Applied Organometallic Chemistry (1989) 3 31–47
© Longman Group UK Ltd 1989

0268-2605/89/03102031/$03.50

Distribution and fate of tributyltin in the United States marine environment

Peter F Seligman,*† Joseph G Grovhoug,† Aldis O Valkirs,‡ Peter M Stang,‡ Roy Fransham,‡ Martha O Stallard,‡ Bradley Davidson‡ and Richard F Lee§
†Naval Ocean Systems Center (Code 522), San Diego, California 92152-5000, USA, ‡Computer Sciences Corporation, San Diego, California 92110, USA, and §Skidaway Institute of Oceanography, Savannah, Georgia 31416, USA

Received 15 August 1988 Accepted 1 October 1988

Tributyltin (TBT) has been measured in water in 12 of 15 harbors studied during US Navy baseline surveys. The highest concentrations of TBT (some exceeding laboratory toxicity limits) have been found in yacht harbors and near vessel repair facilities. Many sites (75%) in harbors and estuaries had no detectable (<5 ng dm^{-3}) TBT. TBT monitoring studies with increased detection limits (<1 ng dm^{-3}) have documented a high degree of TBT variability associated with tide, season and intermittent point source discharges. Although yacht harbors were shown to be the principal TBT source in most regions, dry-docks can be significant sources. Tributyltin degradation studies were conducted using unfiltered seawater from four geographic regions and incubated under natural conditions. Degradation half-lives were always in the range of 4–19 days, providing evidence that TBT is not highly persistent in the water column at environmental concentrations. Preliminary degradation experiments suggest that TBT has a longer residence time in sediment with a half-life of several months. Tributyltin is primarily in the dissolved form in unfiltered seawater, although the association with particulate fractions may increase in samples collected near yacht repair facilities. Partition coefficients for particulate TBT versus bulk water are frequently near 3000 and vary with the particulate concentration, salinity and presence of natural organics.

Keywords: Tributyltin, monitoring, persistence, degradation, seawater, partitioning, sediments, half-life, environmental concentration

INTRODUCTION

The use of tributyltin (TBT) compounds in marine hull coatings as a biocide to prevent the growth of fouling organisms has increased significantly during the last decade. The release of this compound from hulls and vessel repair facilities into the marine and estuarine environment is a major source and principal pathway of TBT into aquatic ecosystems. Tributyltin concentrations in the water column, particularly in marinas, have been reported at levels which exceed acute (≥ 400 ng dm^{-3} TBT) and chronic (≥ 50 ng dm^{-3}) laboratory toxicity values for certain sensitive invertebrates.[1,2] Investigators in the UK,[3–5] Canada,[6] and the US[7–13] have documented high concentrations of TBT in the range from 50 ng dm^{-3} to several μg dm^{-3} in small boat harbors and high-use estuaries. Concentrations were generally less than 20 ng dm^{-3} and frequently not detectable in open, well-flushed regions of bays and estuaries. Reports of TBT concentrations in several regions of the USA which exceeded toxic limits for several sensitive marine species precipitated both regulatory[14] and legislative[15] action in the USA to restrict the use of TBT antifouling coatings to larger craft (>25m) (aluminium hulls are exempted) and low-release-rate paints (< 5 μg cm^{-2} day^{-1}), and to remove TBT from retail sale.[16].

Several coastal states also moved to restrict its use to larger craft and to require low-release rate paints. These laws and regulations in the USA were preceded

---

*Author to whom correspondence should be addressed by similar restrictions in France in 1982[17] and in the UK in 1985 and 1986[18,19] based on the association of shell malformations and reduced productivity in the Pacific oyster *Crassostrea gigas* with TBT in the water column and tissues.

The US Navy decided in the late 1970s to evaluate the use of copolymer TBT antifouling coatings for its Fleet use. Subsequently, a broad program was initiated to investigate the toxicology, ecological effects, degradation and persistence, and toxicant loading and transport to the environment, as well as starting a TBT baseline and monitoring effort. An Environmental Assessment of the proposed fleet use of organotin antifouling hull paints, required by the US National Environment Policy Act (NEPA), was published in 1985[20] and fate-and-effects research and monitoring have continued through 1988 to update information and conclusions drawn in that assessment. Two important questions in assessing the environmental risk of a xenobiotic biocide are:

(1) What are the sources, concentration, and distribution in the environment? and
(2) What is the biogeochemical fate of the biocide?

Our TBT studies encompassing these two areas are summarized below.

MATERIALS AND METHODS

Sample collection and storage

At each sampling station, three collocated water samples were collected using a polycarbonate plastic sampling device at depths of approximately 0.5 m from the surface and 1 m off the bottom. Baseline samples and those collected for the Norfolk, Virginia, regional study were collected in surface waters only. Samples were stored frozen after collection in 1-dm^3 polycarbonate bottles. Polycarbonate plastic has previously been shown to be essentially nonadsorptive to butyltins.[21] Frozen storage of water samples has been shown to be effective for a period of at least three months with respect to loss of TBT.[22] Other investigators have had similar success with refrigeration.[10] The results of unpublished data in our laboratory indicate that frozen storage of seawater samples may be extended to a period of 4.3 months with no more than a 15% loss of the initial amount of TBT measured. This degree of loss is consistent with the relative standard deviations of methods employing hydride derivatization for analysis of TBT in seawater.[22]

Seawater analysis

Analysis of TBT, dibutyltin (DBT), and monobutyltin (MBT) in seawater samples was performed by hydride derivatization with atomic absorption detection (HD AA). The method has been used successfully by other investigators previously,[23,24] and has recently been modified in our laboratory to permit detection of butyltins at picogram amounts in environmental samples.[25] Briefly, a sample is placed in a 500-cm^3 modified gas washing bottle and acidified to pH 5.0–5.5 with 2 mol dm^{-3} acetic acid. Hydride derivatives are formed by the addition of 4% sodium tetrahydroborate(III) prepared in a 1% sodium hydroxide solution in distilled water. A ratio of 1 cm^3 of sodium tetrahydroborate(III) to 100 cm^3 of sample is used to generate hydride species which are subsequently purged from solution and trapped in a glass U-tube (3mm i.d. with 2.5–3-inch sides). The U-tube is packed with 20–30 mg of 3% OV-1 on 80/100 mesh Chromosorb W HP and immersed in liquid nitrogen during the purging period. The butyltin species are separated and detected sequentially according to their boiling points as they distill from the U-trap upon its removal from the liquid nitrogen bath. Detection is accomplished in a quartz tube burner mounted in a spectrophotometer using a hydrogen–air flame at 286.3 nm. Complete details of the analytical process and quartz burner design are described by Stallard *et al.*[25]

Monobutyltin trichloride, dibutyltin dichloride and tributyltin chloride were used as standards without further purification. Standard solutions were prepared in methanol or ethanol and added to seawater free of butyltins in appropriate concentrations for calibration purposes. Butyltin peaks in selected environmental samples were verified by addition of butyltin standards. Butyltin values are expressed as the chlorides uncorrected for recovery as addition of TBT standards (typically 1–5 ng dm^{-3}) to environmental samples has exhibited percentage recovery values of 78% or more in 88% of samples collected from Norfolk, VA, San Diego Bay, CA, and Pearl Harbor, HI, where standard additions were made to samples. Recent modifications in our analytical system[25] have resulted in significant improvements in butyltin detection limits over those previously achieved.[7,22] Current detection limits calculated from three standard deviations of five replicate analyses of seawater solutions spiked with 0.5 ng each of MBT, DBT, and TBT are 120, 80, and 180 pg at the detector respectively as the cation, or 0.24, 0.16, and 0.36 ng dm^{-3} in seawater. A slight nonsignificant negative bias (6% of the mean TBT value) was calculated from the TBT replicate measurement data.

Sediment analysis

Butyltin species in sediment samples were analyzed by direct analysis using HD AA.[26] Sediment MBT, DBT, and TBT concentrations in degradation and adsorption–desorption studies were also determined by HD AA.[26]

Degradation experiments

Microcosms (0.5–8.0-dm^{-3} polycarbonate plastic or Pyrex glass bottles) were filled with ambient unfiltered seawater from selected sites and spiked with either unlabelled tributyltin chloride (TBTCl) or with radiolabeled bis(tri-n-butyltin) oxide (butyl-l-^{14}C-TBTO). The microcosms were then incubated for 3–9 days in light and dark treatments under natural temperature conditions. The containers were sequentially sampled and the loss of parent compound and the appearance of degradation products was measured by HD AA (TBTCl spiked bottles), or by extraction followed by thin-layer chromatography and liquid scintillation counting (^{14}C-TBTO). Abiotic controls were run using either filtered, autoclaved or poisoned systems.[27]

RESULTS AND DISCUSSION

Tributyltin baseline

Measurements of butyltins (MBT, DBT and TBT) were carried out in 15 US harbors from 1984 to 1986. A substantial range of concentrations was found from nondetectable values (< 5 ng dm^{-3}) in many regions to 350 ng dm^{-3} in a marina in San Diego Bay.[11] To compare regional differences broadly, regions in each bay and estuary were divided into three major-use categories: commerical and recreational; areas of resource or ecological importance; and areas near Naval facilities. Mean TBT concentrations for each region for the 15 harbors are presented in Fig. 1. For comparative purposes, 10 ng dm^{-3} (the proposed US EPA water quality criterion)[28] is shown on the key applied to Fig. 1.

In 3 of 15 harbors no detectable TBT was measured and 75% of the 468 samples were below detection limits; 5% of the samples had TBT concentrations ≥ 50 ng dm^{-3} and all of these samples were collected either within yacht harbors or small boat basins, or adjacent to TBT-coated hulls or dry-docks. In some cases, mean regional concentrations of less than the 5 ng dm^{-3} detection limit are reported because nondetectable values were considered as being 0 ng dm^{-3} in calculating mean TBT levels. The two harbors with the highest TBT levels in commercial and recreational regions were San Diego Bay, CA, and Honolulu, HI, both with approximate mean concentrations of 100 ng dm^{-3}.

Seven of the 15 harbors had commercial and recreational regions which exceeded 10 ng dm^{-3} TBT. Marinas and small boat harbors represented the major source of butyltin loading to most of the harbors surveyed. Dry-dock facilities were associated with elevated TBT levels in Honolulu Harbor, and Norfolk, Virginia. The occurrence of DBT and MBT in marine and estuarine waters, at concentrations approaching or sometimes exceeding those of TBT, suggested a process of rapid degradation.

Over a five-year period beginning in 1982, we have measured TBT concentrations in Shelter Island Yacht Harbor, a marina within San Diego Bay containing about 2200 vessels. Tributyltin concentrations increased substantially (by five- to ten-fold) between 1982 and 1986. We believe this increase is consistent with greater use of TBT-containing coatings during this time period.[7,12] Other investigators have also found elevated levels of tributyltin in marinas and boat harbors ranging up to several μg dm^{-3} in both marine and freshwater systems.[4,8,29,30] The extent of TBT contamination, outside of source regions, in areas of ecological resources that might be impacted is an important environmental issue. Based on data from our limited baseline surveys in 15 harbors, we have not observed mean TBT concentrations above 10 ng

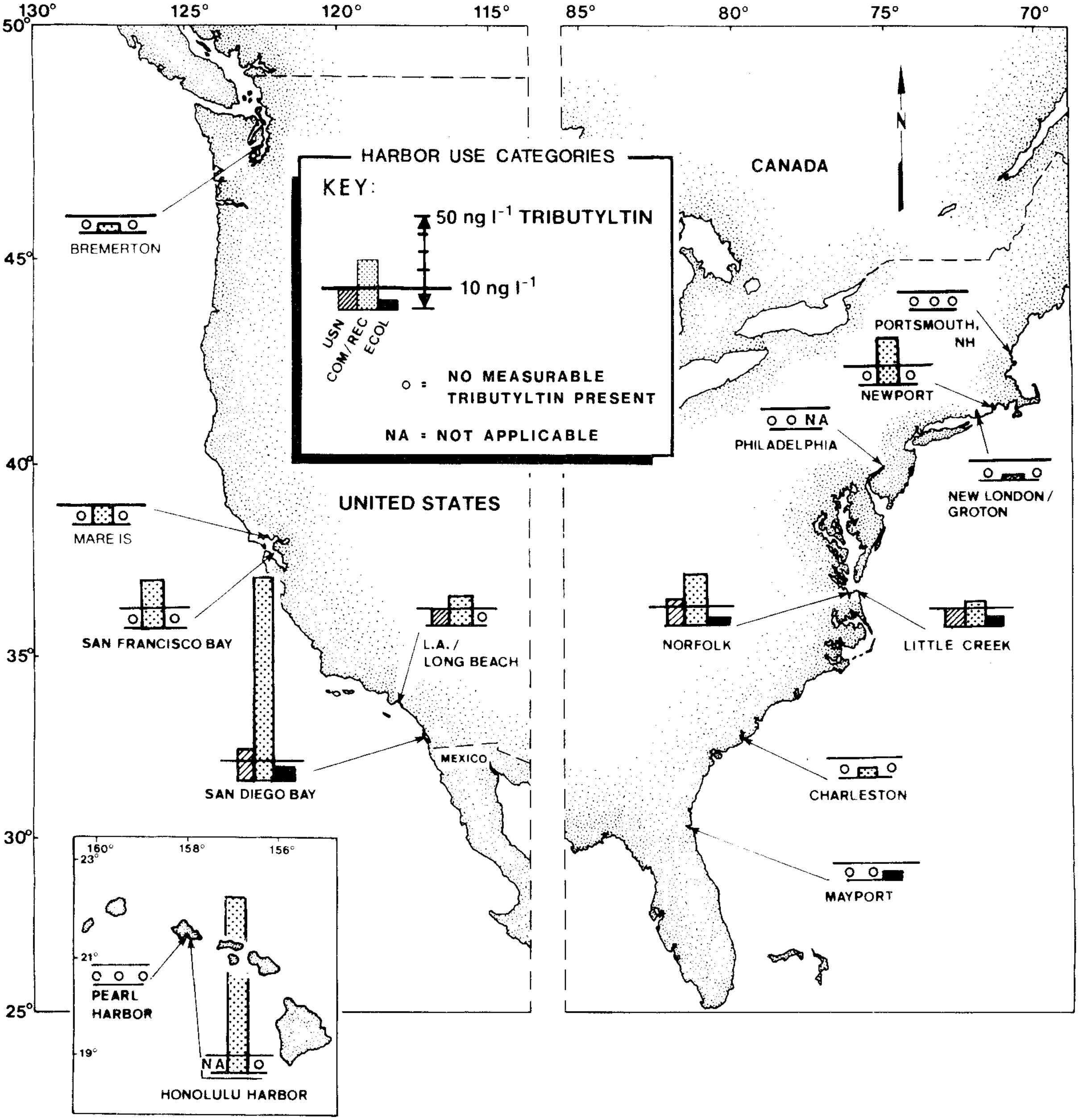

Figure 1 Mean surface water concentrations of TBT at 15 US harbors averaged for regions based on use categories.

dm^{-3} in ecological resource areas. However, further monitoring in these and other important estuaries is needed to determine if measurable TBT concentrations are now present or increasing.

Monitoring

A monitoring program was initiated in 1986 to follow butyltin concentrations during the early stages of the US Navy's use of TBT coatings. Although the implementation of these coatings has been delayed, and the monitoring effort reduced, several regions have been intensively surveyed over the last several years.

San Diego Bay

Water column sampling for TBT in San Diego Bay was designed to evaluate major sources, to differentiate short-term temporal (tidal), vertical and spatial variability components and to optimize future sampling strategy.[12] Ultimately, the monitoring data will be used to evaluate long-term trends and compliance with regulatory actions. Sampling stations were combined into four regions to facilitate statistical comparisons. A total of 867 samples were collected and analyzed. Station selections were based on a combination of flushing characteristics and use patterns (Fig. 2). The northern region (I) is characterized by high current velocities and rapid flushing rates, and includes most of the shipping channels and dredged areas of the bay. The southern region (II) is largely shallow with low-velocity currents and longer water residence times. South Bay is ecologically important as a nursery-ground for numerous fish and invertebrate species. Navy-use areas (region III), including several Navy berthing areas, are moderately well flushed. Marinas and commercial boat basins (region IV) are generally characterized by moderate-to-dense aggregations of boats in enclosed embayments with reduced flushing. Yacht harbors and marinas had by far the highest TBT concentrations ranging from one to nearly two orders of magnitude greater than concentrations in open areas of the bay, which averaged 5–15 ng dm^{-3} (Fig. 3). Over the two-year study period, the average concentration (combining deep and shallow measurements made in triplicate) in the eight surveyed yacht harbors was 77 ng dm^{-3} TBT.

Tributyltin measurements taken in surface water (0.5 m) from yacht harbors generally exceeded deeper values (1 m off-bottom) by as much as ten-fold.[12] Vertical stratification of TBT was less apparent in other regions of the bay. The maximum TBT concentration observed during the sampling period was 340 ng dm^{-3} in surface waters of Shelter Island Yacht Harbor. Shelter Island has consistently had the highest TBT concentrations within San Diego Bay. The maximum value ever observed in this marina was 930 ng dm^{-3} in September 1985.[7]

The lowest TBT concentrations in San Diego Bay were found in the southern portion of the bay where the water residence time was longest. The average concentration was 7.3 ng dm^{-3} (Fig. 3). Concentrations increased with time, averaging 3 ng dm^{-3} in February 1986 to about 11 ng dm^{-3} in February 1988. This increase likely resulted from expansion of South Bay marinas and increased use of this portion of the bay for long-term anchorage of yachts.

The northern (I) and Navy (III) regions of the bay had nearly identical mean TBT levels of 10.5 and 11.0 ng dm^{-3} respectively. The importance of tidal fluctuations on TBT variability was dependent on sampling location. In areas close to source regions, particularly at the mouths of yacht basins, tidal TBT variation can be extreme (Fig. 4), with maximum differences of up to 20-fold (e.g. 17–332 ng dm^{-3} about 300 m from the entrance to Shelter Island Yacht Basin).[31] Other regions distant from sources, such as south San Diego Bay, had low TBT concentrations, high percentages of degradation products and little short-term variability from tidal influences.

Norfolk region, Virginia

Over a three-year period, samples were collected from near-surface water (0.5 m) in the Elizabeth River and Hampton Roads estuaries at eight stations (Fig. 5). This region is an area of major shipbuilding and repair activity as well as a port with as many as 3000 ships per year passing through Hampton Roads. The Elizabeth River is part of the intercoastal waterway and has very little freshwater inflow. Transport of pollutants therefore, is predominantly tide-driven. The large freshwater influx from the James River has a major influence on the transport, dispersion and dilution of pollutants within the Hampton Roads area. The study was directed towards investigating the relative contributions of TBT from large vessels and repair activities rather than from small craft and marinas.[13] Figure 5 gives sampling locations within the Norfolk region. The larger dark circles, stations 3, 4, 9, 10, 11, 32, 19 and 17, represent the sampling stations monitored during the study period. Stations 3, 4 and 9 are in the vicinity of the Naval Station where five US Navy vessels with TBT test paints were stationed.

Figure 6 gives the mean TBT concentrations at the eight stations over 14 sampling periods summarizing a total of 336 samples. TBT concentrations were highly variable in the Elizabeth River over the study period, suggesting intermittent kilogram inputs from commercial dry-docks or other sources.[13] The large fluxes of TBT in the river appeared unrelated to season and were likely associated with individual or closely spaced dry-dock releases. Other authors have reported a large flux of TBT in late spring and summer related to seasonal use of recreational craft.[4,8,10] Maximum loading was observed in December 1985, with a TBT mass exceeding 6 kg calculated for the segment of the river including stations 10, 11, 32 and 19 near the shipyards, where concentrations ranged from 40 to 209 ng dm^{-1} TBT.[13] In general, TBT concentrations in the highly flushed region of Hampton Roads and the large Naval complex were low, usually <5 ng dm^{-3}, and

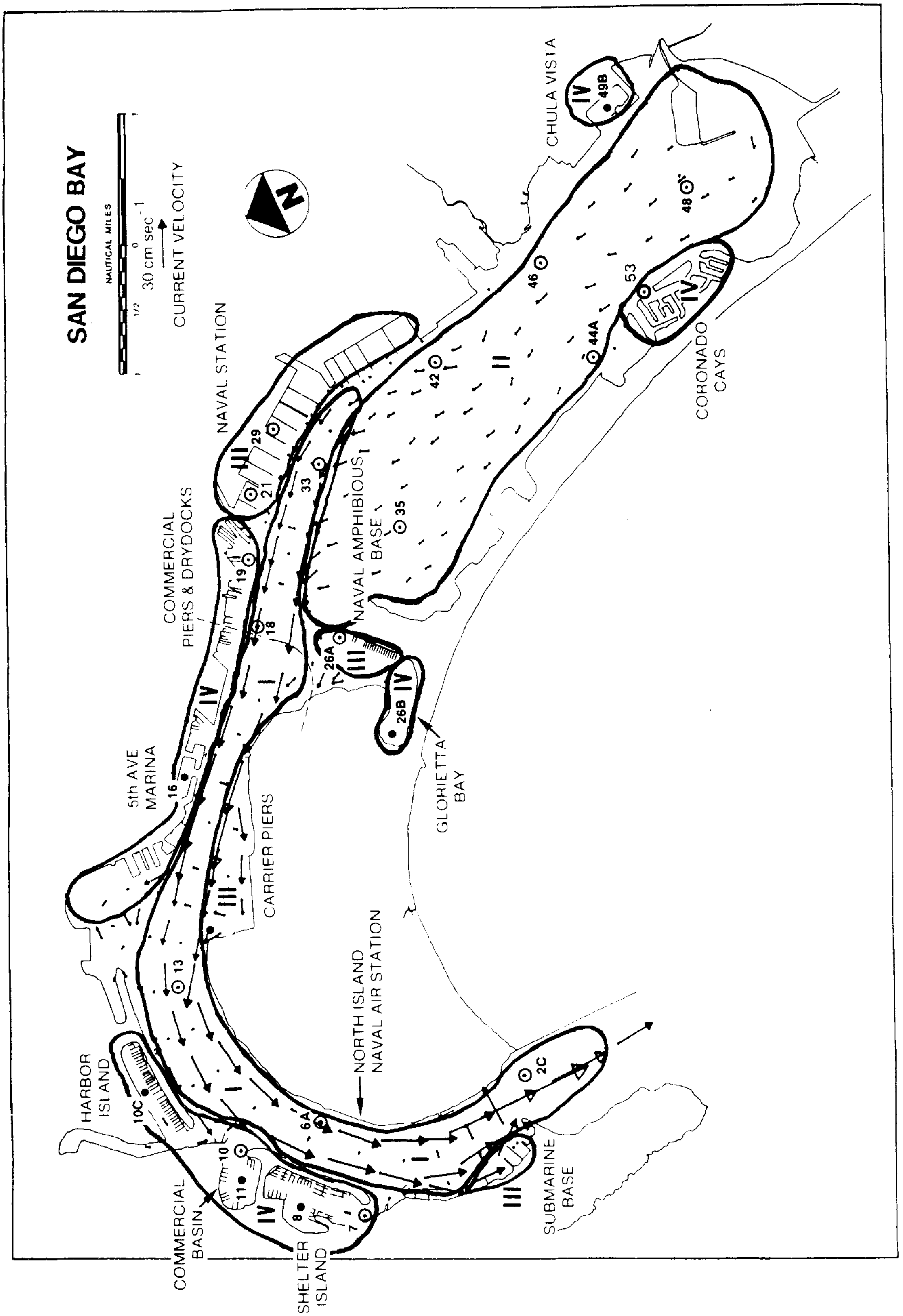

Figure 2 Regional association of monitoring stations in San Diego Bay, California: region I, North Bay; region II, South Bay; region III, Navy; region IV, yacht basins. Arrows document average current velocity.

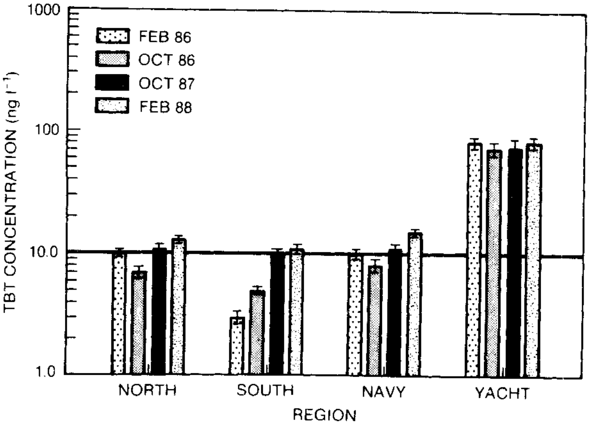

Figure 3 Regional mean TBT concentrations in San Diego Bay, California, during a two-year monitoring period. Error bars are 1 standard error.

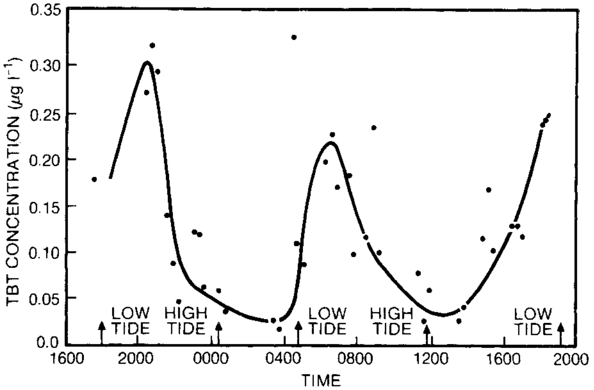

Figure 4 Variation in TBT concentrations in surface water samples during a 24-h tidal cycle (modified from Ref. 31).

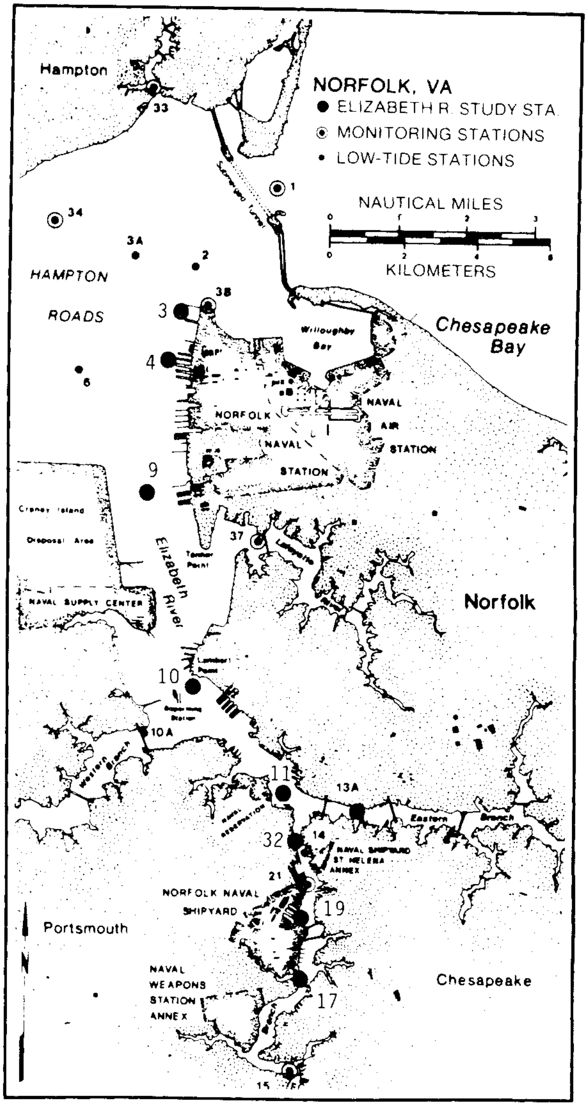

Figure 5 Location of water sampling stations (3, 4, 9, 10, 11, 32, 19, 17) in the Norfolk, Virginia, region.

showed less fluctuation than the Elizabeth River, which varied maximally by nearly two orders of magnitude (Fig. 6). A similar TBT distribution was reported by Huggett *et al.* in the Elizabeth River and Hampton Roads region.[10] The lowest TBT levels were measured in the spring and summer of 1986 and March 1987 when mean estuary concentrations were < 10 ng dm^{-3}. These lower values suggest that even though the river is not well flushed, during periods of low TBT input concentrations drop rapidly suggesting that improved environmental management practices could be successful in lowering concentrations to levels within acceptable limits. High concentrations during December may reflect seasonal painting of cruise ships in local Norfolk shipyards. Mean TBT concentrations in the Elizabeth River for the December 1985 and 1986 time periods were 87 and 48 ng dm^{-3} respectively. Intermittent high TBT concentrations in the Elizabeth River suggest that improved commercial dry-dock clean-up procedures are necessary and would greatly

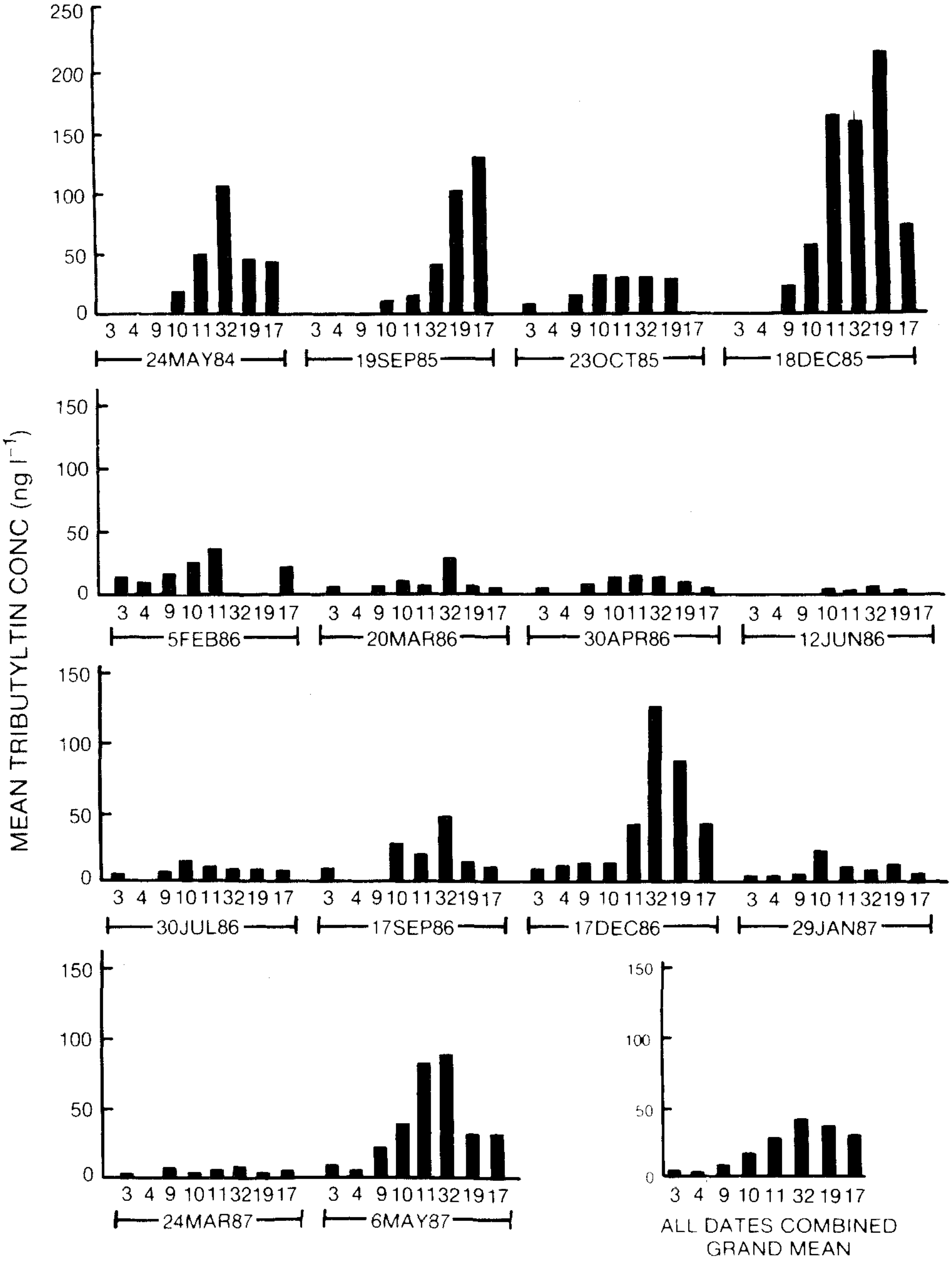

Figure 6 TBT concentrations in surface waters of the Elizabeth River estuary and Hampton Roads from May 1984 to May 1987. Sampling locations are shown and relate to Fig. 5 monitoring stations.

reduce the flux of TBT into the estuary. Numerical model simulations of optimized hull and dry-dock releases from a dynamic estuary model support this conclusion by predicting a low (<10 ng dm^{-3}) river concentration.[13]

Pearl Harbor, Hawaii

A series of monitoring surveys was conducted in 1987 and 1988 to investigate changes in butyltin concentrations in Pearl Harbor during a period in which three US Navy ships were painted with TBT-containing

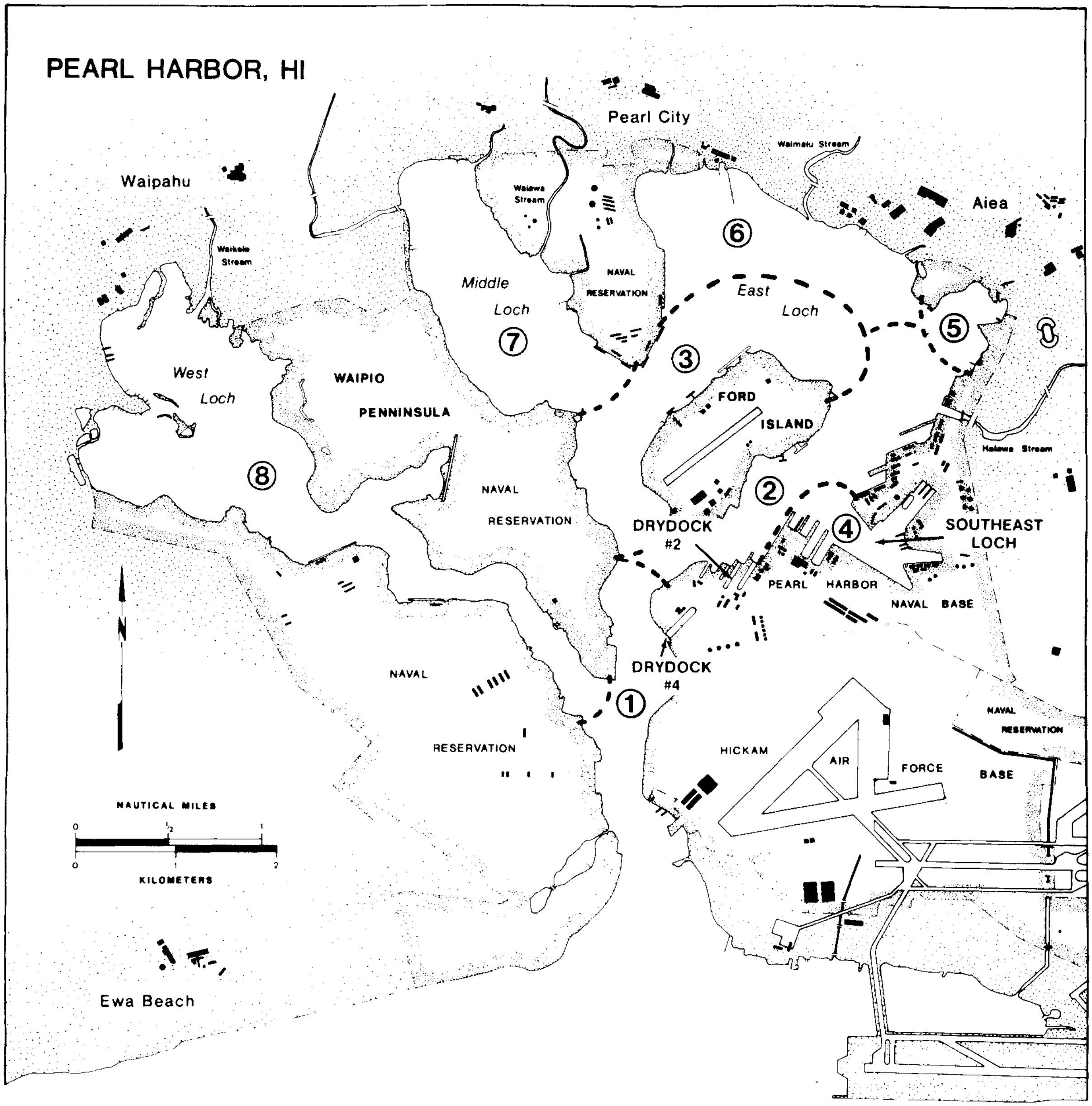

Figure 7 Location of water sampling regions in Pearl Harbor, Hawaii

coatings. The Harbor was selected for these studies because it is almost entirely a Navy port with unambiguous TBT sources. Pearl Harbor is characterized by weak tidal flow, with a mean tidal range of 0.4 m. Circulation is primarily wind-driven. For temporal comparisons the harbor was divided into eight regions, selected on the basis of circulation and use patterns (Fig. 7). The harbor has three main embayments, West, Middle and East lochs. The principal Navy activity is in Southeast Loch (region 4); a small marina is located in East Loch (region 5). The channel areas (regions 1, 2 and 3) were combined as 'Main Channels' for comparison with other regions in Fig. 8. The results of these surveys will be compared to simulations from a numerical dynamic estuary model to predict future TBT concentrations from US Navy utilization of these coatings.

During a baseline study conducted in April 1984, no detectable TBT (<5 ng dm^{-3}) was measured in Pearl Harbor (Fig. 1).[11] At the time of the survey, no US ships with TBT coatings were berthed in the Harbor. Conversely, TBT levels in Honolulu Harbor, Hawaii's principal commercial shipping port, averaged 97 ng dm^{-3}. Figure 8 provides mean regional TBT concentrations in Pearl Harbor for six sampling periods between February 1987 and January 1988. The figure is a summary of 612 samples with triplicated deep and shallow measurements averaged. Each region had from one to several sampling locations. During this time period, six Navy ships coated with TBT paints were based in Pearl Harbor with varying in-port periods. Three of the six were painted during the time period starting in March 1987.

During the first three sampling periods, February–April 1987, TBT concentrations in the Navy berthing area in Southeast Loch averaged close to 10 ng dm^{-3}. During July and October concentrations dropped to 4 and 2 ng dm^{-3}, respectively, followed by an increase to 6 ng dm^{-3}. The changes in concentration are consistent and linear with the total loading of TBT from hull releases measured by an *in situ* leach rate measuring device (unpublished data). A generally similar pattern was observed in the outer regions of the Harbor including the channel areas, West Loch, and Middle and East Lochs. TBT concentrations in the water column in these regions were generally less than 5 ng dm^{-3}. TBT concentrations were frequently less than 1 ng dm^{-3} in the West and Middle Lochs. During the painting and undocking of a Navy Frigate in early March 1987, small increases in TBT concentrations were measured outside dry-dock (no. 2). However, no changes in TBT concentrations were observed in outlying areas of Pearl Harbor. The total release from the dry-dock of approximately 13 g TBT into the harbor represented a 99.8%-effective clean-up effort,[32] documenting that dry-docks can be successfully cleaned to reduce significantly the flux of TBT to the environment from shipyard activities. The release was approximately one to two orders of magnitude less than discharges estimated in the Elizabeth River.[13] Two additional ships were subsequently painted (one in dry-dock no. 2 and one in dry-dock no. 4 in September 1987). Because of rigorous clean-up efforts these vessels released less than 1 g TBT into the harbor. No measurable increases in TBT levels in the harbor waters were noted. Outlying areas of Pearl Harbor consistently had TBT levels below 5 ng dm^{-3} both prior to and after undocking of these TBT-coated vessels. Surface waters generally contained two to three times the TBT concentration of near-bottom water, particularly in regions near TBT sources such as Southeast Loch and Rainbow Marina. This is consistent with findings in other harbors.

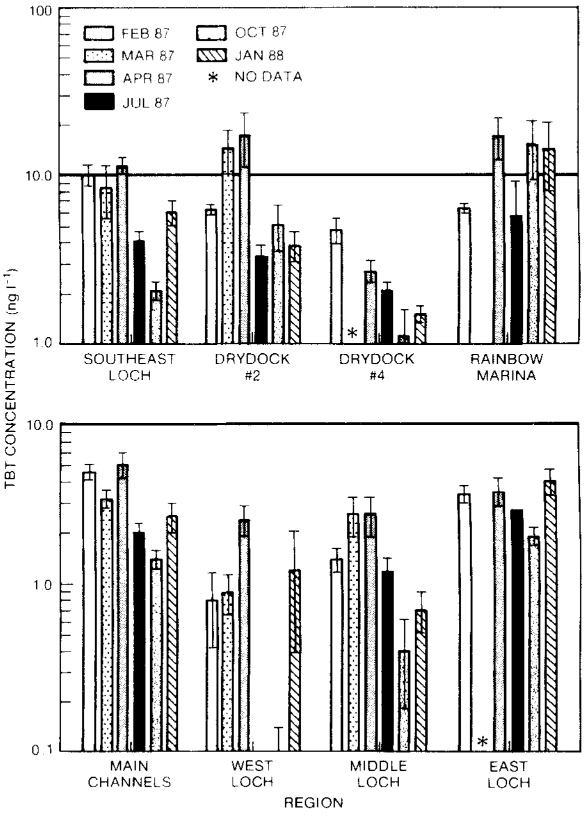

Figure 8 TBT concentrations in Pearl Harbor, Hawaii, during February 1987 to January 1988. Error bars are 1 standard error.

Honolulu Harbor, Hawaii

Honolulu Harbor is the primary commercial port for the State of Hawaii. It is located east of Pearl Harbor and is composed of two broadly connected basins (Fig. 9). The diurnal tidal range in Honolulu Harbor is 0.4 m. The four regions selected for comparison (each having one to several collection sites sampled in triplicate) were the entrance channel (1), the main harbor basin (2), the commercial dry-dock facility (3) and the Ala Wai Boat Basin (6), a marina separated from Honolulu Harbor. In general, TBT concentrations in Honolulu Harbor were an order of magnitude higher than Pearl Harbor (Fig. 10). The data set presented represents 134 sample analyses. TBT concentrations

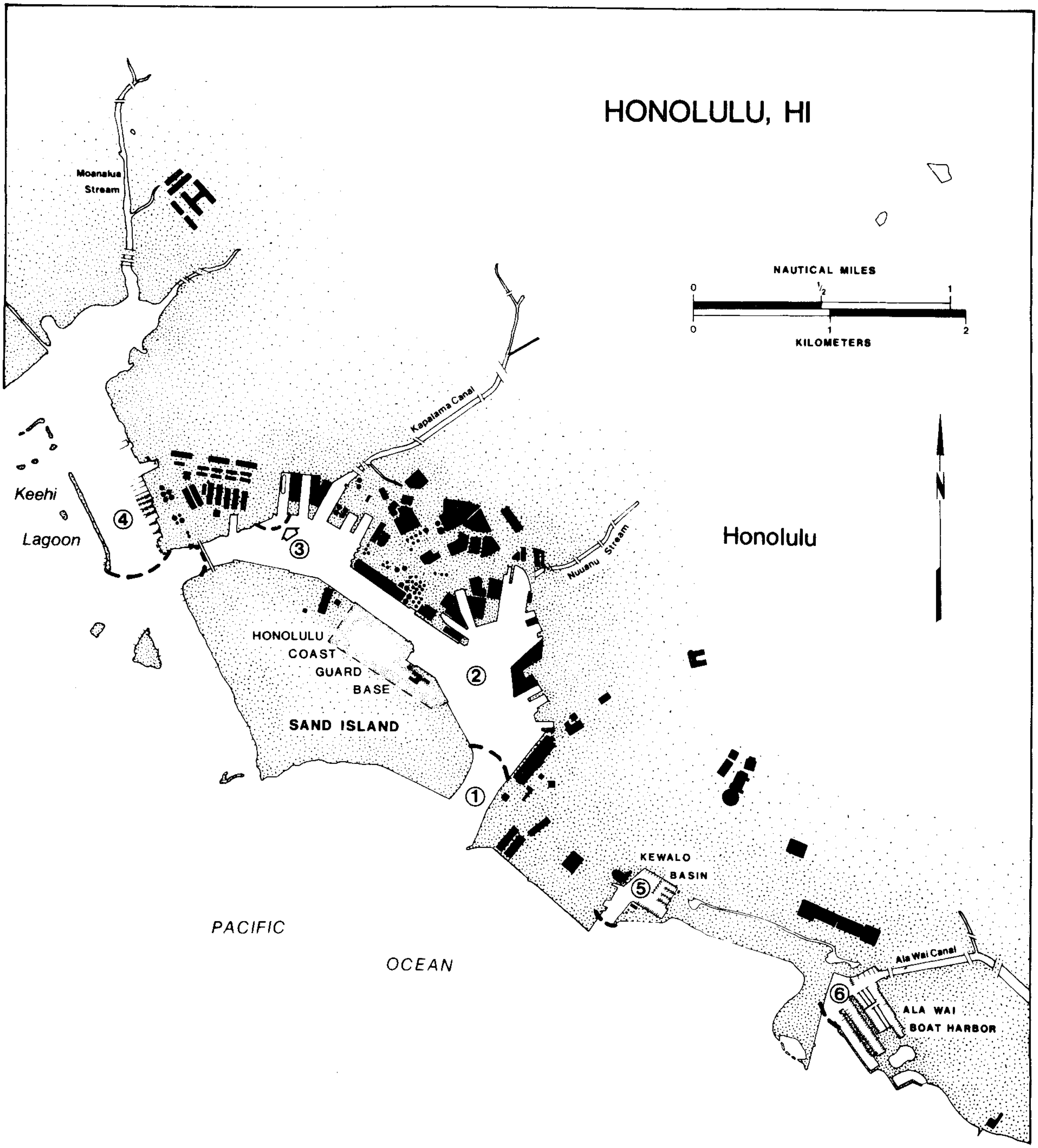

Figure 9 Location of water sampling regions in Honolulu, Harbor, Hawaii.

varied from 5 to 35 ng dm^{-3} in the entrance channel, from 16 to 64 ng dm^{-3} in the main harbor basin and from 74 to 375 ng dm^{-3} near the dry-docks. In the Ala Wai Boat harbor, average TBT concentrations varied from 105 to 210 ng dm^{-3}. Surface values, however, were as high as 390 ng dm^{-3} in Ala Wai with near-bottom concentrations about one-tenth of surface values. The highly variable concentrations at the dry-dock suggest intermittent discharges similar to those observed in the Elizabeth River (Fig. 6). The

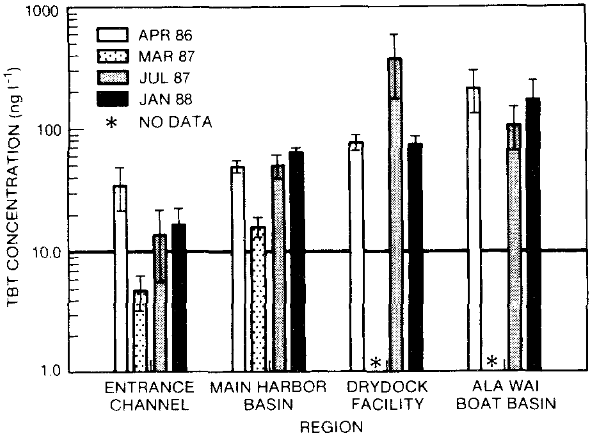

Figure 10 TBT concentrations in Honolulu Harbor, Hawaii, during April 1986 to January 1988. Error bars are 1 standard error.

relatively high TBT concentration observed in the main harbor basin, averaging 45 ng dm^{-3}, likely results from heavy use by commercial bulk carriers and cruise ships, the majority of which use TBT antifouling hull paints.

Fate of TBT in marine and estuarine waters

Degradation in water The persistence of a pesticide in the environment is a critical element in assessing the long-term environmental risk from use of that pesticide. As an example, DDT was banned in the USA in 1972 because of its persistence in the environment (several-year half-life) and its extremely high lipophilic character combined with an inability of invertebrate and vertebrate organisms to metabolize the pesticide. Severe biomagnification of DDT via food-chain accumulation and concomitant declines in reproductive success in several bird species due to manifestations of a DDT-related shell-thinning process were reported in numerous studies. In contrast, it has been reported that a variety of estuarine organisms, including crabs, fish and shrimp were able to rapidly metabolize TBT by forming a number of hydroxylated metabolites.[33,34] Oysters, however, metabolized TBT at a much slower rate, which may relate to molluscan sensitivity to this compound.

We have conducted numerous TBT degradation experiments using microcosms with ambient unfiltered water to evaluate TBT half-lives at four diverse harbors and estuaries at environmental concentrations. These experiments have yielded a highly consistent range of half-lives for TBT in the water column of

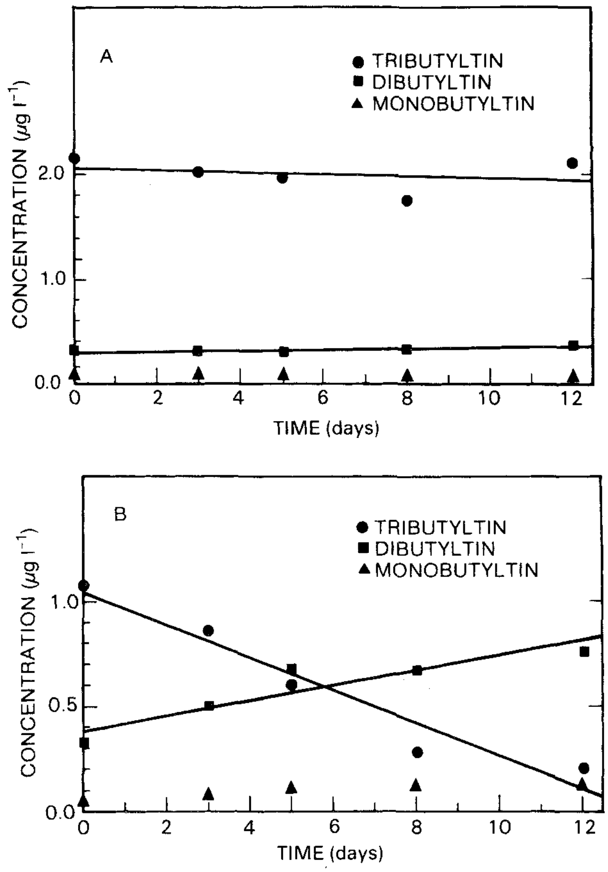

Figure 11 Concentration of TBT and degradation products in (A) filtered seawater control and (B) ambient unfiltered seawater over time (modified from Ref. 35).

4–19 days.[27,35,36] The principal degradation product in both light and dark treatments is DBT with much slower formation of MBT. Figure 11 shows results of a typical degradation experiment in which seawater is spiked with TBT (1.1 μg dm^{-3} TBTCl) and the change in butyltin species is compared in a filtered control (Fig. 11A) with an unfiltered system (Fig. 11B).

The rate of loss of parent compound (TBT) was determined by regression analysis and a half-life was calculated. The rapid formation of DBT and a slower production of MBT were generally observed concomitantly with the loss of TBT (Fig. 11B). Figure 12 gives a summary of 46 degradation experiments, conducted in nine locations in four harbors and estuarine regions in both the east and west coasts of the USA (including Hawaii). The studies were conducted during various seasons between 1985 and 1988. Degradation

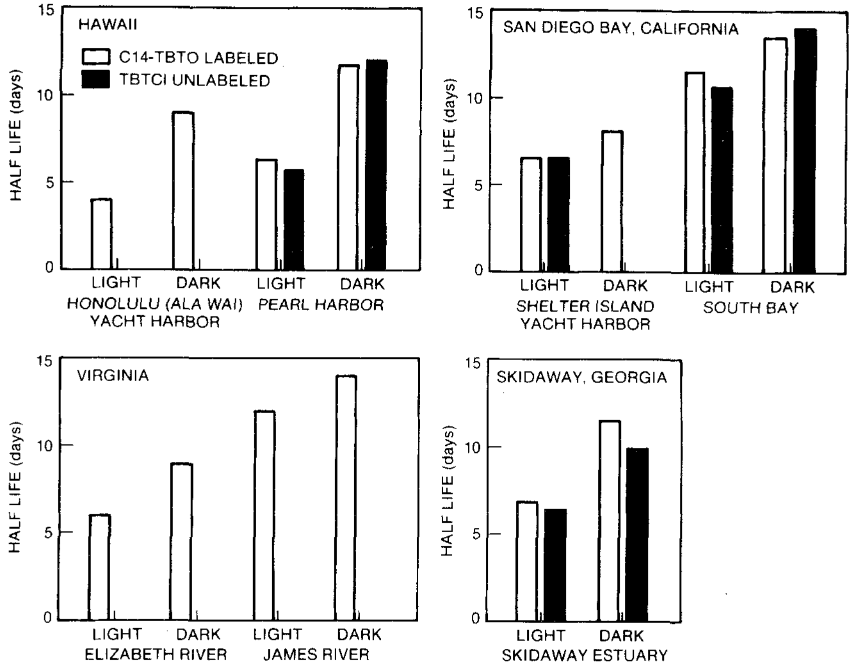

Figure 12 Mean TBT degradation half-lives calculated from labeled (carbon-14) and unlabeled experiments under light and dark conditions.

half-lives of spiked ^{14}C-labeled TBTO compared closely with parallel experiments using unlabeled TBTCl. Mean TBT half-life values varied from four days in the Ala Wai Yacht Harbor in Hawaii to 14 days in south San Diego Bay and the James River in Virginia. In general, experiments conducted in the dark, simulating near-bottom conditions, had half-lives that were longer by an average of 40% over treatments exposed to ambient near-surface light conditions, suggesting that algae populations may be significant in the degradation process. Maguire found that a freshwater green alga could degrade TBT to DBT.[37] More recently, we have found that marine diatoms can rapidly metabolize TBT to hydroxylated derivatives (e.g. hydroxybutyldibutyltin) which are formed in the light treatments. Diatoms, therefore, may play a significant role in the fate of TBT in marine and estuarine systems.[36] Olsen and Brinckman also found accelerated TBT degradation under light conditions suggesting that photosynthetic organisms are important.[38] Although bacteria likely play a major role in the degradation process, eukaryotic organisms such as fungi may be important, particularly in benthic environments.

Within a harbor or estuary, areas of higher TBT concentration (e.g. source regions such as marinas) typically had faster TBT decay rates by a factor of approximately 2. The faster decay rates in water from areas of high ambient TBT concentration suggest a selection process favoring TBT-metabolizing microbes and alga.[36] We observed this phenomenon in Ala Wai Yacht Harbor relative to Pearl Harbor, in Shelter Island Marina compared with South San Diego Bay and in the Elizabeth River versus the James River where TBT concentrations were less than 5 ng dm^{-3} (Fig. 12).

Although spring and winter TBT degradation rates were generally slightly less than summer and autumn rates, the differences are less than expected on the basis of normal thermal kinetics. We measured TBT degradation in water temperatures ranging from 11 to 29°C in Skidaway with half-lives of 8 and 6 days, respectively. In summary, water column degradation rates are generally in the range of 5–14 days (13–5% loss per day) showing that in the environments studied, TBT is not a persistent compound in the water column.

Other investigators have measured similar half-lives (6 days) at water temperatures of 20°C (freshwater, UK) and 28°C (Baltimore Harbor, Maryland, seawater).[39,38] In winter conditions (5°C), however, degradation rates were much slower, yielding half-lives of 60 days or longer.[38,39] Maguire has reported TBT half-lives in fresh water of 6 weeks to several months.[40] The high TBT concentration used in these experiments may have contributed to the longer half-lives reported by causing toxic inhibition of bacteria capable of metabolizing TBT.[27]

Partitioning and degradation in sediments Tributyltin concentrations in aquatic sediments, although variable, have generally been found to be approximately 5×10^2 to 10^4 times overlying water column values.[26,30,41,42] This range of concentration factors is generally consistent with measured partitioning coefficients (Kp),[41–43] although the Kp is dependent on sediment load, salinity, particle size and organic content.[44] Preliminary results of TBT desorption experiments are equivocal: 24-h desorption isotherms suggest that TBT sorption to sediments is reversible,[45] whilst our *in situ* studies, using diver-positioned domes in areas of TBT-impacted sediment, suggested a net adsorption of ambient TBT to the sediments.[42] In addition, it has been demonstrated that the distribution of TBT between sediment and water in an estuary is directly related to salinity and turbidity.[44] The evidence indicates stronger TBT sorption in salinities approaching those of seawater and weaker sorption and potential desorption of TBT in less saline waters.

Degradation studies of TBT associated with sediments suggest half-lives at least an order of magnitude longer than those found in water. A TBT half-life for sediment from a freshwater harbor in Canada has been calculated at approximately 4 months,[40] with DBT as the primary degradation product. Our work with marine sediments has documented a similar decay rate of about 5.5 months with MBT as the principal degradation product.[26] Sediment cores taken in San Diego Bay show increasing percentage MBT values with depth, providing field evidence of TBT debutylation to MBT. *In situ* dome studies at the sediment–water interface indicate a potential for DBT desorption from sediment.[42] This observation is in accord with other work[46] indicating DBT partitioning coefficients are an order of magnitude or more lower than those for TBT; consequently, the potential for TBT-to-DBT degradation at the sediment–water interface and subsequent DBT release to the water column may exist.

In addition to the above-reported biotic degradation of TBT in sediment, recent evidence suggests rapid abiotic degradation of TBT by some sediment types.[47] Several types of sediment from three different marine basins have been shown to dealkylate TBT to DBT in the absence of biota. Preliminary evidence indicates that the dealkylation is physical or chemical in nature and can occur at rates of DBT formation of 10–20% per day after a 24-h incubation period.

The bioavailability of TBT associated with sediments, defined as uptake rate and inducement of toxic effects, is a very important element in evaluating risks associated with sediment TBT concentrations.[48] Bioavailability of TBT under natural conditions has generally not been addressed in reports focusing on its toxicity, and requires further investigation prior to making environmental judgments and regulatory decisions based on TBT sediment concentrations.

Partitioning in suspended particulate TBT exists in the water column in a dissolved form as well as in association with suspended particulates.[41,43,49] Association of TBT with suspended particulates has been shown to be dependent on the particulate concentration, on salinity and on natural organics.[41,44–46] In studies conducted with environmental samples, generally less than 5% of the total TBT measured in unfiltered water samples was found in the particulate fraction separated by in-line filtration.[41] Centrifugation of bulk water samples did not indicate a significant change in the TBT concentration measured, suggesting that TBT was primarily in the dissolved form.[49] Adsorption experiments with ^{14}C-labeled TBTO have shown that no more than 17% of the added TBT sorbed to particulate from the Skidaway estuary, Georgia, in a 10-h period. Experiments with unfiltered seawater from San Diego Bay having significantly less suspended particulate showed that 6–11% of the added TBT sorbed to the particulate fraction.[41]

We have found that partition coefficient values (Kp) determined for TBT associated with suspended particulate are near 3000 at suspended particulate concentrations of 5.8–6.7 mg dm^{-3}.[41] This is in agreement with the work of Maguire in Canadian waters.[50] Sediment/water partition coefficient values in some areas in San Diego Bay are less than particulate/water Kp values, suggesting that degradative processes are also occurring in marine sediments where TBT was deposited. An inverse relation was seen with increasing suspended particulate concentration and Kp.[41] Subsequent measurements of particulate separated from water samples collected from a site near yacht repair facilities have shown higher percentages of TBT associated with suspended particulate (22%). Partition coefficient values were near 4×10^4 in some of the samples measured, indicating location of the sampling site near yacht repair facilities was a significant factor regarding exposure to particulate TBT and is likely related to suspended particulate paint.[43]

CONCLUSIONS

Our initial baseline measurements in 15 harbors and more extensive monitoring surveys have documented that the primary sources of TBT in the US are the same as those overseas.[4] These sources are small boat harbors, marinas and ship repair facilities where TBT paints are applied or removed with inadequate containment of residues. In seven of 15 harbors TBT concentrations exceeded the proposed US EPA Water Quality Criteria of 10 ng dm^{-3} in commercial/recreational regions. Elevated harbor concentrations resulting from small craft (<25 m) should be significantly reduced over the next several years as a result of State and Federal legislation and regulation. The waters of San Diego Bay (where concentrations in all regions are near, or exceed 10 ng dm^{-3}) will provide an excellent test case for the efficacy of the legislation because of the major influence of yachts on TBT concentrations in the region. In regions such as the Elizabeth River and Honolulu Harbor, where drydocks and large vessels are primary TBT sources, improved clean-up measures and use of low-release-rate paints would significantly decrease TBT levels, as has been demonstrated in Pearl Harbor.

TBT is not a persistent biocide in marine and estuarine waters. Degradation experiments conducted in various areas by independent measurement methods have consistently shown that TBT biodegrades rapidly (generally 1–2 week half-life) to DBT at environmental concentrations. At very low temperatures (5 °C) some authors have documented longer half-lives; however, given reduced release rates and lower TBT inputs from yachts in winter, this may not be of significance relative to water column TBT concentrations. TBT degradation in sediments appears to be somewhat slower, with a half-life due to biodegradation of several months. Sediments may then represent a temporary sink and short-term source of TBT as water column levels decline.

The important environmental issue regarding TBT is to ensure that the steady-state concentration remains below levels where significant chronic or population effects can occur, particularly in areas of important ecological and economic resources. Future monitoring programs should be directed towards this goal, keeping in focus the large spatial, temporal and vertical variability that has been documented. The sporadic nature of point-source discharges must also be considered. To date, many of the monitoring efforts have focused primarily in source regions, particularly in marinas and areas of boating activity. More work is needed in ecologically important resource regions outside of boat harbors to evaluate accurately the scope of the TBT problem and the effectiveness of regulatory and legislative action.

Acknowledgements This work was sponsored by the Office of the Chief of Naval Research and David Taylor Research Center under the Navy Energy Research and Development Program. Additional support for methods development was provided by the Naval Facilities Engineering Command, Environmental Protection Program. We gratefully acknowledge the talented technical support of Cesar Clavell, Giti Vafa, Steve Frank and Mark Kram, and typing skills of Deborah DeMasse. We also thank Carl Adema, Gordon Smith and Bill Thomas of the David Taylor Research Center for collecting samples and modelling efforts in the Norfolk region.

REFERENCES

1. Davidson, B M, Valkirs, A O and Seligman, P F Acute and chronic effects of tributyltin on the mysid *Acanthomysis sculpta* (Crustacea, Mysidacea). In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986*, Vol 4, IEEE, New York, pp 1219–1225
2. Bryan, G W, Gibbs, P E, Hummerstone, L G and Burt, F R *J. Mar. Biol. Assoc. UK*, 1987: 525
3. Waldock, M J and Miller, D *The Determination of Total And Tributyl Tin in Seawater and Oysters in Areas of High Pleasure Craft Activity*, Marine Environmental Quality Committee Report CM 1983/E:12, Ministry of Agriculture, Fisheries and Food, Fisheries Laboratory, Remembrance Avenue, Burnham-on-Crouch, Essex CM0 8HA UK
4. Waldock, M J, Thain, J E and Waite, M E *J. Appl. Organomet. Chem.*, 1987, 1:287
5. Cleary, J J and Stebbing, A R D *Mar. Pollut. Bull.*, 1985, 16:350
6. Maguire, R J, Chau, Y K, Bengert, G A, Hale, E J, Wong, P T S and Kramar, O *Env. Sci. Technol.*, 1982, 16:698
7. Valkirs, A O, Seligman, P F, Stang, P M, Homer, V, Lieberman, S H, Vafa, G and Dooley, C A *Mar. Pollut. Bull.*, 1986, 17:319
8. Hall, L W, Lenkevich, M J, Hall, W S, Pinkey, A E and Bushong, S J *Mar. Pollut. Bull.*, 1987, 18:78
9. Stallard, M O, Hodge, V and Goldberg, E D *Environ. Monitoring and Assessment*, 1987, 9:195

10. Huggett, R J, Unger, M A and Westbrook, D J Organotin concentrations in the Southern Chesapeake Bay. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1262–1265

11. Grovhoug, J G, Seligman, P F, Vafa, G and Fransham, R L Baseline measurements of butyltin in US harbors and estuaries. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1283–1288

12. Seligman, P F, Grovhoug, J G and Richter, K E Measurement of butyltins in San Diego Bay, CA: a monitoring strategy. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1289–1296

13. Seligman, P F, Adema, C M, Stang, P M, Valkirs, A O and Grovhoug, J G Monitoring and prediction of tributyltin in the Elizabeth River and Hampton Roads, Virginia. In: *Proc. Organotin Symposium of the Oceans '87 Conference, Halifax, NS, Canada, 1987,* Vol 4, IEEE, New York pp 1357–1363

14. US Environmental Protection Agency Initiation of a special review of certain pesticide products containing tributyltins used as antifoulants; availability of support document. *Federal Register* 1986, 51:778

15. US Public Law 100–330 102 Stat.605 *Organotin Antifouling Paint Control Act of 1988* 16 June, 1988

16. US Environmental Protection Agency Tributyltin Antifoulants; Notice of Intent to Cancel; Denial of Applications for Registration; Partial Conclusion of Special Review. *Federal Register* Vol. 53 No. 192, pp 39022–39041, 4 October, 1988

17. (France) *Decree 82-782* 14 Sept 1982

18. *Control of Pollution Act, 1974,* Her Majesty's Stationery Office, London, UK, 1974

19. Anon, *Organotin in Antifouling Paints, Environmental Consideration,* Pollution Paper No. 25, Department of the Environment, London, UK, 1986

20. US Dept of Navy Fleet Wide Implementation of Organotin Antifouling Hull Paints. *Fed. Register* 1985, 50:25748

21. Dooley, C A and Homer, V Organotin compounds in the marine environment: uptake and sorption behavior, Naval Ocean Systems Center Technical Report No. 917, San Diego, CA, 1983

22. Valkirs, A O, Seligman, P F, Olson, G J, Brinckman, F E, Matthias, C L and Bellama, J M *Analyst,* 1987, 112:17

23. Braman, R S and Tompkins, M A *Anal. Chem.,* 1979, 51:12

24. Hodge, V F, Seidel, S L and Goldberg, E D *Anal. Chem.,* 1979, 51:1256

25. Stallard, M O, Cola, S Y and Dooley, C A *Appl. Organomet. Chem.,* 1989, 3: 105

26. Stang, P M and Seligman, P F Distribution and fate of butyltin compounds in the sediment of San Diego Bay. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1256–1261

27. Seligman, P F, Valkirs, A O and Lee R F *Environ. Sci. Technol.,* 1986, 20:1229

28. US Environmental Protection Agency *Ambient Aquatic Life Water Quality Advisories for Tributyltin* USEPA Office of Research and Development, Environmental Research Laboratories, 14 September 1987

29. Waldock, M J TBT in UK estuaries, 1982–1986. Evaluation of the environmental problem. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1324–1330

30. Maguire, R J, Tkacz, R J, Chau, Y K, Bengert, G A and Wong, P T S *Chemosphere,* 1986, 15:253

31. Clavell, C, Seligman, P F and Stang, P M Automated analysis of organotin compounds: a method for monitoring butyltins in the marine environment. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1152–1154

32. US Naval Sea Systems Command *The US Navy's Organotin Environmental Program, Fiscal Year 1987,* NAVSEA Tech Rep. 050-050R-TR-0387, Washington, DC, 1987

33. Lee, R F *Mar. Environ. Res.,* 1985, 17:145

34. Lee, R F Metabolism of bis(tributyltin) oxide by estuarine animals. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp. 1165–1170

35. Seligman, P F, Valkirs, A O and Lee, R F Degradation of tributyltin in marine and estuarine waters. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1189–1195

36. Lee, R F, Valkirs, A O and Seligman, P F Fate of tributyltin in estuarine waters. In: *Proc. Organotin Symposium of the Oceans '87 Conference, Halifax, NS, Canada, 1987,* Vol 4, IEEE, New York, pp 1411–1415

37. Maguire, R J, Wong, P T S and Rhamey, J S *Can. J. Fisher. Aquat. Sci.,* 1984, 41:537

38. Olson, G J and Brinckman, F E Biodegradation of tributyltin by Chesapeake Bay microorganisms. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1196–1201

39. Thain, J E, Waldock, M J and Waite, M E Toxicity and degradation studies of tributyltin (TBT) and dibutyltin (DBT) in the aquatic environment. In: *Proc. Organotin Symposium of the Oceans '87 Conference, Halifax, NS, Canada, 1987,* Vol 4, IEEE, New York, pp 1398–1404

40. Maguire, R J and Tkacz, R J *J. Agric. Food Chem.,* 1985, 33:947

41. Valkirs, A O, Seligman, P F and Lee, R F Butyltin partitioning in marine waters and sediments. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1165–1170

42. Stang, P M and Seligman, P F *In situ* adsorption and desorption of butyltin compounds from Pearl Harbor, Hawaii sediment. In: *Proc. Organotin Symposium of the Oceans '87 Conference, Halifax, NS, Canada, 1987,* Vol 4, IEEE, New York, pp 1381–1391

43. Valkirs, A O, Stallard, M O and Seligman, P F Butyltin partitioning in marine waters. In: *Proc. Organotin Symposium of the Oceans '87 Conference, Halifax, NS, Canada, 1987,* Vol 4, IEEE, New York, pp 1375–1380

44. Harris, J R W and Cleary, J J Particle–water partitioning and organotin dispersal in an estuary. In: *Proc. Organotin Symposium of the Oceans '87 Conference, Halifax, NS, Canada, 1987,* Vol 4, IEEE, New York, pp 1370–1374

45. Unger, M A, MacIntyre, W G and Huggett, R J Equilibrium sorption of tributyltin chloride by Chesapeake Bay sediments. In: *Proc. Organotin Symposium of the Oceans '87 Conference, Halifax, NS, Canada, 1987,* Vol 4, IEEE, New York, pp 1381–1385

46. Randall, L and Weber, J H *Sci. Tot. Env.*, 1986, 57:191

47. Lee, R F and Stang, P M unpublished data, 1988

48. Salazar, M H and Salazar, S M In: *Proc. Organotin Symposium of the Oceans '88 Conference, Baltimore, MD, 1988* (in press)

49. Johnson, W E, Hall, L W, Bushong, S J and Hall, W S Organotin concentrations in centrifuged versus uncentrifuged water column samples and in sediment pore waters of a northern Chesapeake Bay tributary. In: *Proc. Organotin Symposium of the Oceans '87 Conference, Halifax, NS, Canada, 1987,* Vol 4, IEEE, New York, pp 1364–1369

50. Maguire, R J Review of the occurrence, persistence and degradation of tributyltin in fresh water ecosystems in Canada. In: *Proc. Organotin Symposium of the Oceans '86 Conference, Washington, DC, 1986,* Vol 4, IEEE, New York, pp 1252–1255