Butyltin compounds were investigated in surface sediments from 17 stations in Todos os Santos Bay. Analytical conditions for organotin determination in marine sediments were optimized for GC with pulsed flame photometric detection. Detection limits were: 5.4 μg kg⁻¹ for TBT; 0.2 μg kg⁻¹ for DBT; and 2.1 μg kg⁻¹ for MBT, using a 610-nm filter. In general, TBT concentrations were low and in the range of <DL to 15.9 μg kg⁻¹. Only in one of the investigated stations DBT and MBT were above detection limit despite the oxic to slightly anoxic conditions in the sediments. The presence of paint particles in the sediments and degradation in the water column during resuspension events followed by removal of the more soluble DBT and MBT may explain these observations.

Keywords: butyltin speciation; sediments; Todos os Santos Bay.

INTRODUCTION

There is an increasing interest and concern about the wide spread use of antifouling paints containing tributyltin (TBT)¹.² Such substances intentionally used to eliminate certain organisms that infest ship hulls also act as endocrine disrupters in non target organisms leading to the appearance of imposex in gastropods and to reproductive failure¹-⁴. Because of proven threats to marine organisms several countries banned or have imposed restrictions to the use of TBT although there are still doubts on the efficacy and possible adverse effects of alternative paints⁵-⁷.

In Brazil, no legislation is currently in place to control the use of TBT-based paints. Studies conducted in Guanabara Bay, Rio de Janeiro, that houses the second largest harbor in Brazil and several shipyards and marinas, showed concentrations of TBT in sediments as high as 500 μg kg⁻¹. Also in Guanabara Bay Almeida et al report lack of evidences of TBT degradation in the anoxic sediments of the bay⁸. Limaverde showed that mussels and gastropods from the bay contain high concentrations of TBT and that imposex in Stramonita haemastoma results from exposition to TBT contaminated waters⁹. Godoi et al investigating butyltins in sediments from São Paulo coast found highest TBT levels in Santos harbor (360 μg kg⁻¹ TBT) and in Guarujá marina (670 μg kg⁻¹ TBT)¹⁰.

The aim of the present work was to extend the evaluation of TBT contamination in surface sediment of coastal Brazilian areas to the Todos os Santos Bay (TSB) located in the northeastern region of Brazil. Organotin speciation in sediments has been used to evaluate the extent of marine environment contamination as well as on going remobilization and degradation processes¹¹.

With an area of approximately 1000 km², the Todos os Santos Bay is the largest bay in the Brazilian coast. It has an extensive intertidal zone and a narrow opening to the ocean between Itaparica Island and Salvador City (Figure 1). The tidal regime, characterized by NNE high tidal currents and SSW low tidal currents, is the principal determining factor of water circulation within Todos os Santos Bay. This region is influenced by tropical climate with a well defined rain season from April to June. During summer, predominant winds are from SE, whereas during winter NE winds prevail¹².

EXPERIMENTAL

Reagents

All reagents used were analytical grade. Tributyltinchloride (TBTCl) 96%, dibutyltindichloride (DBTCl) 96%, mono-
butyltrinchloride (DBTCl) 95%, tetrabutyltin (TeBT) 93% and pentylmagnesiumbromide (CH₃(CH₂)₄MgBr, Grignard reagent) 2 mol L⁻¹ in diethyl ether were purchased from Aldrich (Milwaukee, WI, USA). Tripropylchloride (TPrCl) 98%, neutral aluminum oxide (Al₂O₃, 70-230 mesh), Na₂SO₄, HOAc and HCl were obtained from Merck (Darmstadt, Germany); ammonium pyrrolidinedithiocarbamate (APDC - C₅H₈NS₂.NH₄) 97% was purchased from Fluka (Buchs, Switzerland), toluene and methyl alcohol (ChromAR® HPLC) from Malinckrodt, 95% n-hexane HPLC/GC UltimAR® and acetone Nanograde from Malinckrodt or Merck; sílica gel (0.063 – 0.200 mm) and silver nitrate PA (ACS Iso) were from Merck. For organic carbon determination, H₃PO₄ (p. a., Merck) was used.

Standard preparation

Organotin chlorides and TeBT stock standard solutions were prepared at 1.000 mg kg⁻¹ (as Sn) in hexane and remaining stable over a period of six months stored at -20 °C. Pentylated working solutions were prepared by diluting the stock solutions with hexane before derivatization with Grignard reagent.

Sampling

In January 2003, 5 cm of sediments were collected with a Van Veen sampler of 4.2 L specially designed to avoid sediment-water contact during retrieval. Sediments were collected at each station and sub-samples were separated for the determination of organotin compounds, organic carbon, grain size, pH and redox potential (EH), and thereafter immediately sealed and maintained in aluminum box at 4 °C during the transport to the laboratory. The sub-samples for organotin speciation and organic carbon determination were stored in the dark at -20 °C. In station 15, sample was collected in July 2003 using a Kullenberg core sampler.

Sample treatment

Redox potential and pH were measured immediately after arrival in the laboratory using an Ag/AgCl/Pt combined electrode and a glass combined electrode, respectively. Measurements were performed under inert atmosphere, inserting the electrode directly in the sediment. The sub-samples for organotin speciation and organic carbon determination were stored in the dark at -20 °C. Samples were not sieved as to avoid contamination.

Organic carbon determination

Organic carbon was measured in 1–2 g of dry sediment, after acid treatment (1:2 H₃PO₄ aqueous solution, as recommended in the Shimadzu TOC manual) to eliminate carbonates. A Shimadzu SSM-5000A solid sample combustion unit coupled to a Shimadzu TOC-5000A Total Organic Carbon Analyzer was utilized for determination. Quantification was performed using analytical curves and potassium biphtalate as standard.

Butyltins determination

Extraction

The adopted extraction methodology (Figure 2) was modified from Abalos et al. and Fernández-Escobar et al. as appropriate to the sediments characteristics and to the detection by PFPD¹⁷-²⁰. Two grams of sediment (dry mass) were transferred to a glass centrifuge tube. Tripropylchloride (TPrCl) was added as surrogate at a spiking level of 0.2 g. The extraction step was accomplished by sonication with toluene/HOAc (10:4, v/v) for 5 min followed by centrifugation at 2000 rpm, for 5 min, and transfer of the supernatant to a separation vessel. This process was repeated twice.

To the extracts 10 mL of 0.5% APDC aqueous solution were added to partition the HOAc to the aqueous phase and improve the solubility of the mono- and disubstituted organotins in the organic phase. This step was repeated two more times and the separated organic phase was percolated through activated Na₂SO₄ and rotaevaporated to a few milliliters at about 38 °C.

Figure 2. Flow diagram of the analytical procedure for organotin speciation

Derivatisation, alumina cleanup and sulfur elimination

After addition of 2 mL of Grignard reagent, the extract was shake for 1 min and left standing for 20 min. Elimination of excess of Grignard reagent was carried out in an ice bath by adding 12 mL of Milli-Q water and 2 mL of concentrated HCl. The derivatised extract was isolated with a Pasteur pipette and then percolated through activated Na₂SO₄ recovered in a vessel and rotaevaporated to a few milliliters at 38 °C.

The cleanup was made by alumina adsorption chromatography in a glass column filled with 3 g of alumina, 2% water deactivated, and 1 g of activated Na₂SO₄ packed on the top. The organic phase was percolated through the column, using hexane as eluent, and the extract recovered was evaporated under a gentle stream of nitrogen down to 1 mL and TeBT was added as internal standard prior to the GC-PFPD determination. Finally, for sulfur elimination, 100 mg of 25% AgNO₃ – coated silica gel, were put into vials containing the concentrated extract (1 mL). After sonicating for 10 min the mixture was allowed to stand for 2 h at room temperature.
**RESULTS AND DISCUSSION**

Results are given under Table 3 and the space distribution of concentrations appears in Figure 4. A remarkable result was the absolute dominance of TBT in all stations except in Bimbarras Sul (station 13) where TBT was below detection limit and DBT appeared as the main species. The predominance of TBT is usually associated to recent inputs. Spearman and Pearson statistical tests were applied to verify possible correlations between TBT and the other variables in Table 3. The absence of significant correlations indicates that processes controlling the concentration of TBT and its degradation products are occurring outside the sediment environment, as will be discussed below.

The degradation of TBT through dealkylation to tin occurs via biotic and abiotic reactions\(^2\). Photolysis is the most important abiotic degradation process with a half-life of about 3 months\(^2\). According to Batley and Maguire the half life for the biotic degradation of TBT in waters varies from 6 days to several weeks, while the total mineralization occurs within 50-75 days\(^2\). Only in anoxic sediments the degradation is significantly slower ranging from 2 years to decades\(^2\). Therefore, the virtual absence of TBT

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**Table 1. Butyltin concentrations in the reference material PACS-2 in \(\mu g \text{ kg}^{-1}\) as Sn (dry weight)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Determined Value (n=3)</th>
<th>Certified Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBT</td>
<td>1041.9 ± 21.1 (2.0)</td>
<td>980 ± 130</td>
</tr>
<tr>
<td>DBT</td>
<td>1001.3 ± 58.5 (5.8)</td>
<td>1090 ± 150</td>
</tr>
<tr>
<td>MBT</td>
<td>172.5 ± 20.7 (11.9)</td>
<td>300*</td>
</tr>
</tbody>
</table>

* Information value; coefficient of variation, in percent, are given between brackets.

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**Figure 3. Chromatogram of a sample from Ponta do Marinho (station 7) obtained by using GC-PFPD; see text for analytical conditions. TBT, DBT, MBT, TPrT and TeBT stand for tributyltin, dibutyltin, monobutyltin, tripropyltin (surrogate), tetrabutyltin (internal standard), respectively. The peaks of DBT and MBT can be identified in this chromatogram but not quantified**

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**Figure 4. Space distribution of butyltin concentrations in the Todos os Santos Bay**
degradation products in sediments, which in its majority can be considered slightly anoxic, is not expected. In Guanabara Bay, where sediments are strongly anoxic, TBT is also the dominant species although DBT and MBT are found in detectable concentrations.

In the Todos os Santos Bay (TSB) the combination of shallow water depths (average of 6 m), high water transparency (relatively low concentration of suspended matter, 2.15–10.07 mg L\(^{-1}\)) and high water turbulence caused by winds and tidal currents may concur for the observed results. Fent found from studies in seawater that high water turbulence caused by winds and tidal currents may concur for the observed results.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>pH</th>
<th>E(<em>{\text{H}</em>{\text{2}}\text{O}})</th>
<th>Grain size &lt; 0.63 μm (%)</th>
<th>C(_{\text{org}}) (%)</th>
<th>Concentration (μg kg(^{-1})) TBT</th>
<th>DBT</th>
<th>MBT</th>
<th>BTs (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Salvador Harbor</td>
<td>7.25</td>
<td>53</td>
<td>8.70</td>
<td>0.74</td>
<td>13.5 &lt;dl &lt;dl &lt;dl 13.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Itapagipe (2)</td>
<td>7.79</td>
<td>341</td>
<td>3.21</td>
<td>5.46</td>
<td>11.7 &lt;dl &lt;dl &lt;dl 11.7</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3. Tainheiros</td>
<td>7.35</td>
<td>30</td>
<td>75.61</td>
<td>2.79</td>
<td>12.1 &lt;dl &lt;dl &lt;dl 12.1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>4. Paripé</td>
<td>7.32</td>
<td>21</td>
<td>72.28</td>
<td>4.59</td>
<td>9.6 &lt;dl &lt;dl &lt;dl 9.6</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5. Aratu Bay (South)</td>
<td>7.46</td>
<td>48</td>
<td>41.17</td>
<td>2.78</td>
<td>11.6 &lt;dl &lt;dl &lt;dl 11.6</td>
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<td></td>
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<tr>
<td>6. Aratu Bay (North)</td>
<td>7.35</td>
<td>22</td>
<td>89.15</td>
<td>1.99</td>
<td>6.7 &lt;dl &lt;dl &lt;dl 6.7</td>
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<td></td>
<td></td>
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<tr>
<td>7. Ponta do Marinho</td>
<td>7.19</td>
<td>55</td>
<td>98.09</td>
<td>2.30</td>
<td>14.7 &lt;dl &lt;dl &lt;dl 14.7</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>8. Caboto (North)</td>
<td>7.49</td>
<td>89</td>
<td>87.46</td>
<td>2.33</td>
<td>10.2 &lt;dl &lt;dl &lt;dl 10.2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>9. Ponta da Cabimina</td>
<td>7.42</td>
<td>35</td>
<td>80.13</td>
<td>0.73</td>
<td>7.8 &lt;dl &lt;dl &lt;dl 7.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. Maré/São Paulo</td>
<td>7.29</td>
<td>32</td>
<td>93.98</td>
<td>2.91</td>
<td>7.0 &lt;dl &lt;dl &lt;dl 7.0</td>
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<td></td>
<td></td>
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<tr>
<td>11. Mataripe</td>
<td>7.26</td>
<td>-248</td>
<td>55.40</td>
<td>1.33</td>
<td>15.9 &lt;dl &lt;dl &lt;dl 15.9</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>12. Maré/channe</td>
<td>7.29</td>
<td>72</td>
<td>63.58</td>
<td>1.73</td>
<td>5.5 &lt;dl &lt;dl &lt;dl 5.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. Bimbarras Sul</td>
<td>7.17</td>
<td>-15</td>
<td>28.51</td>
<td>1.62</td>
<td>&lt;dl 28.8 4.0 32.8 &lt;dl</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>14. Near Fontes Island</td>
<td>6.74</td>
<td>32</td>
<td>95.43</td>
<td>2.33</td>
<td>6.9 &lt;dl &lt;dl &lt;dl 6.9</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>15. Near Porcos Island</td>
<td>7.44</td>
<td>24</td>
<td>13.95</td>
<td>3.27</td>
<td>6.2 &lt;dl &lt;dl &lt;dl 6.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in Iguape Bay</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16. Near Frades Island</td>
<td>7.69</td>
<td>110</td>
<td>3.61</td>
<td>2.68</td>
<td>5.5 &lt;dl &lt;dl &lt;dl 5.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17. Salvador Channel</td>
<td>7.89</td>
<td>55</td>
<td>3.61</td>
<td>3.81</td>
<td>6.0 &lt;dl &lt;dl &lt;dl 6.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The BT concentrations for each site are the average of two determinations per sample; standard deviations are in the range of 0.1 to 2.3 μg kg\(^{-1}\), dl (detection limit): TBT = 5.4 μg kg\(^{-1}\), DBT = 0.2 μg kg\(^{-1}\) and MBT = 2.1 μg kg\(^{-1}\).

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Table 4. Examples of OT concentrations reported for different areas of the world (μg kg⁻¹ as Sn)

<table>
<thead>
<tr>
<th>Location</th>
<th>TBT</th>
<th>DBT</th>
<th>MBT</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Western Mediterranean</td>
<td>nd – 9260</td>
<td>nd – 960</td>
<td>nd – 1591</td>
<td>32</td>
</tr>
<tr>
<td>Perth, Australia</td>
<td>1.0 – 1350</td>
<td>n.i.</td>
<td>n.i.</td>
<td>33</td>
</tr>
<tr>
<td>Auckland, New Zealand</td>
<td>&lt; 4.9 – 3318</td>
<td>n.i.</td>
<td>n.i.</td>
<td>34</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>8.8 – 3900</td>
<td>&lt; 2.0 – 5800</td>
<td>&lt; 1.5 – 260</td>
<td>35</td>
</tr>
<tr>
<td>Sta. Monica, USA</td>
<td>nd – 7.4</td>
<td>nd – 27</td>
<td>nd – 12</td>
<td>36</td>
</tr>
<tr>
<td>Otsuchi Bay, Japan</td>
<td>5.6 – 82</td>
<td>n.i.</td>
<td>n.i.</td>
<td>37</td>
</tr>
<tr>
<td>Coast of India</td>
<td>nd – 1280</td>
<td>1.3 – 394</td>
<td>1.6 – 393</td>
<td>38</td>
</tr>
<tr>
<td>Coast of São Paulo, Brazil</td>
<td>17 – 847</td>
<td>14 – 421</td>
<td>36 – 367</td>
<td>12</td>
</tr>
<tr>
<td>Guanabara Bay, Brazil</td>
<td>nd – 742</td>
<td>nd – 90</td>
<td>nd – 21</td>
<td>10</td>
</tr>
<tr>
<td>Coast of India</td>
<td>2.8 – 1100</td>
<td>3.8 – 310</td>
<td>5.0 – 360</td>
<td>39</td>
</tr>
<tr>
<td>Guanabara Bay, Brazil</td>
<td>10 – 522</td>
<td>nd – 395</td>
<td>nd</td>
<td>11</td>
</tr>
<tr>
<td>TSB, Brazil</td>
<td>nd – 15.9</td>
<td>nd – 28.8</td>
<td>nd – 4.0</td>
<td>This work</td>
</tr>
</tbody>
</table>

nd = not detected; n.i. = not informed

CONCLUSIONS

The presence of TBT as the dominant OT species in TSB is a rare feature since even in anoxic environments, where TBT is more stable, measurable levels of DBT and MBT have been reported for other areas. TBT concentrations are relatively low even in areas of intense navigation. The combination of these two facts leads to the conclusion that TBT released into the water is rapidly degraded, possibly to tin, before reaching final sedimentation. TBT half life under the environmental conditions of the Todos os Santos Bay may be remarkably smaller than those so far reported in the literature. The fraction that resists degradation must be embedded in a protective medium, most probably paint particles. These results show that monitoring contamination and possible hot spots in TSB needs a different strategy given that concentration records in sediments do not discriminate sites in the near of potential sources from others. Measurements in the water column or in organisms that accumulate TBT or adversely react to its presence at low concentration, as for instance gastropods that develop imposex, are more appropriate for use in future environmental assessments.

ACKNOWLEDGEMENTS

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