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# Simultaneous butyltin determinations in the microlayer, water column and sediment of a northern Chesapeake Bay marina and receiving system

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**Butyltins were determined in the microlayer, water column and sediment of a northern Chesapeake Bay marina and its receiving system. Concentrations of the toxicant species tributyltin (TBT) ranged from 60 to 4130 ng dm$^{-3}$ in the microlayer, from 34 to 367 ng dm$^{-3}$ in the water column and from $<0.05$ to 1.4 $\mu$g g$^{-1}$ (dry weight) in sediment. TBT concentrations in all three environmental compartments were higher in the marinas than in the receiving system. Concentrations of TBT in the microlayer and water column of the study area were potentially toxic to sensitive aquatic biota. The microlayer appears to be depleted in dibutyltin relative to tributyltin compared to both water column and sediment.**

**Keywords: Butyltins, microlayer, water column, sediment, analysis**

## INTRODUCTION

The presence of marine fouling organisms on ship hulls increases hydrodynamic drag which leads to reduction of maximum attainable speed and to significantly decreased fuel efficiency. For thousands of years, ship hulls have been treated with a variety of substances to minimize fouling.[1] Paints containing copper oxide have been used since the late nineteenth century; however, these formulations have serious limitations due to short effective lifetimes and high costs. The use of organotin coatings such as tributyltin (TBT) has been promoted in recent years because of their excellent antifouling action, long lifetimes (up to seven years) and absence of corrosion problems.[2]

Tributyltin antifouling paints have potential negative environmental effects due to the toxicity of this compound to non-target organisms. To assess adequately the potential risk of this compound to non-target aquatic biota, it is necessary to know the concentrations of tributyltin and other butyltin species (dibutyltin and monobutyltin) that are present in the environment. Various butyltin monitoring studies have been conducted in the northern[3–5] and southern[6,7] waters of Chesapeake Bay. Butyltin concentrations measured in these monitoring efforts were primarily evaluated in the water column. Although the water column is an important environmental compartment for butyltin species, other habitats such as the microlayer and sediment are also potential compartments for these contaminants. At the present time there are no butyltin data available for microlayer, water column and sediment evaluations taken simultaneously in the same locations of a Chesapeake Bay marina and its respective receiving system. Until recently, the lack of analytical methods for butyltin analysis in sediments has limited monitoring of this environmental compartment.

The objectives of this study were to evaluate monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) and tetrabutyltin (TTBT) in the microlayer, water column and sediment of a Chesapeake Bay

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marina and receiving system. A series of seven stations were evaluated during one sampling period in July 1987.

## MATERIALS AND METHODS

### Sample collection

Microlayer, water column and sediment samples were collected on 8 July 1987 from a series of seven stations in the Port Annapolis Marina, Back Creek and Severn River area in northern Chesapeake Bay (Fig. 1). Back Creek contains 13 marinas and has a high level of boating activity.

Microlayer samples were collected by lowering a glass plate (30 cm × 30 cm) vertically below the water surface, then raising the plate vertically to collect the hydrophobic layer.[8] The collected material was drained into acid-washed 250-cm$^3$ polycarbonate containers with the aid of a Teflon squeegee. Five to ten repetitions of this procedure were required at each sampling site to collect a sample volume of 50–100 cm$^3$. Two microlayer samples were taken at each location.

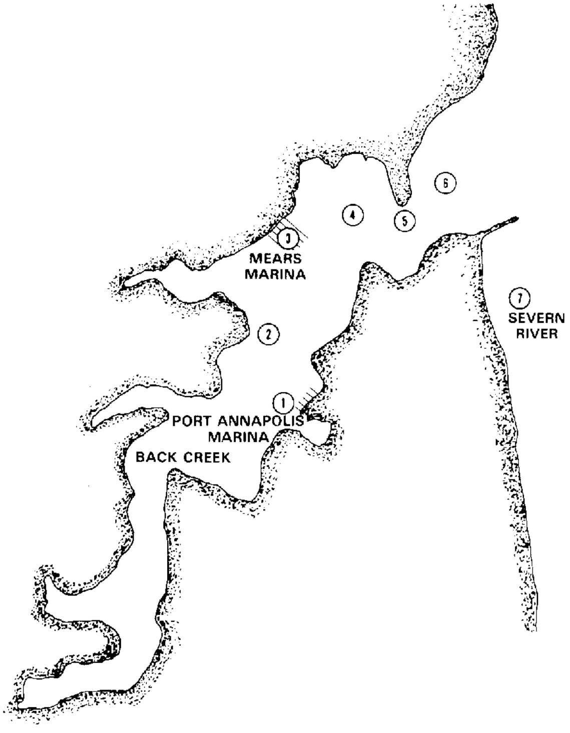

**Figure 1** Map of seven sampling stations in the Port Annapolis Marina, Back Creek and Severn River study area.

Water column samples were taken by lowering a 1-dm$^3$ polycarbonate bottle at arm's length below the water surface. The cap of the bottle was then removed and the sample was collected. Duplicate samples were collected at each station.

Sediment samples were collected with a polycarbonate corer of diameter 5 cm. The upper 2–3 cm of the core was removed with a Teflon spatula and placed in an acid-washed 250 cm$^3$ polycarbonate bottle. Duplicate samples were taken at each station.

Suitable field blanks were prepared for each sample matrix and carried through the complete sample storage and analysis procedure. All samples were frozen on dry ice immediately after collection and maintained at −20 °C until analysis. Analysis of the water column and microlayer samples was accomplished within seven days of collection. The sediment samples were analyzed within 60 days of collection.

### Analytical methods

All glassware was cleaned prior to use by washing with laboratory detergent followed by 12–24 h of leaching with 10% nitric acid. The clean glassware was then rinsed with copious amounts of deionized water.

A Hewlett–Packard (HP) (Avondale, PA) Model 5730A gas chromatograph equipped with an HP flame photometric detector (FPD) (Model 18764A) was used with chromatographic separation carried out on a 2 mm i.d. × 6 ft glass column packed with 1.5% OV-101 (liquid methyl silicone) on Chromosorb G HP (Varian, Sunnyvale, CA). Nitrogen gas (zero grade) carrier flowed at a measured rate of 20 cm$^3$ min$^{-1}$. A hydrogen-rich flame was sustained with hydrogen flowing at 150 cm$^3$ min$^{-1}$, air at 50 cm$^3$ min$^{-1}$ and oxygen at 0–5 cm$^3$ min$^{-1}$. Initial column temperature was 23°C. After an initial 2-minute hold, the column was heated at the rate of 32°C min$^{-1}$ to a final temperature of 180°C. The detector temperature was maintained at 200°C and the injection port at 150°C. The GC FPD was equipped with a 600-nm cut-on optical interference filter with a band pass of 600–2000 nm (Ditric Optical Inc., Hudson, MA) to monitor SnH molecular emission.

The microlayer and water column samples were analyzed by the method of Matthias *et al.*[9,10] Briefly, for analysis of water samples with typical TBT concentrations (<250 ng dm$^{-3}$), a sample volume of 200 cm$^3$ is necessary in order to achieve the detection limit of 5 ng dm$^{-3}$. For samples of 200 cm$^3$, the extraction/derivatization procedures were carried out in a 250-cm$^3$ straight-sided separatory funnel equipped with a Teflon-lined screw cap and a Teflon stopcock. These funnels were made to our specification for this work by Wheaton Scientific, based on the design of a 125-cm$^3$ funnel available as a standard item from Wheaton. For microlayer samples, the 125-cm$^3$ capacity funnels were used. The procedure outlined below is that for 200-cm$^3$ samples. For smaller samples, volumes of solvents and reagents are reduced proportionally.

To a 200-cm$^3$ sample of unfiltered water in a 250-cm$^3$ separatory funnel 50 $\mu$l of 0.5 ng $\mu$l$^{-1}$ $Pr_2Sn^{2+}$ in deionized water was added as an internal standard. The samples were then shaken and the internal standard allowed to equilibrate with the sample for 10–15 min. Hydride derivatization was achieved by the addition of 3 cm$^3$ of 4% (w/v) aqueous sodium borohydride (sodium tetrahydroborate). Dichloromethane (6 cm$^3$) was then added, the funnel was capped and shaken by hand for about 30 s and vented. The funnel was then secured to the wrist-action shaker and shaken (240 strokes min$^{-1}$) for 10 min. After shaking, the layers were allowed to separate and the lower, organic layer was removed, either to a Reacti-vial (Wheaton Scientific) or to a 15-cm$^3$ borosilicate glass centrifuge tube (Corning Glass). An additional 3 cm$^3$ of dichloromethane was added and the shaking step was repeated. The second organic portion was combined with the first for a total solvent volume of about 5–6 cm$^3$. In some estuarine water samples, the dichloromethane formed an emulsion with algae and other materials present in the water. This dichloromethane emulsion was considerably heavier than water and could be removed easily from the separatory funnel. The emulsion was then broken by centrifugation at 700 g for 5–10 min using a Sorval Type 2 bench-top centrifuge. The organic (bottom) layer was removed to a glass Reacti-vial using a Pasteur pipet. The dichloromethane was then evaporated under a gentle stream of dry air to 50–200 $\mu$l as required. Generally 5-$\mu$l portions of the concentrated sample were injected on to the GC column, although sample sizes of up to 10 $\mu$l can be used. Quantification was achieved by calibration curves constructed by analysis of 200-cm$^3$ artificial seawater samples spiked to appropriate concentrations with butyltins.

The sediment samples were analyzed by the method described by Matthias *et al.*[11] Briefly, 2–4 g of wet sediment was placed in a 150-cm$^3$ round-bottom flask (water content was detrmined by drying a separate subsample to constant weight in a 100°C oven). Dipropyltin chloride (50 $\mu$L; 50 ng $\mu$L$^{-1}$ in methanol) was added as an internal standard, followed by 0.5 cm$^3$ concentrated hydrochloric acid. The sample was then swirled for about 30 s (in a hood as hydrogen sulphide is evolved) and 25 cm$^3$ methanol was added. A magentic stir bar was then placed in the flask. The mixture was refluxed for 30 min in an 80°C water bath with stirring. After refluxing, the sample was cooled to room temperature and the slurry transferred to a 50-cm$^3$ glass centrifuge tube (Corning Glass, Corning, NY). The sample ws centrifuged for 5 min at 164 g. The supernatant was transferred to a 25-cm$^3$ volumetric flask using a Pasteur pipet, and methanol was added to bring the sample to 25.0 cm$^3$. Subsamples of the resulting green solution (11.0 cm$^3$) were placed in 5-cm$^3$ glass screw-top reaction vials (Reacti-vial, Wheaton Scientitic, Millville, NJ) and 1.0 cm$^3$ of cyclohexane was added. Quantification was done by the method of standard additions, with the di- and tri-butyltin spikes added to three subsamples of the acidified methanol solution at this point in the analysis. The methanol solutions were extracted with cyclohexane for 5 min on a Burrell wrist-action mechanical shaker. The hexane layer was removed with a Pasteur pipet and placed in a second Reacti-vial. An additional 1.0 cm$^3$ cyclohexane was added to the vial with the methanol solution and a second extraction was performed. The cyclohexane layers were combined and evaporated to about 0.7–1.0 cm$^3$ using a stream of dry air. Hydride derivatization was achieved by shaking the cyclohexane layer with 1 cm$^3$ of 0.4% (w/v) sodium borohydride in water for 45 min on the mechanical shaker. The aqueous layer was then removed with a Pasteur pipet and the sample was ready for analysis.

The gas-chromatographic conditions were as previously described, except that the initial temperature was 30°C. The temperature was increased at 32°C min$^{-1}$ to a final temperature of 170°C which was held until the TBT peak eluted. A large, complex, unidentified peak eluted after TBT; the elution of this peak was hastened by increasing the column temperature to 230°C until the baseline was restored.

Two subsamples of each replicate water column and sediment sample taken at each location were analyzed. The values reported in the next section are the mean and standard deviation for the four determinations at each location. Microlayer sample volumes were rather small (50–100 cm$^3$); therefore, the entire sample volume was used for each analysis. The values reported in the next section are the results for each of the two samples collected at each station.

## RESULTS AND DISCUSSION

Butyltin concentrations in the microlayer, water column and sediment are presented in Tables 1–3. Tetrabutyltin (TTBT) was not detected in the microlayer or water column at any sampling station. It was not possible to detect tetrabutyltin or monobutyltin in the sediment by the analytical method employed. Because of the localized and transient nature of the microlayer the sample-to-sample variation is quite large, with the range nearly equal to the mean for some of the sampling locations.

**Table 1** Monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT) concentrations (ng dm$^{-3}$) reported in the microlayer at the seven stations (duplicate samples)

| Station | Sample | MBT | DBT | TBT |
|---|---|---|---|---|
| 1 | A | 1030 | 2020 | 5980 |
| | B | 980 | 1280 | 2280 |
| 2 | A | nd | 128 | 216 |
| | B | 15 | 129 | 396 |
| 3 | A | 13 | 129 | 524 |
| | B | nd | 87 | 217 |
| 4 | A | nd | 72 | 143 |
| | B | 10 | 83 | 194 |
| 5 | A | 13 | 102 | 473 |
| | B | 13 | 66 | 208 |
| 6 | A | 35 | 222 | 775 |
| | B | 23 | 82 | 251 |
| 7 | A | 16 | 8 | 50 |
| | B | 13 | 9 | 70 |

nd, not detected. Detection limit 5–15 ng dm$^{-3}$, depending on species.

**Table 2** MBT, DBT and TBT concentrations (ng dm$^{-3}$) reported in the water column at the seven stations (mean ± SD for four determinations)

| Station | MBT | DBT | TBT |
|---|---|---|---|
| 1 | 102 ± 3 | 233 ± 21 | 367 ± 69 |
| 2 | 18 ± 2 | 165 ± 1 | 182 ± 2 |
| 3 | nd | 203 ± 8 | 257 ± 21 |
| 4 | nd | 182 ± 7 | 222 ± 1 |
| 5 | nd | 158 ± 3 | 163 ± 28 |
| 6 | nd | 133 ± 3 | 142 ± 1 |
| 7 | nd | 25 ± 1 | 34 ± 2 |

nd, not detected. Detection limits are 5–20 ng dm$^{-3}$ depending on species.

Monobutyltin (MBT) was detected in only two of the water column samples but it was detected in all microlayer samples. Because the detection limits differ for the two types of samples the significance of this finding is unclear. Detection limits are 15 ng dm$^{-3}$ for MBT in water and 10 ng dm$^{-3}$ for MBT in microlayer. The values detected range from less than 15 ng dm$^{-3}$ (the detection limit) to 102 ng dm$^{-3}$ in the water column and from 5 ng dm$^{-3}$ to 1000 ng dm$^{-3}$ in the microlayer.

Dibutyltin was detected in all three compartments at all locations except the sediment at Station 7. The highest concentration of DBT in the microlayer (1650 ng dm$^{-3}$) was at Station 1 in the marina. Lowest DBT concentration (8 ng dm$^{-3}$) was at Station 7 in the Severn River. Concentrations of DBT in the water column followed a similar trend, with the highest concentration (233 ng dm$^{-3}$) within the marina and lowest value (25 ng dm$^{-3}$) in the Severn River. Similarly, concentrations of DBT in the sediment were highest at Station 1 in the marina (2.2 μg g$^{-1}$) and decreased along the length of Back Creek to a non-detectable level (<0.05 μg g$^{-1}$) in the Severn River.

TBT concentrations in all three compartments were highest in the marinas and lowest in the Severn River. TBT concentrations in the microlayer were 4130 ng dm$^{-3}$ at Station 1 in the marina and 60 ng dm$^{-3}$ at Station 7 in the Severn River. Highest TBT concentrations in the water column occurred at Station 1 in the marina (367 ng dm$^{-3}$) with the lowest value (34 ng dm$^{-3}$) at Station 7 in the Severn River.

**Table 3** DBT and TBT concentrations (μg g$^{-1}$) reported in the sediments of the seven stations (mean ± SD for four determinations)

| Station | DBT | TBT |
|---|---|---|
| 1 | 2.2 ± 0.05 | 1.4 ± 0.80 |
| 2 | 0.64 ± 0.14 | 0.59 ± 0.16 |
| 3 | 0.57 ± 0.24 | 0.43 ± 0.19 |
| 4 | 0.39 ± 0.02 | 0.62 ± 0.20 |
| 5 | 0.15 ± 0.03 | 0.14 ± 0.05 |
| 6 | 0.86 ± 0.04 | 0.24 ± 0.20 |
| 7 | nd | 0.05 ± 0.01 |

nd, not detected. Detection limit 0.05 μg g$^{-1}$.

Maximum concentrations of 1.4 $\mu$g g$^{-1}$ were reported in the sediment of the marina; lowest values (<0.05 $\mu$g g$^{-1}$) were found in the Severn River.

The ratio of DBT to TBT in the water column and sediment are both approximately one (Table 4). In the microlayer, DBT is depleted relative to TBT with a mean ratio of 0.32. The depletion of DBT in the microlayer could be the result of poor partitioning of the more highly charged, hydrophillic DBT cation ($Bu_2Sn^{2+}$) compared with the partitioning of TBT cation ($Bu_3Sn^+$). There have been reports of TBT enrichment in the microlayer by values of up to $10^4$ in fresh water.[12] The highest enrichment of TBT in the microlayer relative to the water column in this study was 11.2 at Station 1 (Table 5). The other stations show no or only minimal enrichment of 0.8 to 3.6.

**Table 4** Ratio of DBT to TBT in each compartment at the seven sampling stations.

| Station | Microlayer | Water column | Sediment |
|---|---|---|---|
| 1 | 0.40 | 0.63 | 1.44 |
| 2 | 0.42 | 0.91 | 1.08 |
| 3 | 0.29 | 0.80 | 1.32 |
| 4 | 0.46 | 0.82 | 0.63 |
| 5 | 0.25 | 0.97 | 1.07 |
| 6 | 0.30 | 0.94 | 1.70 |
| 7 | 0.13 | 0.73 | — |
| Mean ± SD | 0.32 ± 0.11 | 0.83 ± 0.11 | 1.20 ± 0.37 |

**Table 5** Microlayer enrichment factors for the MBT, DBT and TBT expressed by the concentration in the microlayer/concentration in the water column

| Station | MBT | DBT | TBT |
|---|---|---|---|
| 1 | 9.8 | 7.1 | 11.2 |
| 2 | 0.4 | 0.8 | 1.7 |
| 3 | — | 0.5 | 1.4 |
| 4 | — | 0.4 | 0.8 |
| 5 | — | 0.5 | 2.1 |
| 6 | — | 1.1 | 3.6 |
| 7 | — | 0.3 | 1.8 |

**Table 6** Sediment enrichment factors for DBT and TBT expressed as concentration in the sediment ($\mu$g g$^{-1}$)/concentration in the water column ($\mu$g g$^{-1}$).

| Sediment | DBT | TBT |
|---|---|---|
| 1 | 9400 | 3800 |
| 2 | 3900 | 3200 |
| 3 | 2800 | 1700 |
| 4 | 2100 | 2800 |
| 5 | 950 | 860 |
| 6 | 650 | 1700 |
| 7 | — | 1500 |

Both DBT and TBT are enriched in the sediment relative to the water column by a factor of approximately $10^3$ (Table 6). For DBT there is a fairly smooth decrease in enrichment along the length of Back Creek from the marinas into the Severn River. For TBT, the sediment is enriched relative to the water column by $1 \times 10^3$ to $4 \times 10^3$, values consistent with the water–sediment partition coefficient of 3715 reported by Dooley and Homer.[13]

TBT concentrations reported in the microlayer and water column of the present study can be compared with laboratory toxicity data reported for various Chesapeake Bay biota. Laboratory toxicity data for sediments are not available. TBT concentrations ranging from 60 to 4130 ng dm$^{-3}$ were reported in the microlayer of all seven stations. TBT concentrations of 88 ng dm$^{-3}$ have been reported toxic to Chesapeake Bay zooplankton.[14] These organisms can be found in the microlayer during a portion of their life history and would therefore be susceptible to the toxic effects of TBT as reported in this study. TBT concentrations ranging from 34 to 367 ng dm$^{-3}$ in the water column of the study area could also be potentially toxic to these sensitive Chesapeake Bay biota.

## CONCLUSIONS

TBT is found in the microlayer and water column at concentrations that have been shown to be harmful to certain sensitive biota in controlled environments. The marina sediments studied showed a thousand-fold enhancement of TBT over water column and microlayer concentrations. It is not known if these contaminated sediments will act as a source of TBT to the water column after TBT inputs are minimized as a result of legislative action.

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