# Butyltins in sediments from Santa Monica and San Pedro basins, California

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## Abstract

Butyltins have been measured for the first time in sediments from the deeper waters of the Santa Monica and San Pedro (SM/SP) basins of Southern California borderland. Core samples were collected from water depths ranging from 458 m in the shelf to 906 m in the central basin. Surficial and a few subsurface sections from selected cores were analyzed for butyltins. The dominant components are generally dibutyl and monobutyltins (DBT and MBT, respectively). Microbial degradation of Tributyltin (TBT, the most toxic of the butyltin species) to DBT and MBT during the long range transport to deeper basins, as well as a lack of continuing inputs of TBT in the present times could justify the butyltins signatures found in the region. The levels of butyltins are in the lower range (below detection level, <1, to 14 ng of Sn g$^{-1}$) relative to nearshore sediments. However, the results demonstrate that the butyltins are, indeed, found even in the sediments of the central basins of the Southern California borderland suggesting that deeper global oceanic regimes need to be further investigated for these compounds. © 1998 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Organotin compounds are used in numerous industrial products such as polymer additives, biocides and fungicides, besides antifouling paint (e.g. Blunden et al., 1985). Despite their restricted use in antifouling paints to larger vessels in some European countries and in the United States, the versatile use of these toxic components has resulted in a significant increase in industrial output. Eventually, the parent and degradation products end up in the marine environment, e.g. via agricultural applications and sewage discharges, impacting non-target marine life. Though these concerns are not novel, questions are still open relating to their toxicity, stability and fate of these chemicals buried in sediments.

Sediments could accumulate hydrophobic contaminants such as organotins and thus serve as long-term sink (Unger et al., 1988). They may even be remobilized into the water column through diffusive flux and resuspension/desorption phenomena (Stang and Seligman, 1987; Dowson et al., 1993). The extent to which open seas and deep oceanic waters have been

contaminated by butyltins is rather unclear because recent studies of organotin in sediments and waters have focused mainly on coastal areas near centers of intense boat use or fish farms (Grovhoug et al., 1986; Stang and Seligman, 1986; Seligman et al., 1986; Maguire et al., 1986; Dahab, 1988; Wade et al., 1990; Alzieu et al., 1991; Tolosa et al., 1992, Cocchieri et al., 1993; Dowson et al., 1992, Sarradin et al., 1994). The only two studies known to us from relatively deeper waters are by Stewart and Thompson (1994) and Coghlan (1994). The former detected butyltins in benthic sediments collected at a water depth of 377 m from Ballenas Basin, Strait of Georgia. Coghlan detected significant amount of TBT in open waters 200 km offshore in the North Sea where typical toxic effects (e.g. imposex) of organotin compounds have recently been reported (Fent, 1996). Here we report the occurrence of organotins from the Santa Monica (SM) and San Pedro (SP) basins in southern California Borderland from water depth ranging from 458 m in the shelf to central basin of ~906 m. The availability of fine resolution core sections collected as part of NOAA/ National Status and Trends Program to investigate organic contaminants provided an unique opportunity

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to measure organotins in the same sample suite. The age of the sediment cores ranged from 1991 to 1900 where some of the sections were post 1988, when the restrictions in the use of organotin-based antifouling paints were imposed in USA (Stewart and Thompson, 1994). This study was initiated to investigate the stability of organotins and the possible long range transport of these compounds to deeper waters from coastal zones considering that the sediment cores in the study sites were found earlier to be enriched in a variety of anthropogenic contaminants (Venkatesan and Kaplan, 1990; Chalaux et al., 1992; Venkatesan, 1994).

## 2. Materials and Methods

### 2.1. Sample collection

Sediment cores from sites illustrated in Fig. 1 were collected in September of 1991 on board R/V Seawatch using Soutar's Slow-entry Box core from SM and SP basins (Venkatesan, 1994). A brownish-orange floc layer was observed in all the cores, indicating that there was no or only minimal disturbance of the surface layer during coring. Surface sections from all the six cores and selected sections from two cores were analyzed. Specific sections chosen were determined by their availability in sufficient quantities for analysis as well as their Pb-210 chronology. Sediment sections have been stored frozen in glass jars with teflon lined caps since collection.

Nearsurface sections were of fine resolution, each dating to 2–5 years by $^{210}$Pb chronology (Huh, 1996). Sedimentation rates were determined by linear regression except for the top layers of NOAA-I, III and VI. Some sediment mixing is indicated by the $^{210}$Pb gradient and $^{228}$Th profiles of NOAA-I and III cores underlying oxic bottom waters. Chronologies of these cores were determined based on the sedimentation rates from below the surface mixed layer, assuming that the rates have remained constant at the top horizons. The turbidite layer centering at 1–1.5 cm in NOAA-VI probably reflects the winter storms of 1979–1980. The age of the top layer was therefore estimated from two preset time points, e.g., the time of core collection at Z = 0 (1991.68 A.D.) and at 1.25 cm (1980). The sedimentation rate in NOAA-IV, closer to the JWPCP outfall, is the highest among the cores studied here and it is, indeed, high enough to swamp the effect of mixing in influencing the downcore distributions of $^{210}$Pb as well as trace metals (Huh, 1996). NOAA-V was collected from the deep SP Basin underlying anoxic bottom waters and the $^{234}$Th and $^{228}$Th data dispense the possibility of sediment mixing in this core.

Three grab sediment samples were collected by the Southern California Coastal Water Research Project (SCCWRP) in July of 1986 from the San Diego Naval Station dock at the mouth of the Chollas Creek (32° 41.02′ N; 117° 00.03′ W, farther southeast of the San Pedro Basin, not shown in Fig. 1). The samples were taken from 9 m of water and was composed of silty clay.
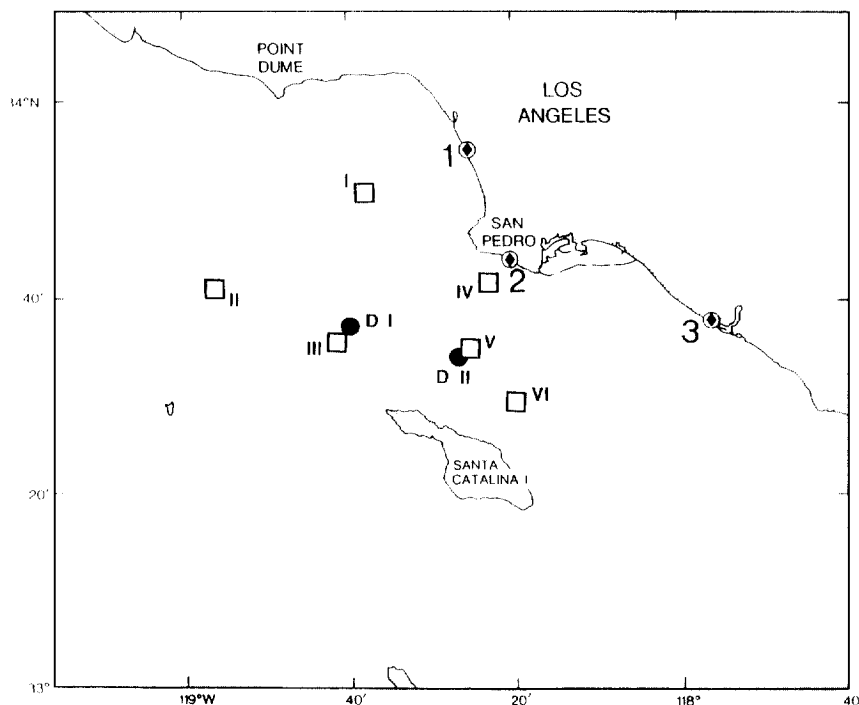


Fig. 1. Station locations in SM/SP basins (□). Also indicated are dumpsites DI and DII (●). 1, 2 and 3 are the Los Angeles City (Hyperion), County (JWPCP) and Orange County Sanitation Districts. Water depths: I 593 m; II 906 m; III 586 m; IV 458 m; V 888 m, VI 889 m.

These samples were collected mainly for PAH study (Anderson and Gossett, 1987) and were stored frozen since then until analysis in 1992. Runoff from C. Creek and the naval ship activities are the major potential sources of contaminants in these sediments. Significant amounts of butyltin species, therefore, could be expected from these samples.

Sediment standard reference material PACS 1 was obtained from the National Research Council (Halifax, NS; Canada) for analysis. Sample processing and hexylation were performed after combining and modifying the procedures of Wade et al. (1990) and Tolosa et al. (1992).

### 2.2. Sample extraction

Sediments were freeze-dried and analyzed soon after to avoid loss of the components (Quevauviller and Donard, 1991; Gomez-Ariza, 1994). About 1000 ppm of propyltin chloride (TPT) was added as recovery spike to ~7 g of freeze-dried sediment sample in a 50 ml Erlenmeyer flask with stopper. About 600 ppm each of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) were used as matrix spikes. The pH was lowered to ~1 with 6 N HCl, stirred with glass rod and 15 ml of diethyl ether with 0.25% w/v tropolone (Aldrich Co.) was added and sonicated for 15 min. The organic layer was decanted and the extraction repeated two more times. The extract was dried with ~20 g $Na_2SO_4$ and rotoevaporated. The residue was dissolved in 2 ml of hexane and transferred to a 12 ml centrifuge tube.

### 2.3. Hexylation

Two ml of Grignard Reagent (hexylmagnesium bromide, 2.0 M solution in diethyl ether, Aldrich Co.) was added to the above centrifuge tube, sealed and heated for 2 h at 70°C. While the tube was cooled and shaken in crushed ice and water, 3 ml of HCl (6 N) was added dropwise. The supernatant hexane layer was collected in a 25 ml Erlenmeyer flask. Extraction with hexane was repeated two more times. The combined extract was dried with 10 g of $Na_2SO_4$ and transferred to 10 ml round bottom flask and blown down to about 1 ml with $N_2$. Reagent blank and spike blank were processed in the same way.

The hexane extract was charged to a 1 g (preheated and stored at 120°C) silica column (0.7 mm I.D.) topped with ~1 g of $Na_2SO_4$. The organotins were eluted in 10–11 ml of hexane:ether (9:1). Solvent was stripped off under nitrogen and transferred into 2 ml vial in hexane.

### 2.4. Gas chromatography

The butyltin fraction was coinjected with tetrabutyltin as internal standard. A Fisons Mega Series gas chromatograph was equipped with a single flame photometric detector (FPD) with a bandpass filter at 610 nM. A DB-17 column of 30 m×0.25 mm i.d. and 0.25 micron film thickness was used. The chromatographic conditions are as follows: the temperature was programmed from 70 to 290°C at 6°C $min^{-1}$ holding for 5 min at the final temperature. Hydrogen as carrier gas at 50 cm $s^{-1}$ and nitrogen as makeup gas at 30 cm $s^{-1}$ were used. Flow rates of fuel gases were 120 ml $min^{-1}$ of hydrogen and 100 ml $min^{-1}$ of air. Injector and detector temperatures were held at 225°C. The identification of compounds was confirmed by GC/MS analysis in both the scan and selected ion mode with a Finnigan 4000 equipped with a Varian chromatograph model 9600. The GC/MS conditions were as follows: DB-5 (0.25 mm I.D.) column was programmed to hold for 4 min at 35°C and at 6°C $min^{-1}$ to 310°C.

## 3. Results and discussion

Butyltin concentrations are reported here as ng of tin per gram of dry sediment to enable direct comparisons of the three butyltin species. The reproducibility of the GC/FPD analysis was tested by repeatedly injecting the same amount of the standard mix of hexylated tins, synthesized at UCLA. The percent relative standard deviation of tetrabutyltin, TPT and the target analytes ranged from 5 to 11. The percent average recoveries of TBT, DBT, MBT and TPT from matrix spike analyses were 50, 84, 40, and 67, respectively. Our recoveries of TBT are lower than, while those of DBT, MBT and TPT are comparable to, reported values (e.g. Wade et al., 1988; Tolosa et al., 1991). The wider range in the recoveries is not unexpected due to the difficulty of extracting these components from sediment matrices. In particular, the low recovery of MBT is because it is the most difficult analyte to be measured. For example, Zhang et al. (1991) have evaluated 10 different extraction procedures for MBT none of which proved to be satisfactory (see below for more details). Further, we did not shake the samples for extended hours like in other studies, but resorted to sonication for only 15 min to avoid any artifact during the analysis, especially possible degradation of TBT to other species. This precaution was taken in view of the published range of half lives for TBT from a few days to several months which could imply that analytical steps also could contribute to conflicting data (Donard and Michel, 1992). Further, the goal of the study was to explore the presence or absence of organotins in the basin sediments which could be accomplished by a milder extraction technique.

Average concentrations of TBT, DBT and MBT respectively in the standard reference sediment PACS 1 from four replicate analyses were as follows: 0.97 ± 0.22, 0.96 ± 0.17 and 0.35 ± 0.17 $\mu$g of Sn $g^{-1}$ dry sediment.

These values fall within 76–125% of the certified values (1.27± +0.22; 1.16±0.18; 0.28±0.17 µg Sn g⁻¹). Many other groups (e.g. Chau et al., 1995; Kuballa et al., 1995) have reported much higher concentrations of MBT (150–200%) relative to certified values. The wide range of value certified in reference material PACS 1 (Abalos et al., 1997) further demonstrates the difficulty of analyzing this compound. The value for MBT could not even be certified in the CRM-462 (Bureau Community of Reference, Europe) due to lack of agreement in the quantitative results (Quevauviller et al., 1994). It has to be noted, however, that most of the published data report spiked samples only, usually at high concentration levels, which results in the overestimation of the accuracy and precision.

Considering the above limitations in the methodology, the precision of the method developed at UCLA was documented by the triplicate analysis of the three Chollas Creek samples. For example: DBT in Chollas Creek 1, 2, and 3 were 65.1(±9), 58.8(±3), and 84.6(±3) and that of MBT 34(±5), 28.4(±6) and 14.3 (±0.5) ng of Sn g⁻¹, respectively. TBT ranged from 2–3.5 ng g⁻¹ in the samples. The very low TBT might have been an artefact due to prolonged storage of the C. Creek samples in the freezer since 1986. These were analyzed only to demonstrate the reproducibility of the analysis at UCLA since they were available in large quantities. However, data from these three samples will not be considered further for geochemical interpretations. The recovery of the surrogate (TPT) ranged from 40 to 82% in all samples. The butyltin contents were corrected for the recovery of TPT.

Total butyltins were calculated as the sum of the concentrations of tin from TBT, DBT and MBT in the SM/SP basin sediment samples (Table 1). The concentrations of butyltin species range from 1 to 14 ng of Sn g⁻¹ (average=4 ng Sn g⁻¹) with SP Basin sediments relatively more enriched in the butyltins than those from SM Basin as expected from the distribution patterns of other contaminants (Venkatesan et al., 1995). The butyltin contents are comparable to the levels in the sediments from southwestern coastal British Columbia, Canada (Stewart and Thompson, 1994), and Gulf of Mexico and in some west coast sediments and generally lower than east coast sediments of the USA where it is as high as 187 ng Sn g⁻¹ (Wade et al., 1990). An order of magnitude lower concentrations measured in the current study than those found in San Pedro Harbor (butyltins 282 ng Sn g⁻¹; Wade et al., 1990) are consistent with the sampling locations in deeper waters, farther offshore from coastal inputs and remote from areas of high boating activity.

As high as ~550 ng Sn g⁻¹ near yacht facilities (Seligman et al., 1986) and ~2000 ng Sn g⁻¹ near ship building and repair facilities in Puget Sound (Krone et al., 1989) have been found, confirming the observations of

Table 1
Concentration of organotins in sediments (ng of Sn g⁻¹, dry sediment)

| Sampling site | Subbottom depth (cm) | Pb-210 Age[a] | TBT | DBT | MBT | Σ Butyltins |
|---|---|---|---|---|---|---|
| SM BASIN I | | | | | | |
| | 0–1 | 1988–1990 | 4 | 4 | 5 | 13 |
| | 1–2 | 1982–1985 | 3 | 5 | 2 | 10 |
| | 2–3[b] | 1977–1980 | 2 | 5 | 2 | 9 |
| | 3–4 | 1972 | 1 | 2 | <LD | 3 |
| | 5–6 | 1957 | <LD | <LD | <LD | <LD |
| | 8–9 | 1932 | <LD | <LD | <LD | <LD |
| | 9–10 | 1923 | <LD | <LD | <LD | <LD |
| SM BASIN II | | | | | | |
| | 0–1 | 1985–1990 | 7 | <LD | 2 | 9 |
| SM BASIN III | | | | | | |
| | 0–1 | 1987–1990 | <LD | <LD | <LD | <LD |
| SP BASIN IV | | | | | | |
| | 0–1[b] | 1990–1991 | 2 | 4 | 3 | 9 |
| | 1–2 | 1987–1989 | 4 | 5 | 6 | 15 |
| | 6–7 | 1970 | 2 | n.q. | n.q. | 2 |
| | 8–9 | 1950 | <LD | <LD | <LD | <LD |
| | 11–12 | 1917 | <LD | <LD | <LD | <LD |
| SM/SP BASIN V | | | | | | |
| | 0–1 | 1989–1991 | 4 | 2 | 3 | 9 |
| SP BASIN VI | | | | | | |
| | 0–1 | 1984–1987 | 5 | 14 | 4 | 23 |

LD: Limit of detection of the analytical procedure was calculated from the LOD of the FPD (S/N = 3)×extraction recovery/dilution for the GC determination. LD in ng of Sn/g for TBT=1.0; DBT=1.0; MBT=1.2. n.q. Not quantitated because of interfering peaks.
[a] Pb-210 dates from C. Huh (Oregon State University).
[b] Average of two replicate analyses.

Schatzberg (1987) and Thompson et al. (1985) that the antifouling paints leached from boats and vessels are the major contributors of butyltins to the marine environments. The dominant components are generally DBT and MBT in the samples analyzed. This is in contrast to many of the coastal and harbor sediments studies (e.g. Stang and Seligman, 1986; Krone et al., 1989; Wade et al., 1990). Only one sediment sample (SM Basin II, 0–1 cm) contains TBT as the major component comparable to other studies quoted above. Interestingly, our results are similar to those observed from freshwater lake and river sediments (Maguire et al., 1986) and from selected sites of Arcachon Bay, France (Sarradin et al., 1994) which contained MBT as the predominant tin species, with DBT often present in greater amounts than TBT. Higher DBT than TBT levels have also been found in Lake Biwa sediments (Tsuda et al., 1986).

Several factors such as types and rates of degradation reactions, sediment characteristics, butyltin signature of sources, processes such as resuspension, adsorption and desorption can influence the relative proportions of butyltin species in sediments. Significant amounts of DBT comprise certain paint formulations (Blair et al., 1986) which could be eventually deposited in sediments. DBT is also used as a PVC stabilizer, which could finally be transported to coastal waters via sewage (Tolosa et al., 1992). However, the sediments in this study are from SM/SP basins from water depths ranging from 458–906 m and the results are consistent with those found in most of the east coast sites from relatively greater water depths which contained higher proportions of DBT and MBT than the Gulf and West coast sites studied (Wade et al., 1990). Near-surface sections in all the cores dating from 1984–1991 contain only comparable or much less TBT relative to DBT and MBT. It appears that the long range transport to the deeper basins has resulted in the gradual degradation of TBT and accumulation of its metabolites in the study region (Maguire et al., 1983). It is not surprising that surface section of Core III did not contain detectable levels of organotins which is consistent with the presence of lowest level of contaminants such as polycyclic aromatic and chlorinated hydrocarbons (Venkatesan, 1994) in this core relative to the other cores analyzed. This is probably because this site is not located along the main California Counter Current trajectory which transports anthropogenic contaminants along the coast and offshore of the California borderland.

DBT and MBT detected in sediments may be generated in the water column from TBT degradation by algae or bacteria (Hinga et al., 1987; Olson and Brinckman, 1986; Lee et al., 1987). Thus, microbial degradation of TBT to DBT and MBT, as well as a lack of continuing inputs of significant amounts of TBT, could result in the butyltins signatures found in the surface

sediments studied here. This phenomenon could become increasingly important with longer water column residence times where elevated levels of TBT degradation products could be accumulating (Seligman et al., 1988). The presence or absence of TBT-metabolizing bacteria or microalgae could, therefore, play a major role in the environmental preservation and composition of butyltins in different waters and sediments. However, the presence of TBT and its degradation products in the shelf, slope and in the center of the SM and SP basins reinforces the findings of others that sediments could be a sink for TBT as well as a chronic source of TBT and its degradation products to the marine environment (Huggett et al., 1986; Unger et al., 1988). It is likely that this long-range transport of butyltins from nearshore to the central basins has occurred via tidal effects as well as advection of fine-grained particles to offshore regions, especially during storm events. The distribution and dynamics in the SM/SP basins of other chemicals originating from land as well as nearshore coastal water activities document the transport of particles to deeper waters of the central basins (Crisp et al., 1979; Venkatesan et al., 1980, 1995; Venkatesan and Kaplan 1990). Additional data is required in order to resolve fully the mode of degradation of TBT and, transport and occurrence of these components in deeper waters.

Of the two cores analyzed, one (Core I) exhibits only a slight decline in organotin content with increasing depth. Core IV shows a marginal subsurface maximum around 1987–1989 which interestingly coincides with the period when restrictions in their use in antifouling paints were imposed in USA (Stewart and Thompson, 1994). A few other studies have followed depth profiles of organotins in sediments. De Mora et al. (1989) observed exponential decrease in TBT concentrations with depth, whereas others have found no clear depth trends (Astruc et al., 1989; Stewart and de Mora, 1992). A half-life of around 2 years for TBT and a first order degradation kinetics were considered by de Mora et al. (1989) to explain the rapid decrease in TBT with depth. In comparison, it appears that degradation of TBT is much slower in southern California sediment cores as expected from the hypooxic or anoxic conditions of the sampling sites (Venkatesan and Kaplan, 1990). Although much of the organotins is probably degraded during their transit to offshore basin sites, they seem to be better preserved once being incorporated in the sediment matrix (Stewart and de Mora, 1990). In general, the presence of uniformly low levels of the target compounds in the core sections and the limited number of cores measured preclude extensive discussion of historic deposition. However, it is evident that sediments prior to 1960 did not contain detectable levels of these compounds. This observation is consistent with the fact that organotin-based antifouling paints were first used in the 1960s (Stewart and Thompson, 1994) further suggesting

minimal mixing of the sediment column. Based on the limited data, subsequent degradation of TBT into its metabolites within the sedimentary column cannot be entirely ruled out either. Further, the sorption and desorption behaviour of the butyltin moieties are believed to be different (Stang and Seligman, 1987; Hermosin et al., 1993), which could significantly impact their history of deposition and degradation. Perhaps, a high resolution core from shallow waters (yet, relatively nonbioturbated) could help better document the extent of their historic inputs.

## 4. Conclusions

The current study demonstrates that butyltins are found even in the deeper basins in southern California Borderland and thus are not confined to nearshore environments suggesting that butyltins survive reasonably during their long-range transport to offshore sites. It is likely that TBT and its degradation products are remobilized by tidal effects and transported to deeper basins and further degraded during transit through the water column as well as after deposition in the sedimentary strata. More data are needed to understand the mechanisms involved in the transport and occurrence of butyltins in the deeper ocean sediments. TBT, the most toxic of the butyltin species, is not generally the dominant component in the basin sediments and the levels of all butyltin species are in the lower range relative to several other coastal sediments studied so far. However, in general, organometallics are much more toxic than their inorganic counterparts and the recommended acceptable level in the waters (e.g. $2 \, \text{ng Sn l}^{-1}$) is close to the detection limits of most analytical setups (Donard and Michel, 1992). The detection of low levels of the butyltins in offshore sediments emphasizes a dire need for a technique to measure ultra-trace levels of butyltins and further investigations in other deep ocean waters.

## Acknowledgements

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