ABSTRACT

A monitoring survey of butyltin concentrations was conducted in San Diego Bay in February, 1986. Intensive sampling was designed to differentiate tidal, vertical and regional variability components. Yacht harbors and marinas had by far the highest concentration of tributyltin within San Diego Bay, ranging from 0.027 to 0.235 ug/l. The lowest tributyltin concentrations, frequently below detection, were found in the southern part of the bay, where water residence time was longest. Navy berthing areas and the northern part of the bay had intermediate values, usually in the range of 0.005-0.015 ug/l. Compared to data from a 1984 baseline survey, 1986 tributyltin concentrations decreased in all regions, however, total butyltin increased slightly, suggesting accumulation of degradation products. Tide and depth were important in determining tributyltin concentration variability but the degree of effect was sample station dependent. Yacht harbors and marinas can regionally be considered a tributyltin source while the southern bay can regionally be considered a sink.

INTRODUCTION

National and international attention has recently been focused on the use of organotin antifouling coatings because of their potential toxicity and not their occurrence of tributyltin (TBT) paint leachates. A number of authors have reported acute and chronic toxicity values for marine organisms in the range of 0.1 to 1 ug/l TBT concentrations for mussels and mussel larvae [1, 2], copepods [3], oysters [4], algae [5] and mysid shrimp [6]. In response to the concern about the potential effects of TBT on the aquatic environment, the Environmental Protection Agency (EPA) has initiated a Special Review of pesticide products containing TBT used as antifoulants [7]. In addition the EPA is developing a water quality criteria and several states are in the process of establishing water quality standards and point source discharge limits under the National Pollution Discharge Elimination System (NPDES) permitting process.

Several authors have documented the presence of TBT in the aquatic environment. Concentrations as high as 2.25 ug TBT/l have been measured in marinas in the U.K. during summer months [8, 9]; lower to non-measurable values were found in open areas of estuaries and during the winter months, documenting a seasonal effect relatable to boating activity. Tributyltin concentrations as high as 29 ug TBT/l were reported in freshwater marinas and 0.84 ug TBT/l in Toronto Harbor (10) with significant concentrations in the surface microlayer (up to 60.7 ug TBT/l in one marina).

During the last several years we have measured TBT levels in San Diego Bay where the highest concentrations were found in yacht harbors (summer maximum of 0.93 ug TBT/l) and increases in TBT levels in marinas were indicated over a 2 1/2 year period [11]. Reported work documenting environmental concentrations of organotins has not focused on the statistical aspects of monitoring nor on short-term variability (e.g., influence of tides) nor has the effect of depth (e.g., 2 layer estuarine systems) been addressed. Very little information on the reliability and variability of measured butyltin values has been reported.

The objective of the work reported here was to evaluate the importance of depth and short-term tidal variability on butyltin concentrations based on nearly synoptic sampling in San Diego Bay. We also wanted to evaluate whether groups of sampling stations could be combined to compare regional differences based on flushing and TBT use characteristics. These regional data could then be compared to baseline and future monitoring data to evaluate significant changes in water column butyltin concentration over time that may be relatable to changes in environmental flux (e.g., paint leach rates) or use.

Based on predicted large fuel savings and increased capabilities, the U.S. Navy has proposed to slowly implement tributyltin containing coatings into the fleet over the next 5 to 10 years. An Environmental Assessment (EA) was completed to evaluate potential impacts to the marine environment from fleet use of these coatings (12). As outlined in the EA, the Navy intends to monitor butyltins at major Navy harbors during the early stages of fleet implementation. The monitoring program has three primary objectives: (1) measure organotin concentrations in selected harbors during fleet implementation to determine if critical levels are being approached or exceeded in sensitive areas, (2) monitor long-term changes in TBT levels and estimate Navy contribution to cumulative TBT loading and (3) provide a data base to test predictive dynamic estuarine models. The
work reported here represents a prototype monitoring survey the results of which will be used to evaluate vertical, spatial and temporal variability and to estimate the adequacy of sample size for future monitoring efforts.

METHODS AND MATERIALS

Survey Methodology

A subset of the San Diego Bay baseline survey stations [13] were selected for monitoring during February 1986. Seventeen stations (Figure 1) were chosen for intensive water sampling. Samples were collected in triplicate during three tidal stages at two depths, 0.5m below the surface and 1m above the bottom. To facilitate statistical comparisons, four regions were selected based on a combination of flushing characteristics and use patterns (Figure 1). The northern bay region (North) is characterized by high current velocities and rapid flushing rates and encompasses most of the shipping channel and dredged areas in the central and western portions of the bay. Monitor stations 2C, 6A, 13, 18 and 33 were included in this region. The southern bay (South) is mostly shallow, with low velocity currents and longer water residence times. South Bay is also ecologically important as a nursery ground for numerous fish and invertebrate species. Monitoring stations 35, 42, 44A, 46 and 48 were included in this region. The areas of Naval use (Navy) include the Naval Station, carrier piers on North Island Naval Station, the Naval Amphibious Base and the Submarine Base at Ballast Point. These areas are moderately well flushed and include the regions within and adjacent to berthing areas. Stations 15, 20, 26 and 29 make up this region. Marinas and commercial boat basins (Yacht) are the principal TBT source areas and are characterized by moderate to dense aggregations of yachts and small commercial craft in enclosed embayments. Stations 7 and 10 were considered Yacht stations. These regions were chosen as probable sources (Yacht and Navy regions) and sinks (North and South regions) of butyltins. At two stations, near the harbor entrance (station 2C) and at midbay (station 18), intensive vertical sampling and measurement of physical/chemical parameters were conducted to evaluate the vertical distribution of butyltin. Two boats were used to collect approximately simultaneous (within 20 minutes of high, mid- and low tide) water samples at the other 15 stations. In addition to the monitoring stations a single set of triplicate samples was collected from 6 yacht harbors 0.5 m below the surface at low tide (stations 8, 11, 10C, 16, 26B and 49B). Water samples were collected with a recently developed sampling device in which the samples are frozen and stored in 1 liter polycarbonate bottles until analysis, reducing the chance of contamination when transferred from sampler to container. Briefly, the device consists of three polycarbonate bottles attached to a line 1 m above a 4 kg weight. The polypropylene caps have 1.5 cm holes drilled in the tops, a neoprene stopper is placed in the hole of each bottle and attached to a secondary line. The system is designed so that the bottles remain vertical due to their buoyancy with the tops up as they are lowered by hand to the desired depth. The stoppers are pulled, the bottles fill within 45 seconds and are then raised in the inverted
(sum of mono-, di-, and tributyltin) concentrations respectively. Deep [D], (in above bottom sediments) and shallow [S], (0.5m deep) data are compared for each region. Sample sizes for each mean ranged from 20 to 48. The most distinctive characteristic of the data was that the mean TBT concentration in yacht basins was approximately an order of magnitude greater than the remainder of the bay and secondly that there was substantially higher mean TBT concentrations in the surface water (0.139 ug/l) than in the deep water (0.046 ug/l). The south bay region had very low to non-measurable TBT with mean values in the range of 0.002 ug/l to 0.004 ug/l. Navy and north bay regions were nearly identical with mean values close to 0.01 ug/l with no significant differences between mean deep and shallow TBT data. Total butyltin levels varied from about 1.7 times the tributyltin uniform in the yacht harbors to a range of 6.5 to 13 times the TBT levels in the south bay. The navy and northern regions were similar with total butyltin ranging from 2.5 to 4 times the TBT levels. The higher percentage of mono- and dibutyltin in the south bay may be explained by longer residence times, and greater accumulation of decay products as discussed elsewhere in these proceedings [19]. Regional means of total butyltin throughout most of the bay were similar, ranging from 0.023 ug/l to 0.036 ug/l in Navy, North and South regions. This suggests that mixing processes and the numerous sources from marinas, commercial and military areas have resulted in steady state concentrations that are relatively constant throughout the bay.

Figure 5 compares February, 1984 baseline data for surface tributyltin with February 1986 monitoring data for the four regions defined within San Diego Bay. The 1986 mean TBT data is consistently lower than the 1984 TBT concentrations, significantly so in the south and north bay regions. A plausible explanation for significant TBT reductions in the south bay may be the reduced release of TBT from the San Diego Gas and Electric power plant in south bay. Approximately 930m3 of water intake conduit were painted with organotin paint between 1981 and 1983 (Joseph Dietz, SDGE, personal communication). In 1984 the coating was actively releasing TBT but it is unlikely that much active paint remains because of the high flow rates in the intake. We measured mean TBT levels of 0.012 ug/l in the discharge water (unpublished data) in February, 1994. Given the modeled sensitivity of south bay to local source TBT inputs [20] suspected reduction in power plant TBT release may explain the reduction of TBT concentrations in the region. It is not clear, however, why the north bay and navy regions would show a reduction in TBT, particularly since sources in those areas have increased. Two Navy test ships and two hospital ships, coated with organotin paint, were berthed near station 29 and 19 respectively. Apparently system flushing dynamics are such that even a fairly large, constant input of TBT did not cause measurable regional increases. Figure 6 compares February surface total butyltin data from the 1984 baseline study with the 1986 monitoring study for the four regions. In contrast to surface tributyltin, all regions except the yacht basins showed an increase in concentration. It appears that, concurrent with a reduction in tributyltin levels, an accumulation of degradation products is taking place. Tidal flushing of the yacht basins may prevent such accumulation.

Shelter Island Yacht Basin, which has been monitored over several years, showed a significant (approximately 10 fold) increase in surface TBT concentration during summer months between 1982 and 1983 (Figure 7). The same increase was not apparent during the 1982 and 1981, suggesting significant seasonal differences, presumably due to the reduction in release rate at lower winter temperatures and possibly reduced boat activity, including painting and hull maintenance.

The effects of tide and depth are most apparent in the TBT concentrations from the yacht basins (Figure 8). Near surface concentrations were significantly higher than near bottom concentrations, particularly at high and low tide. At mid-tide (inter) the difference was less apparent. The large difference in vertical distribution is presumably due to the TBT leaching from hulls in surf zones 1 to 2 m below the surface, further below in shallow areas and at mid-tide. The influence of depth on variability is also apparent in Figure 9 which shows individual station data. The highest concentrations of TBT were observed in the surface samples, presumably due to high concentration water flushing from the marinas. This
position (bottom up) through the surface layer. Samples are placed in a pre-chilled ice chest and frozen within 8 hours.

Analytical Methodology

Samples were analyzed directly by hydride derivatization of the seawater, followed by butyltin concentration in a purge and trap system with detection of the volatile butyltin hydrides in a modified hydrogen flame atomic absorption spectrophotometer. The analytical procedure used here was a modification by our laboratory [11, 14] of methods developed previously [14, 15].

Detection limits of mono-, di- and tributyltin are approximately 5 ng at the detector or 5 ng/l using 1 liter samples. Detection limits range slightly depending on trap condition, gas flow rates and instrument parameters. Sample concentrations below detection limits were considered to be 0.00 ug/l. This may skew the data, reduce its normality, and thus potentially reduce statistical power of our analysis. However, this approach was taken to give equal weight to measurements below detection limits.

Analytical accuracy and precision were evaluated by analysis of a pure tributyltin cation solution in distilled water prepared by the National Bureau of Standards for a laboratory intercomparison exercise [17]. A recovery value of 103% with a coefficient of variation of 6.8% was determined. Laboratory analytical variability is generally 10% or less. We have demonstrated that water samples can be frozen in polycarbonate bottles for several months without significant loss, redistribution or degradation of the butyltins [18]. In addition, we have documented close inter-comparability in environmental samples of trace level butyltin concentrations in split samples compared with a solvent extraction, hydridization method with GC/flame photometric detection [18].

RESULTS AND DISCUSSION

Distribution of Butyltins in San Diego Bay

A summary of butyltin concentrations at individual monitoring stations and the additional yacht surface stations is provided in Table 1. The data presents means and standard deviations of means (standard errors) across both tide and depth. The mean coefficient of variation for triplicate measurements of mono-, di- and tributyltin concentrations measured during the 1986 monitoring study were 25%, 17% and 25% respectively. This variance resulted from both laboratory analytical variability and environmental heterogeneity, but was small relative to variability contributed by station location, sample depth and tidal condition, as discussed below.

Figure 2 presents shallow data at low tide (plus or minus 20 minutes of low slack water) collected approximately 0.5 m below the surface during February 1986. Tributyltin concentrations were by far the highest in the marinas, ranging from 0.03 ug/l (station 26B) to 0.23 ug/l (stations 8 and 11), low, but generally measurable concentrations were found in the central and northern portions of the bay (0.005-0.02 ug/l TBT). Very low to non-detectable concentrations were measured in the south bay region (<0.01 ug/l), at stations removed from tributyltin sources. One tail t-test results indicated that station mean (all depths and tidal conditions) tributyltin concentrations at stations 8, 10, 10C, 11, and 16 exceeded 0.050 ug/l (p<0.026, 0.001, 0.050, 0.013, 0.004 respectively). These stations, all in marinas, were the only areas in San Diego Bay which significantly exceeded the proposed safety limit [12] of 0.05 ug/l TBT.

The four regions are compared in Figures 3 and 4 which give mean tributyltin and total butyltin concentrations and the ratio of tributyltin to total butyltin over all depths and tides in the monitoring and baseline stations.

Table 1. Mean and standard error (SE) for mono-, di-, and tributyltin concentrations and the ratio of tributyltin to total butyltin over all depths and tides in the monitoring and baseline stations.

<table>
<thead>
<tr>
<th>Station</th>
<th>n</th>
<th>MBT</th>
<th>DBT</th>
<th>TBT</th>
<th>TOTAL</th>
<th>RATIO</th>
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Figure 3. February, 1986 regional mean tributyltin concentrations for deep (D) and shallow (S) depths over all tidal conditions (see text). Error bars are standard deviations of the means.

The effect may be magnified in our data because two of the monitoring stations (7 and 10) were located at the entrance to yacht harbors where the effects of tide on the concentration of butyltin was previously found to be large [21]. Evidence of surface TBT transport out of the yacht harbors is discernible at the bay entrance (station 2C, figure 9) where concentrations at low tide were significantly greater than those at high tide and at depth. This flushing characteristic appears related to the net transport of warmer surface water out of the bay. Maximum difference between near-surface and deep concentrations occurs at station 7 at the entrance to Shelter Island Yacht Basin and is less intense at station 10 (Figure 8).

Figure 4. February, 1986 regional mean total butyltin concentrations for deep (D) and shallow (S) depths over all tidal conditions (see text). Error bars are standard deviations of the means.

Figure 5. February, 1984 and February, 1986 regional mean tributyltin concentrations at the surface at low tide. Error bars are standard deviations of the means.

Figure 6. February, 1984 and February, 1986 regional mean total butyltin concentrations at the surface (0.5m) at low tide. Error bars are standard deviations of the means.
Figure 7. Mean surface (0.5 m) tributyltin concentrations during summer and winter months in Shelter Island Yacht Basin.

9). Station 19 (North) and 42 (South) do not show significant tributyltin depth dependent concentrations.

Figure 8. February, 1986 mean tributyltin concentrations in the Yacht region per depth and tidal condition. Error bars are standard deviations of the means.

Figure 9. February, 1986 mean tributyltin concentrations at 5 selected stations across depths per tidal condition. Error bars are standard deviations of the means.

Statistical Considerations

One objective of the monitoring program is to refine and optimize sampling strategy. A three-way analysis of variance examining tributyltin variability contributed by monitoring station location, depth and tidal condition was conducted in order to explore possible reduction in sample number and frequency. Triplicate sample variability was used to generate the mean square error term. The two Yacht stations 7 and 10 were eliminated from the analysis because preliminary review of the data indicated that tributyltin concentrations at these stations, located at the mouths of Shelter Island Yacht Basin and Commercial Basin respectively, were obviously sensitive to tidal flushing of the basins. Results indicated that all three factors were important in determining tributyltin concentrations (p<0.05 in all cases) and that there was significant interaction between station location and tide, and between station location and depth (p< 0.01 for both interactions). Interactions were not limited to stations in particular regions, which were selected on a priori expectations of probable sources and sinks of tributyltin, but rather depended on station hydrography.

The number of samples required in order to detect a 50% change through time in mean tributyltin concentrations between two sets of samples was calculated. The sample number, based on tributyltin sample variability in the 1986 monitoring data, was calculated to assure a 95% confidence level that a real change (≥50%) could be detected, if occurred, and a 90% confidence level that no change (<50%) would not be misinterpreted as a change (i.e., assuring that type 1 and type 2 errors would not occur). Triplicate values in the monitoring data were treated as independent sam-
samples. Figure 10 plots sample numbers calculated for an average station in each region and an overall average San Diego Bay station against varying knowledge concerning the sample site; conditions which would be kept consistent between the two sets of samples. For example, keeping the station location and depth consistent between two sample sets for an average station in the North region would require three more samples per sample set in order to be confident that an apparent 50% change in TBT concentration had occurred than would be required if station location, tide and depth had been kept consistent. While biased by the variable number of stations in each region on which the sample size is calculated, Figure 10 emphasizes the importance of tide and depth in determining TBT concentrations, particularly for the two Yacht stations located at the mouth of yacht basins. If only the region is kept consistent where samples are taken, an average of 28 samples would be needed at any point in time to detect a 50% change in tributyltin concentration at some later date.

The data suggest that the information contributed by taking triplicate samples at a particular sampling site is small relative to the information contributed by sampling over depth and the tidal cycle when estimating TBT concentration variability at a sampling station. Until the interaction effects are better understood and to insure the consistency of our data base we feel it prudent to maintain existing sample stations and to continue sampling through the water column and tidal cycle.

Conclusions

Yacht harbors and marinas, grouped as a region, are presently the most important sources of tributyltin in San Diego Bay, with surface concentrations reaching 0.23 μg/l. The south bay region, in contrast, generally exhibit very low to nondetectable levels of TBT.

Tributyltin degradation products comprised a larger fraction of the total water column butyltin concentration in the south bay than in any other region. The lowest fraction was found in the yacht harbors and marinas. Mean 1986 levels of surface tributyltin were consistently lower than 1984 levels for all regions. All regions except the yacht basins and marinas exhibited an increase in total butyltin concentration over this period, presumably due to an accumulation of degradation products. Accumulation was felt to be a function of water residence time; longest in the south bay and probably shortest in the small volume, tidally flushed yacht harbors.

Tide and depth were very important in determining tributyltin concentrations and their effect was station dependent. A clear example of this was found at stations 7 and 10 in the mouths of the Shelter Island yacht basins, though an analysis of variance revealed their influence at other stations as well. Since there is strong interaction between station and tide and station and depth in determining tributyltin variability which is station specific, we are hesitant to eliminate station number, sample depths or sampling frequency. However, since triplicate sample TBT variability was much less than that due to sample station location, depth or tidal condition, we feel the total number of replicates can be reduced substantially. The stations in the yacht and south bay regions appear quite similar in their mean tributyltin concentration, flushing characteristics and accumulation of degradation products within region. The stations in these regions can probably be lumped together to represent a source and a sink of TBT. The stations in the north and navy regions are relatively more heterogeneous and specific attention should be paid to each.

Figure 10. Required number of samples to detect a 50% change in tributyltin concentration between two sample sets for an average station in each region and an overall average station. Sample number is plotted against sample conditions kept consistent between sample sets (see text). The number of monitoring stations for each region on which sample number is calculated is shown in parentheses.
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