel, excluding the shell, will be removed for analysis.

Chemistry

The chemical analyses will be performed by CDFG and Battelle laboratories. TBT and DBT residues in sediment and biological tissues will be determined by electron-capture gas chromatography using the method of Tsuda et al. (1986). TBT and DBT concentrations in water will be determined by flame photometric gas chromatography using the method of Matthias et al. (1986). Copper will be analyzed using graphite furnace atomic absorption spectrophotometry.

Quality Control

Water - A portion of the volume from the six replicate water samples from each site will be composited and divided into three split samples for intralaboratory quality control and three split samples for interlaboratory quality control.

Sediment - Sediment cores will be thawed overnight, and homogenized. A portion of the volume from the eight replicate sediment samples from each site will be composited, homogenized, and divided into three split samples for intralaboratory quality control and three samples for interlaboratory quality control.

Biota - Fish from Lake Tahoe and mussels from San Diego Bay will be thawed overnight. A portion of the volume from the eight replicate fish samples will be composited, rehomogenized, and divided into three split samples for intralaboratory quality control and three split samples for interlaboratory quality control. Similar quality control will be done for the mussels.

Sample Allocation

The CDFG Water Pollution Control Laboratory (WPCL) will be responsible for TBT and DBT analysis of replicate water and sediment samples from Lake Tahoe and the CDPR Laboratory will be responsible for analyses of replicate water and sediment samples from San Diego. CDPR will contract analyses to Battelle Laboratory, Sequim, Washington. CDFG will be responsible for replicate tissue samples from both Lake Tahoe and San Diego. The CDFG Laboratory and CDPR will exchange split water and sediment samples for interlaboratory quality control. The U.S. Navy Laboratory in San Diego will be used by CDFG for interlaboratory quality control of tissue samples. CDFG will be responsible for all analyses of copper concentrations in water.

Estimated Number of Samples to be Analyzed for TBT and DBT

	<u>CDFG</u>		<u>CDPR</u>		<u>Navy</u>
	<u>Rep.</u>	<u>Split (OC)</u>	<u>Rep.</u>	<u>Split (OC)</u>	<u>Split (OC)</u>
Tahoe Keys					
Water	6	3		3	
Water (Cu)	6				
Sediment*	24	9		9	
Sediment (Cu)	24				
Fish	8	3			3
Shelter Island					
Water		3	6	3	
Water (Cu)	6				
Sediment		3	8	3	
Sediment (Cu)	8				
Fish	8	3			3
Total:	<u>90</u>	<u>24</u>	<u>14</u>	<u>18</u>	<u>6</u>

* 3 sites in Tahoe Keys Marina.

Harrington, J.M. 1991. Tributyltin residues in Lake Tahoe and San Diego, California. 1988. Environmental Services Branch Administrative Report No. 91-2, Sacramento, California

Tsuda, T., H. Nakanishi, T. Morita, and J. Takebayashi. 1986. Simultaneous gas chromatographic determination of dibutyltin and tributyltin compounds in biological and sediment samples. J. Assoc. Off. Che. 69:9181-984.

Matthias, C., J. Bellama, G. Olson, and F. Brinkman. 1986. Comprehensive butylmethtin species at ultratrace levels using simultaneous hydridization/extraction with gas chromatography-flame photometric detection. Environ. Sci. Technol. 20:609-615.