Applied Organometallic Chemistry (1989) 3 411–416
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0268-2605/89/03505411/$03.50

Stratification and tributyltin variability in San Diego Bay

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Received 10 April 1989 Accepted 13 June 1989

Tributyltin (TBT), a biocidal antifoulant in many marine paints, was measured in near-surface and near-bottom water over a 25 h period at the entrance to a marina in San Diego Bay, USA. Surface water concentrations varied from 20 to 225 nanograms per liter (ng dm^{-3}) as TBT chloride and bottom water varied from non-detectable (<1 ng dm^{-3}) to 77 ng dm^{-3}). Surface water concentrations varied, with highest concentrations associated with ebbing tides, and lowest concentrations with flooding tides, indicating that the yacht basin is a source of TBT. Bottom water TBT concentrations were almost always lower than corresponding surface water concentrations. The highest bottom water concentrations were associated with flooding tides and lowest surface water TBT concentrations. Physical water column measurements indicate that vertical stratification developed during ebbing tides and dissipated during flooding tides. This accounted for maximum bottom water and minimum surface water TBT concentrations during flooding tides, due, at least in part, to vertical mixing and dilution during flood tides.

Keywords: Tributyltin, stratification, tide, temperature, thermocline, San Diego Bay, USA, hydride generation

INTRODUCTION

Butyltin compounds are currently entering marine waters, primarily as a result of tributyltin (TBT)-containing antifouling paints.[1] Recent reports[2,3] have indicated enclosed recreational vessel anchorages as significant source regions; that is, areas with high pleasure craft densities, significant TBT hull paint usage, and restricted water circulation. Interviews with yacht owners and San Diego marine paint retailers resulted in an estimate of approximately 75% TBT paint usage in Shelter Island yacht basin during this study.

Tidal variation in TBT concentrations of surface water (0.5 m) 400 m outside the entrance to Shelter Island yacht basin have been reported.[4] Low TBT concentrations were associated with flooding tides and high concentrations with ebbing tides. TBT was apparently flushed from the basin during ebb tides and more diluted water from the northern portion of San Diego Bay entered the area during flood tides. Similar tidal variability of copper and zinc concentrations in San Diego Bay surface waters near enclosed vessel anchorages have been reported.[5] This report examines the variability of TBT concentrations in surface and bottom water in relationship to selected chemical and physical measurements at the entrance to Shelter Island yacht basin in San Diego Bay.

METHODS AND MATERIALS

Sample acquisition

The Naval Ocean Systems Center Marine Environmental Survey Craft (R/V MESC) was secured at the San Diego Harbor Police dock from 1000 PST (Pacific Standard Time) 30 October 1986 until 1200 31 October 1986 (Fig. 1). Seawater was pumped aboard via an intake line of approximately 4 cm internal diameter at a rate of approximately 80 dm^3 min. *In situ* measurements of temperature, conductivity, dissolved oxygen, percentage transmittance, and sample depth were obtained with a CTD (Interoceans model 513D) sampling system. The pump intake was fastened to this device. The *in situ* unit and pump intake were raised and lowered

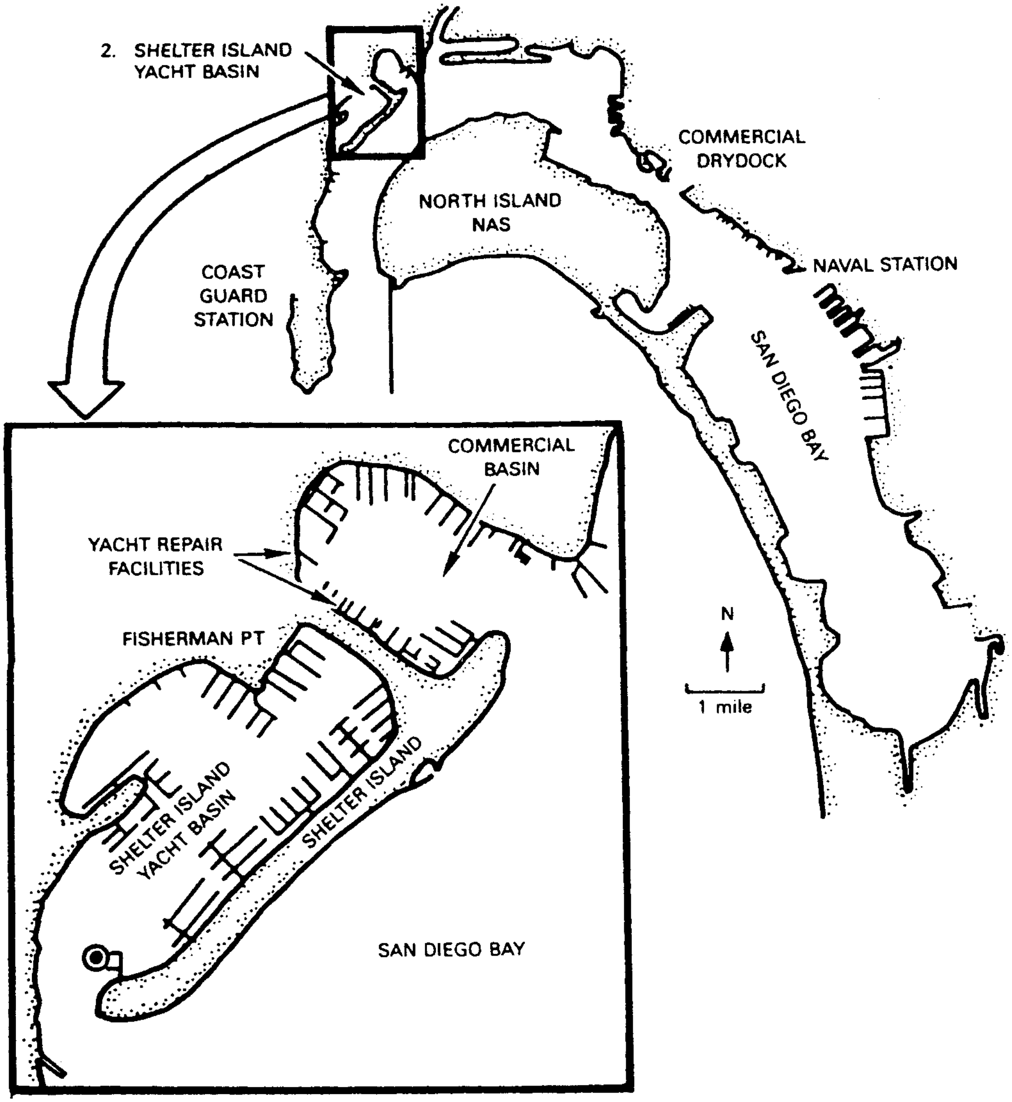

Figure 1 Station location at entrance to Shelter Island yacht basin, San Diego Bay, California.

through the water column using a davit and hand-winch. Aboard the R/V MESC, pH was measured in real time via the pump discharge under flow-through conditions. The parameters listed above, time and bottom depth were logged onto magnetic discs at 2–5 s update intervals.[6] Water samples for subsequent TBT determinations were obtained from an in-line valve aboard the MESC. Approximately 900-cm^3 samples were collected directly in 1 dm^3, clean, polycarbonate centrifuge bottles and immediately frozen for laboratory analysis. Discrete samples were collected hourly on the half-hour at the surface (0.4 m) and approximately hourly near 40 minutes after the hour near the bottom (approximately 0.5 m from the sediment–water interface). Depth profiles were obtained at approximately 30-min intervals.

Analytical procedures

Tributyltin concentrations were determined by the hydride derivatization/atomic absorption spectroscopy technique.[1,2] This method uses sodium borohydride to form volatile tributyltin hydride in an acidified (pH 5–5.5) seawater solution. Helium gas purges inorganic tin hydride (stannane) and all volatile alkyltin hydrides from a reaction vessel into a cyrotrap immersed in liquid nitrogen. After a 5 min collection period, the trap is heated from approximately −180°C to +180°C. The tin hydrides are eluted from the trap as a function of their boiling points and detected in a hydrogen–air flame entrained in a quartz furnace aligned in the beam path of a Buck 200 spectrophotometer with the monochromator set at 286.3 mm. Quantification was performed by comparison to minimum four-point calibration curves. The detection limit for tributyltin chloride was 0.5 ng at the detector or 1.0 ng dm^{-3} for a 500-cm^3 sample using an enhanced sensitivity method.[7]

RESULTS AND DISCUSSION

The TBT concentrations over time for both near-surface and near-bottom water are shown in Fig. 2. TBT in surface water varied from 20 to 225 ng dm^{-3} with a mean of 100 ng dm^{-3}. Bottom water ranged from non-detectable (< 1 ng dm^{-3}) to 77 ng dm^{-3}, with a mean of 25 ng dm^{-3}. The mean TBT concentration in the surface water was four times greater than in the bottom water at the yacht basin entrance. Other investigators have reported statistically significant differences between surface and bottom TBT concentrations.[3] Surface water in yacht basins as well as in San Diego Bay entrance waters contained significantly

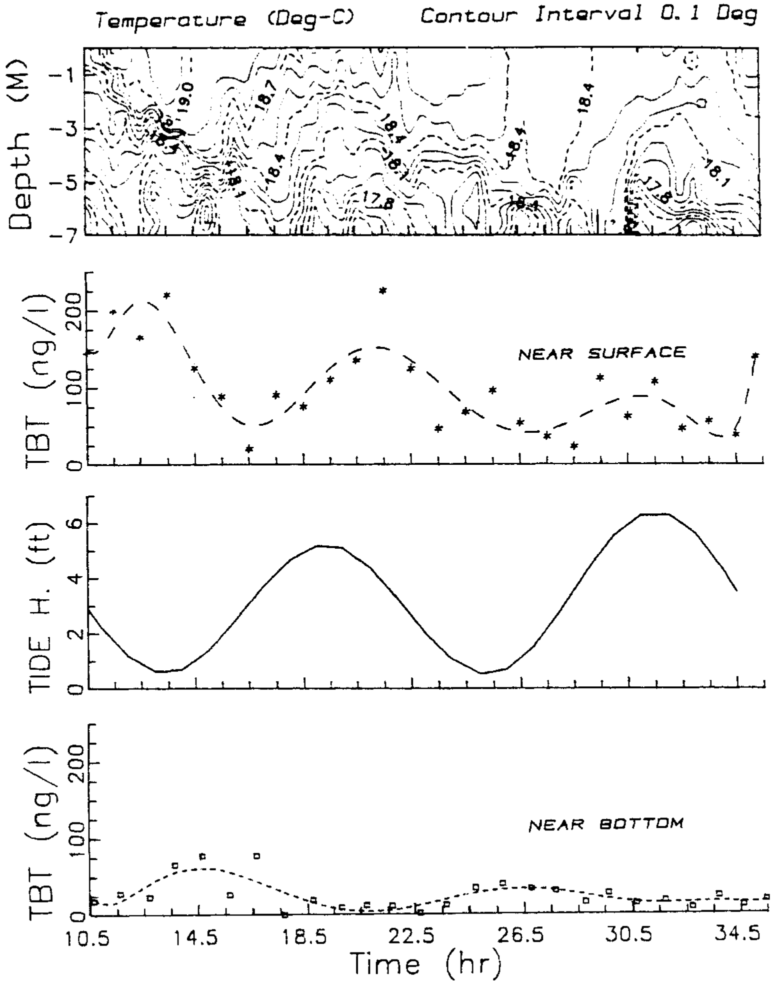

Figure 2 Tributyltin concentrations (ng dm^{-3}), thermal structures (°C), and tidal height (feet above mean lower low water) during survey of 30–31 October 1986.

more TBT than underlying waters, possibly due to the net transport of warmer surface water out of the basins as well as from the bay as a whole.

Weather conditions during the study period were fair. The morning overcast gave way to sunshine from 0800 until after dusk. Temperature at 1200 on 30 October 1986 was 22°C with 85% relative humidity.

Surface warming during the mid-morning and early afternoon resulted in the development of a local thermocline. The thermal structure was apparent at the start of the study near the surface, subsided, and strengthened through the water column during the latter stages of ebb and 2 h into flood tide. The maximum temperature gradient observed during this interval was approximately 0.7°C m^{-1} through the water column. The thermocline was dissipated by the strengthening flood surge at approximately 1530. By 1700 the thermal gradient through the water column was nearly uniform, with a change of approximately 0.1°C m^{-1}. A weaker thermal gradient evolved during the evening ebb tide. The gradient was stable during the mid to later ebb stage and persisted between 2300 and 0100 (2500 elapsed time from 0000 on day one) at a depth of approximately 1–5 m. At its strongest, the gradient at the discontinuity was approximately 0.3°C m^{-1}. The overall surface to bottom temperature differential between 2300 and 0100 was approximately 0.8°C. By 0400 (2800) the tidal surge dissipated the thermal structure. A significant thermal discontinuity was absent between 0500 (2900) and 0700 (3100). During this interval, the change in temperature over the entire water column was no more than 0.1–0.3°C. The development of a thermocline in the near-surface layer observed 3.5 h after slack flood on 30 October was not observed during the same phase on 31 October. The thermal discontinuity probably developed later in the ebb phase, after the termination of the study.

The highest sustained surface TBT concentrations were observed during late ebb and slack low tide on 30 October. Concentrations diminished as flood tide progressed and the thermocline subsided through the water column, reaching minimum levels near full flood tide. These minima coincided with the dissipation of the thermal structure at approximately 1530. Presumably, the decrease in surface concentrations were attributed to dilution caused by the increased volume in the upper mixed layer.

Bottom water concentrations during the same interval increased. Peak concentrations occurred immediately following slack ebb, coincident with minimum surface water concentrations. Concentrations increased as the thermal discontinuity deepened, presumably due to mixing through the lowered mixed layer boundary.

Surface TBT concentrations increased during the ensuing slack high (1920) and over the first half of the ebb cycle. However, levels diminished over the latter half of the ebb tide and increased only slightly during the flood. Bottom water TBT concentrations decreased over the ebb phase until shortly before slack low tide. Peak bottom concentrations again occurred at and just after slack low, coincident with lowest surface concentrations. Bottom water concentrations stabilised at low levels (<20 ng dm^{-3}) during the remainder of flood and the ensuing ebb tide.

Examination of Fig. 2 reveals that the changes in both surface and bottom water TBT concentrations approximate sine functions. These interpolations of TBT concentrations were produced by a tenth-degree polynomial. The two waveforms also appear to be approximately 180° out of phase, as would be expected from the above discussion. That is, with mixing of water vertically, due to the turbulence caused by incoming tides, the surface water would be diluted with low TBT-containing bottom water and the bottom water would receive some high TBT concentration surface water. This trend of increasing TBT concentrations in the bottom water with concomitant decreasing levels of TBT in the surface water is evident after both low tides during the survey. Conversely, the largest differences between the surface and bottom water TBT concentrations occurred on ebbing tides when the vertical stratification was strongest and outgoing tidal velocities were greatest (Figs 2 and 3).

The measurement of pH indicated a trend similar to that of temperature during the first 6 h of the survey: that is, the pH stratification increased with depth with the ebb tide and dissipated during the first flood tide. The pH structure did not exhibit this trend during the second ebb tide. We believe this was due to the fact that the second low tide occurred after sunset; carbon dioxide uptake by phytoplankton in the surface water had ceased, and consequently, pH values decreased. The percentage transmittance structure exhibited stratification during both ebb tides and dissipation of the stratification on flood tides. Dissolved oxygen structure showed a diurnal pattern during the survey. A persistent, well defined gradient existed between depths of 1 and 5 m from the beginning of the survey until approximately midnight (2400). After 0100 (2500 survey time in Fig. 3) on 31 October 1986, the

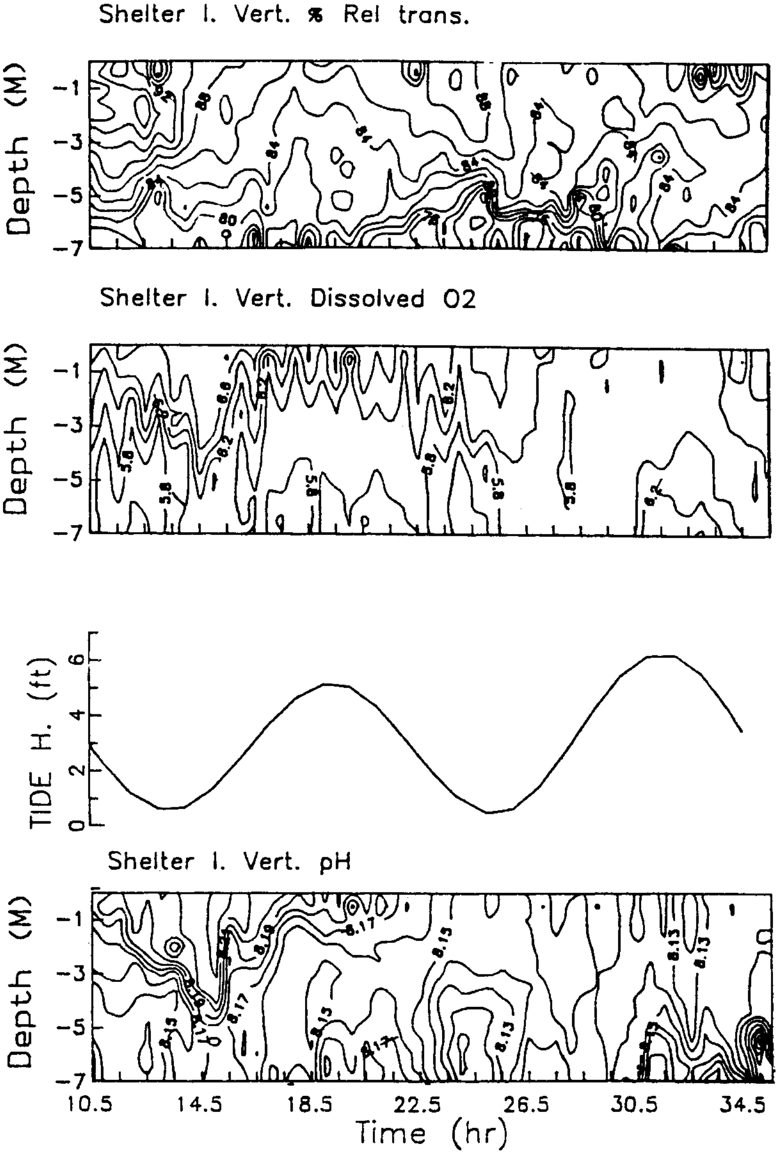

Figure 3 Dissolved Oxygen (mg dm^{-3}), relative transmittance (%), pH (−log [H+]), and tidal height (feet above mean lower low water) during survey of 30–31 October 1986.

dissolved oxygen gradient dissipated. We believe this was due to the observed cessation of the wind at approximately midnight and the consequent loss of wind-driven surface mixing. Salinity exhibited little variability with respect to either depth or tidal state during the survey and is consequently not included in Fig. 3.

The majority of the approximately 2300 yachts in Shelter Island yacht basin are less than 20 m in length and, consequently, the majority of TBT-containing hull paint is located in the uppermost 2 m of the water column. The water column, both at the entrance to the basin (Fig. 3) and within the basin itself,[8] exhibits stratification, with a thermal discontinuity between 1 and 5 m in depth. Our data, and previous basin-wide TBT concentration profiles,[3] indicate a TBT discontinuity as well. A significant portion of the TBT released from the yacht hulls appears to be flushed from the basin on a semidiurnal basis. With minimal vertical mixing, except near the mouth of the basin on flood tides, TBT may have a relatively short residence time in the basin surface waters, exclusive of the rapid degradation of TBT[9,10] in Shelter Island yacht basin.

CONCLUSION

Tributyltin concentrations varied by an order of magnitude in the surface water at the mouth of Shelter Island yacht basin during a 24 h period, averaging 100 ng dm^{-3}. Highest concentrations were associated with ebb tides and lowest with flood tides in the surface waters. Bottom water concentrations were significantly lower than surface TBT concentrations, averaging 25 ng dm^{-3} and varied 180° out of phase with the surface water TBT concentrations. Physical and chemical parameters indicated stratification of the water column at the yacht basin entrance especially during ebb tides. Water high in TBT concentration exited the basin at these times by surface laminar flow.

These data show that at the Shelter Island yacht basin entrance there are significant temporal and spatial changes in TBT concentrations and other physical and chemical parameters. The capability of real time data acquisition and processing allows observation of events as they occur and aids in interpreting complex results. In addition, data such as these indicate the importance of, and need for, comprehensive and specific monitoring strategies when documenting levels of contaminants in dynamic systems.

Acknowledgements This work was sponsored by the Office of the Chief of Naval Research and the David Taylor Naval Ship Research and Development Center, Energy Research and Development Program. This work was done under United States government contract and may be reproduced by or for the U.S. Government.

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