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# Variability of butyltin determination in water and sediment samples from European coastal environments

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**A large amount of data has appeared in the literature within the last few years dealing with the monitoring of butyltin compounds in coastal environments. However, the strategies used strongly differed from one author to another, which led to difficulties in the comparison of contamination levels and the evaluation of long-term trends. In this paper, different causes of pitfalls due to uncontrolled sources of variability are addressed; they involve precautions to be undertaken for the monitoring of butylins in water and sediment, particularly: sample collection; sample pretreatment (filtration/centrifugation, acidification, sieving); sample storage (different methods for storage and drying procedures); variability over the same site; variations over a tidal cycle; and variability due to diffusion (e.g. due to flushing).**

**Keywords: Butyltin compounds, variability, waters, sediments, collection, treatment, storage, monitoring strategy, contamination, assessment**

## INTRODUCTION

Butyltin compounds, especially tributyltin species (TBT) arising from the use of antifouling paints, are known to induce important stresses on a wide variety of marine organisms, particularly in shallow enclosed estuaries which are generally major sites for shellfish production.[1] Such effects were observed on the common oyster (growth inhibition) in France[2] and along the south west coast of the UK.[3] TBT was also suspected of being responsible for similar effects on the Portuguese oyster in the Tejo Estuary[4] and the Sado Estuary (Portugal).[5]

Since this compound appeared to be critical relative to bivalve production and a possible source of economic problems, organotin surveys were needed in estuarine and coastal environments in the past few years. Environmental quality target values (EQT) have been reconsidered within the last three years owing to the evidence of the high TBT toxicity at very low concentrations in water: the EQT value was set at 20 ng $dm^{-3}$ in the UK in 1987 and was recommended to be re-set at 2 ng $dm^{-3}$ in order to achieve complete protection of marine life.[6]

The control and representativity of organotin measurements in various media (waters, sediments and biological tissues) are highly dependent upon a number of factors such as tidal cycles, direct anthropogenic inputs and persistence in waters (see the review by Donard *et al.*[7]). It is clear that butyltin compounds may accumulate in enclosed areas whereas concentrations are diluted in main waterways. This has already been observed in the UK.[6]

When addressing a survey, it appears particularly important to define accurately a set of physico-chemical and physical parameters to allow a possible comparison of data (e.g. tide, hydrodynamics, suspended matter contents, etc.).

The collection and pretreatment of the samples has also to be considered, i.e. suitable methods to avoid losses or contamination—filtration and acidification for water samples and sieving for sediment samples, as well as the storage procedures used.[8] However, if considerable efforts have been made with regard to the analytical developments, little attention has been paid so far to the sampling and sample pretreatment strategies for water or sediment butyltin analyses. Furthermore, there is a wide heterogeneity in the butyltin concentrations reported in the literature.

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Many authors do not filter the water samples; however, butyltin compounds such as TBT display a very high partition coefficient, $K_p$.[9] This may lead to some errors in the interpretation of results. Indeed, the dissolved fraction of a water sample (filtered with a 0.45-$\mu$m mesh) does not have the same dynamics as the particulate fraction, more specifically in estuarine environments. In addition, TBT contained in dissolved or particulate fractions does not have the same biological impact on marine organisms.

Other potential problems are related to the stability of samples prior to analysis; unlike total-metal analyses, the determination of tin species requires suitable storage procedures to preserve chemical forms: micro-organisms bound to particles may methylate inorganic tin or degrade butyltin compounds during storage of samples rich in suspended matter.[8]

Another important aspect with regard to the assessment of butyltin contamination is the location of the sampling site. Organotin contaminations are most often restricted to high point sources such as harbours. The problem is therefore also to estimate the importance of diffusion of these contaminations.

We report in this paper results from several sampling surveys from European coastal environments and parameters likely to affect the evaluation of butyltin impacts in water and sediment samples. Potential sources of over- or underestimation of butyltin contaminations such as sample pretreatment, variability over the same site or over a tidal cycle, and diffusion of the contamination from high TBT point sources will be discussed.

## MATERIALS AND METHODS

### Sampling strategies

It is presently almost impossible to evaluate the most adequate sampling strategies from the data presented in the literature since methods are widely different: many authors do not filter the water samples or use centrifuged waters, bulk sediments are analysed in most of the cases and suspended matter is generally not considered in butyltin monitoring.

In this paper, we have chosen whenever possible to base the determination of butyltin concentrations on filtered water samples ($<0.45\,\mu$m) because acute toxicity tests on marine organisms are most often based on the butyltin concentrations contained in the dissolved phase. However, some attempts were made to assess the effects of suspended particles on the butyltin content in water because many organisms (e.g. filter-feeding bivalves) accumulate toxic elements from particulates and also because of the differing hydrodynamic behaviour of dissolved and suspended phases, e.g. their residence times in the coastal ecosystems.

It was also preferred to base the determination of butyltins in suspended matter on centrifuging large amounts of water rather than using solid residues obtained after filtration. This procedure is more time-consuming but was thought to lead to more accurate results (limitation of risk of adsorption on filter; better reproducibility and homogeneity owing to higher amounts of samples).

Finally, we have chosen to sieve the sediment samples at 60 $\mu$m in order to achieve a better homogeneity and because the relationship between trace metal contents and fine sediment fraction is now well established.

### Water sample collection and treatment

#### Sampling

In general, water sample collection was performed close to major sources of TBT (harbours and marinas) and in nearby flushed areas in main waterways. Samples were collected at slack-water low tide where the highest TBT levels are likely to occur,[10,11] to remove tidal influences (dilution); intertidal samples were collected by submersing 250-cm$^3$ acid-prewashed Pyrex glass bottles with Teflon screw caps which were opened and closed at 50 cm below the surface in order to avoid possible contamination with microlayer waters. Estuarine samples were collected with a close–open–close sampler[12,13] from a rubber boat to avoid risks of contamination from the main ship.

Two samples were collected in the North Sea from a rubber boat, using a precleaned close–open–close sampler.

#### Filtration

Whenever possible, samples presenting a suspended matter content above 10 mg dm$^{-3}$ were filtered at 0.45-$\mu$m mesh in the field with sterile Nalgene filtration units (one per sample) and the bulk and filtered samples were acidified at pH 2 using suprapure hydrochloric acid and stored at 4°C in the dark prior to analysis. This was shown

to be an accurate procedure to preserve the butyltin stability in water over four months.[8] However, it was not possible to carry out this treatment in Portugal: samples were first acidified at pH 2 in the field and stored in dry ice in a container and filtered in the laboratory after two days. The study of the filtration effects on butyltin contents was performed with samples presenting high suspended loads.

### Effects of partitioning

The partitioning of butyltins between dissolved and particulate phases and the effects of filtration were examined using a sample containing a high suspended load. Two water samples from the marina of Boyardville (France) were prepared by mixing fine sediment and water from the same site (with known butyltin contents) to obtain samples containing respectively 251 and 367 mg $dm^{-3}$ of suspended matter. One subsample was acidified to pH 2 and the other was left unacidified. Both samples were homogenized with a mechanical shaker for two days and later filtered at 0.45 $\mu$m. Partition coefficients were calculated after analysis of the dissolved and particulate butyltin (calculated by difference between the concentrations in filtered and bulk samples; Table 1a). This experiment was carried out to address the effect of acidification prior to filtration on the partitioning of butyltin compounds. In addition, recovery of butyltins was assessed between real contents detected in bulk samples and concentrations which should have been obtained considering the butyltin contents in the fine sediment and the respective amounts of particles in each of the samples (Table 1b). Analyses of filtered and non-filtered water samples were also performed (over a tidal cycle) along with suspended matter analyses (collected by centrifugation) in order to better evaluate the butyltin partitioning (Rotterdam Harbour, Netherlands).

### Sample location and the assessment of diffusion effects

Samples were systematically collected in supposed TBT point sources and flushed channels located in their vicinity in order to assess the diffusion of butyltin contamination.

Samples were collected from seven stations in September 1988 in the Sado Estuary (south of Lisbon) and its adjacent coastal areas (Fig. 1a). Sampling sites were harbours and dry docks [samples S1 (Sesimbra harbour) and S4], a poorly flushed channel located near an industrial zone (samples S5 and S6), and well flushed coastal and estuarine areas (samples S2, S3 and S7). Six stations were sampled in the Tejo Estuary (Fig. 1a) including enclosed marinas and dry docks (samples T1, T2 and T3) and well flushed piers (samples T4, T5 and T6) located in the vicinity of shipyards.

In France, three marinas were sampled along with highly flushed adjacent channels, the Boyardville Marina (Fig. 1c) on Oléron Island (marina, samples O1 and O2; channel, samples O3 and O4), the Arcachon Marina (Fig. 1d) in Arcachon Bay (marina, samples A1 and A2; channel, sample A3), and the Le Verdon Marina (marked with a circle on Fig. 1, between Figs. 1c and 1d) located at the Gironde Estuary outlet (marina, sample G1; channel, G2). Some results of an organotin survey performed in the Netherlands[12] (Fig. 1e) are also presented. They involve water, suspended matter and sediment samples collected in July and October 1988 in the upstream zones of the Rhine (samples R0, R1 and R2) and Scheldt Estuaries (sample Sc) and in the Wadden Sea (samples D1 and D2).

### Assessment of other sources of variability

The variability of butyltin concentrations over the same site was addressed in the Boyardville and Arcachon marinas by simultaneously collecting two samples at the same location less than 50 m apart.

The variability over a tidal cycle was assessed in Rotterdam harbour.

## Collection and treatment of sediments and suspensions

Sublittoral sediment samples were collected in some stations to underline the effects of diffusion of contamination from enclosed sites to main waterways.

Samples were collected along the French Mediterranean coast (Fig. 1b), respectively in the enclosed Lazaret Bay located close to Toulon harbour (station M1, −5 m deep), and in well flushed coastal sites located on the continental shelf in front of some harbours such as, that of Marseille (stations M2, −18 m deep and M3, −8 m deep), Cannes harbour (stations M4 and M5, −40 m deep), the Monaco marina (stations M6, −80 m deep and M7, −40 m deep), and a clean site in Corsica (station M8, −15 m deep).

**Table 1** Butyltin partitioning in turbid water samples according to the sample treatment (whether acidified or not)

(a) Effects of filtration

| Station | Non-filtered (ng $dm^{-3}$) | | | Filtered (ng $dm^{-3}$) | | | $K_p$[c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | MBT | DBT | TBT | MBT | DBT | TBT | MBT | DBT | TBT |
| O2 (acidified)[a] | 245 | 226 | 428 | 86 | 130 | 164 | 5035 | 2015 | 4384 |
| O2′ (unacidified)[b] | 110 | 148 | 240 | 16 | 30 | 24 | 23406 | 15670 | 35857 |

(b) Extraction recovery (after Quevauviller and Donard[9])

| Recovery | Particulate (ng $g^{-1}$) | | |
|---|---|---|---|
| | Found | Theoretical | (%) |
| O2 (acidified)[a] | | | |
| TBT | 428 | 3404 | 13 |
| DBT | 226 | 1303 | 17 |
| MBT | 245 | 1810 | 14 |
| O2′ (unacidified)[b] | | | |
| TBT | 240 | 2328 | 10 |
| DBT | 148 | 890 | 17 |
| MBT | 110 | 1238 | 9 |

[a]O2 = acidified, SM (suspended matter) = 367 mg $dm^{-3}$.
[b]O2′ = unacidified, SM = 251 mg $dm^{-3}$
[c]$K_p$ is the partition coefficient in (ng $g^{-1}$)/(ng $dm^{-3}$).
The Kp calculations in Table 1a were done as follows (e.g. with TBT in the sample O2 Oléron acidif): the mass/mass of TBT was calculated according to the amount found by difference between the bulk sample (428 ng $dm^{-3}$) and the filtered one (164 ng $dm^{-3}$ or 0.164 ng $cm^{-3}$), that is 264 ng of TBT bound to particulate in 1 litre water. Considering the amount of suspended matter (0.367 g $dm^{-3}$) in the sample, the resulting mass of TBT bound to particles is therefore 264/0.367 = 719 ng $g^{-1}$. The Kp value is obtained as 719/0.164 = 4384 ng $g^{-1}$ $ng^{-1}$ $dm^{-3}$ (mass of TBT/g of particulate divided by mass of TBT $dm^{-3}$ in dissolved phase).
The sediment used for the preparation of the turbid samples is the sample O1 (Table 4).
The example of TBT explains the calculations: the theoretical concentrations to be found in the bulk turbid samples were calculated on the basis of the organotin concentrations in sediment and the respective amount of particulate matter added, i.e. for TBT in the sample O2 (Oléron) 9274 ng of TBT (as Sn) × 0.367 g were added in 1 litre of water, giving a theoretical concentration 3404 ng $dm^{-3}$ TBT (as Sn). The recovery was obtained by dividing the real concentration found by the calculated value, i.e. 428 × 100/3404 = 13%.

These sediments were sampled with a Petersen grab, freeze-dried, sieved at 60-$\mu$m mesh and ground with an agate mortar and pestle.

Estuarine sediments were collected in the upstream zones of the Rhine and Scheldt Estuaries in July and October 1988[12] with a Reyneck box corer, and wet-sieved at 60 $\mu$m with overlaying water from the sediment sampler to avoid eventual organotin desorption during sieving. In addition, suspended matter was collected by centrifugation of *ca* 500 $dm^3$ of water with a Teflon-lined apparatus over a tidal cycle in Rotterdam Harbour. Sediment and suspended matter samples were thereafter freeze-dried and ground.

Intertidal sediments were sampled in the Arcachon and Boyardville marinas (samples A1 and O1) and their adjacent well flushed channels (samples A3 and O3, O4), as well as in the Tejo Estuary (sample T6) and the Sado Estuary (sample S5).

The variability of organotin concentrations in sediments over the same site was studied in the Sado Estuary by collecting five samples less than

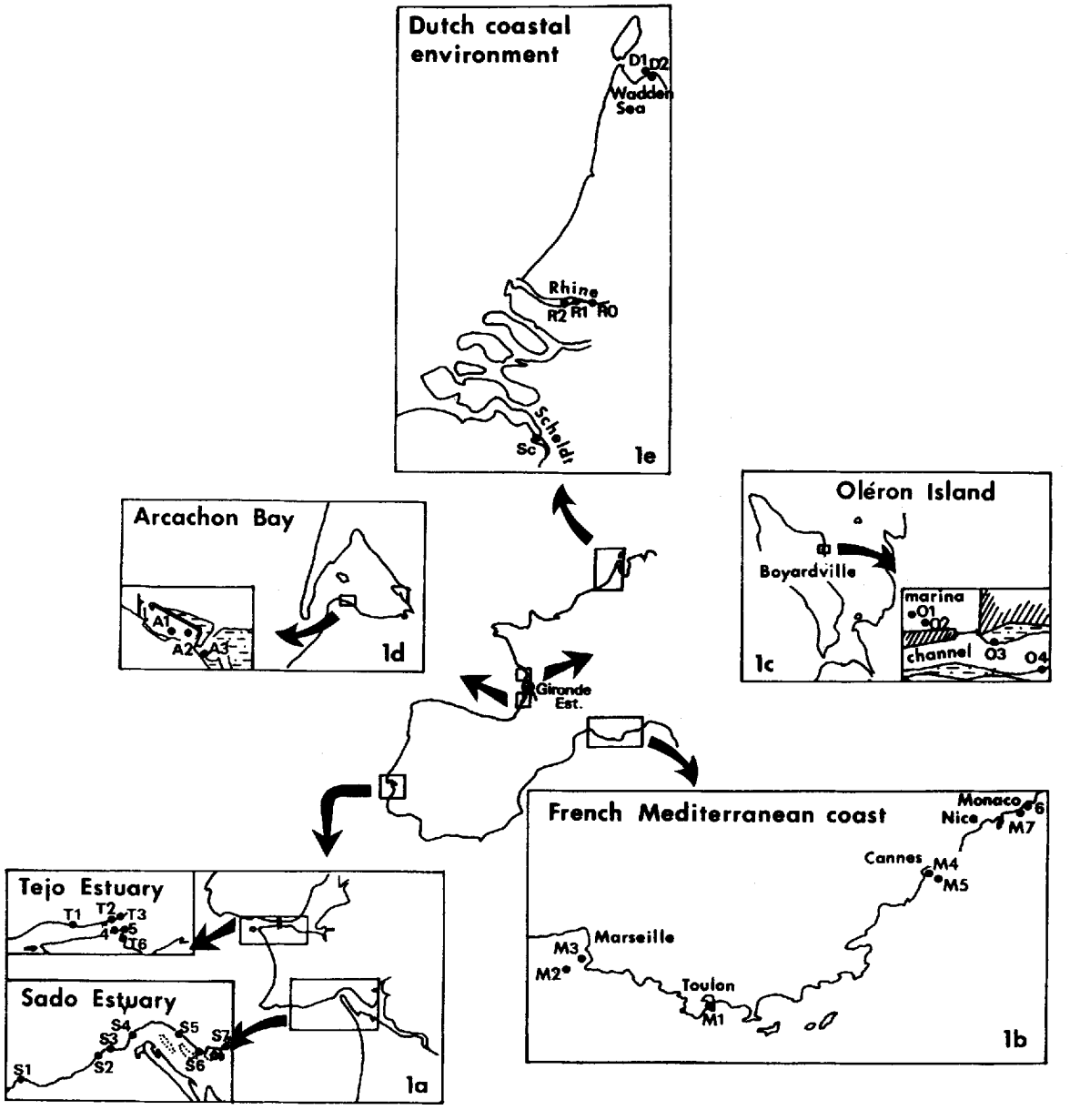


**Figure 1** Sampling locations: 1a, Tejo and Sado Estuaries (Portugal); 1b, French Mediterranean coast; 1c, Boyardville Marina (France); 1d, Arcachon harbour (France); 1e, Dutch coastal environments. The circle on the general map (between locations 1c and 1d) is the position of the Gironde Estuary outlet (samples G1 and G2).

100 m apart. These samples were collected (first-centimetre layer) at low tide, wet-sieved at 60 $\mu$m with water from the area of collection, dried at 40–50°C and ground with an agate mortar and pestle.

Different fractions of some samples (>60 $\mu$m and coarse detrital fragments isolated by flotation) were also analysed in order to determine the butyltin variability in relation to grain size (Sado Estuary, Oléron Island, Arcachon Bay,

Lazaret Bay, Rhine and Scheldt Estuaries). Procedures used were shown to be suitable to preserve the organotin stability in sediment.[8]

## Analytical procedure

### Extraction

Organotin extraction from sediment and suspended-matter samples was performed using analytical-grade acetic acid (1 g in 20 $cm^3$), in two steps:

(1) agitation of the mixtures by stirring overnight;
(2) ultrasonic extraction during 30 min.

The extracts were centrifuged at 4000 rpm during 5 min and the supernatant solutions were collected in acid-prewashed flasks.

Analyses were performed with 1–2 $cm^3$ of the extracts in clean seawater, which permitted both the required acidification (see analyses) and the sample injection.

Filtered water samples do not require special treatment, except for acidification, preferably by acetic acid.[14] However, the experiment carried out with samples rich in suspended matter showed that an extraction step should be necessary for accurate organotin measurements in such matrices. Butyltin extraction recoveries from turbid samples ranged between 9 and 17% only (Table 1b).

### Analyses

Water samples were analysed by hydride generation/cryogenic trapping/GC separation, with detection in a quartz cell in an atomic absorption spectrometer. In this method, which has been developed by Donard *et al.*,[15,16] inorganic tin and alkyltin compounds react with a 5% sodium borohydride solution (15 $cm^3$) under acidic conditions to yield alkyltin hydrides (using a modified Perkin–Elmer MHS 20 hydride system). These hydrides are cryogenically trapped (in liquid nitrogen) and separated on a chromatographic column packed with Chromosorb GNAW 60/80 mesh, coated with 3% SP-2100. Hydride species are sequentially desorbed after heating of the column (−196 to 200 °C), in relation to their specific boiling points. Detection is performed by AA Perkin–Elmer 5000) using an electrothermally heated (1000 °C) quartz furnace and a tin EDL lamp, the AA operating at 224.6 nm. The hydrides are carried by a helium flow (400 $cm^3\ min^{-1}$) and oxygen and hydrogen are introduced in the quartz cell as additive gases with respective flows of 20 $cm^3\ min^{-1}$ and 200 $cm^3\ min^{-1}$. The reproducibility for all the butyltin compounds was assessed with five replicates in water (standard solutions) and four replicates in sediments (Table 2).

**Table 2** Repeatability for the mono-, di- and tributyltin compounds in water samples (five replicates of standard solutions) and sediments (four replicates of a sample).

| | MBT (%) | DBT (%) | TBT (%) |
|---|---|---|---|
| Water | <7 | <6 | <13 |
| Sediment | <7 | <8 | <14 |

Standard deviation relative to mean of 5 replicate analyses for water and for 4 replicate analyses for sediment.

### Calibration

Calibration was performed within each sample by standard addition procedures in order to avoid eventual matrix effects. The results of water and sediment analyses were calculated as the mean values of two replicates. The detection limits in water were respectively 0.6 ng $dm^{-3}$ (as Sn) for monobutyltin (MBT), 0.5 ng $dm^{-3}$ (as Sn) for dibutyltin (DBT) and 1.2 ng $dm^{-3}$ (as Sn) for tributyltin (TBT). For sediments and suspended matters, the detection limits were 1.2 ng $g^{-1}$ (as Sn) for MBT, 1.0 ng $g^{-1}$ (as Sn) for DBT and 1.8 ng $g^{-1}$ (as Sn) for TBT. Standard solutions of 10 $\mu g$ Sn $cm^{-3}$ g mono, di-, and tributyltin in methanol were used for the calibration. Concentrations of 10 ng of the different species (as Sn) were injected in 50 $cm^3$ of water for the assessment of the repeatability of the measurement.

## RESULTS

### Butyltin distribution in water

Except for data from Portugal, all butyltin concentrations are reported for samples filtered immediately in the field (for water containing more than 10 mg $dm^{-3}$ of suspended matter) and stabilized by acidification (Table 3). Results are given for tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT).

**Table 3** Butyltin concentrations in waters from the different areas studied

| Station | Non-filtered (ng dm$^{-3}$) | | | | Filtered (ng dm$^{-3}$) | | |
|---|---|---|---|---|---|---|---|
| | MBT[a] | DBT[a] | TBT[a] | SM[b] | MBT[a] | DBT[a] | TBT[a] |
| *Samples acidified prior to filtration* | | | | | | | |
| Sado Estuary, Portugal | | | | | | | |
| Enclosed | | | | | | | |
| S1 (Sept. 1988) | 46 | 52 | 39 | <10 | —[c] | — | — |
| S4 (Sept. 1988) | 18 | 55 | 80 | <10 | — | — | — |
| S5 (Sept. 1988) | 60 | 110 | 200 | 508 | 28 | 100 | 33 |
| S6 (Sept. 1988) | 60 | 160 | 870 | 318 | 53 | 90 | 160 |
| Flushed | | | | | | | |
| S2 (Sept. 1988) | 6 | 19 | nd[c] | <10 | — | — | — |
| S3 (Sept. 1988) | 21 | 16 | nd | 226 | 8 | 10 | nd |
| S7 (Sept. 1988) | 9 | 23 | nd | 12 | — | — | — |
| Tejo Estuary, Portugal | | | | | | | |
| Enclosed | | | | | | | |
| T1 (Sept. 1988) | 40 | 130 | 430 | <10 | — | — | — |
| T3 (Sept. 1988) | 5 | 22 | 32 | <10 | — | — | — |
| Flushed | | | | | | | |
| T5 (Sept. 1988) | nd | 8 | nd | <10 | — | — | — |
| T6 (Nov. 1988) | 94 | 31 | 13 | 110 | 90 | 14 | 8 |
| *Samples filtered prior to acidification* | | | | | | | |
| Oléron Island, France | | | | | | | |
| Enclosed (Marina) | | | | | | | |
| O1 (Oct. 1988) | 5 | 30 | 91 | <10 | — | — | — |
| O2 (Oct. 1988) | 6 | 34 | 62 | <10 | — | — | — |
| Flushed (Channel) | | | | | | | |
| O4 (Dec. 1988) | 9 | 20 | nd | 103 | 7 | 14 | nd |
| Arcachon Bay, France | | | | | | | |
| Enclosed (Marina) | | | | | | | |
| A1 (Nov. 1988) | 5 | nd | nd | 12 | — | — | — |
| A2 (Nov. 1988) | 3 | nd | 33 | <10 | — | — | — |
| Flushed (Channel) | | | | | | | |
| A3 (Dec. 1988) | 6 | 7 | nd | 122 | 5 | 6 | nd |
| Gironde Estuary, France | | | | | | | |
| Enclosed (Marina) | | | | | | | |
| G1 (Dec. 1988) | 6 | 6 | 16 | 62 | 2 | 4 | 5 |
| Flushed (Channel) | | | | | | | |
| G2 (Dec. 1988) | 3 | 2 | nd | 87 | 3 | 2 | nd |
| Rhine Estuary, The Netherlands | | | | | | | |
| R1 (Jul. 1988) | 7 | 51 | 150 | — | — | — | — |
| R2 (Jul. 1988) | — | — | — | 53 | 2 | 72 | nd |
| R2 (Oct. 1988) | — | — | — | 8 | 2 | 7 | nd |
| Scheldt Estuary, The Netherlands | | | | | | | |
| Sc (Jul. 1988) | — | — | — | 115 | 9 | 17 | nd |
| Sc (Oct. 1988) | — | — | — | 14 | 4 | 7 | nd |
| Wadden Sea, The Netherlands | | | | | | | |
| Enclosed (Marina) | | | | | | | |
| D1 (Jul. 1988) | — | — | — | 16 | 3 | 24 | 1650 |
| Flushed (Channel) | | | | | | | |
| D2 (Jul. 1988) | — | — | — | 1010 | 9 | 10 | 25 |

[a]MBT, DBT, TBT = mono-, di- and tri-butyltin species: concentrations are reported in ng dm$^{-3}$ as tin. [b]SM = suspended matter content in mg dm$^{-3}$. [c]—, Not analysed; nd, not detected.

**Table 3** (continued)

| Sample | | Non-filtered MBT | DBT | TBT | SM | Filtered MBT | DBT | TBT |
|---|---|---|---|---|---|---|---|---|
| *Water (ng dm$^{-3}$)* | | | | | | | | |
| R0 (Oct. 1988) | a | —[a] | — | — | 23 | 2.1 | 2.0 | nd[a] |
| | b | — | — | — | 21 | 1.7 | 1.3 | nd |
| | c | 2.6 | 0.9 | nd | 31 | 1.8 | 1.0 | nd |
| | d | — | — | — | 28 | 1.6 | 1.5 | nd |
| | | MBT | DBT | TBT | Centrifuged volume (dm$^3$) | | | |
| *Suspended matter (ng g$^{-1}$)* | | | | | | | | |
| R0 | (a–b) | 99 | 27 | 176 | 580 | | | |
| | (b–c) | 52 | 22 | 147 | 450 | | | |
| | (c–d) | 41 | 23 | 227 | 442 | | | |

— = Not analysed.

**Variability over the same site**

Results obtained from analyses of two samples collected at the same location revealed that the variability may in some cases be very important. Indeed, whilst concentrations detected in the duplicate samples from Boyardville Marina (station O1) did not show important variations (62–91 ng dm$^{-3}$), data collected from Arcachon harbour (station A1) pointed out high differences (not detected–33 ng dm$^{-3}$).

The butyltin concentrations (MBT and DBT) detected in the Rhine and Scheldt Estuaries at the same stations but in two different periods (July and October 1988) did not display significant variations, considering the low concentrations found in both cases (Table 3).

**Partitioning between the particulate and dissolved phases**

The comparison of filtration effects with a sample rich in suspended matter, both acidified and unacidified (sample O2), revealed strong differences. In the non-acidified sample, TBT was found in the particulate phase (*ca* 90%) whereas MBT and DBT were detected mainly in the dissolved phase (Table 1). The acidification led to a release of TBT in the dissolved phase whereas the partitioning of MBT and DBT remained similar.

In the case of analyses of turbid waters from Portugal, filtration after acidification was shown to induce a high butyltin variability in relation to the suspended matter contents. Mean values of the respective concentrations of butyltins in the 'particulate' phase (amounts in bulk acidified water less amounts in filtered water) and 'dissolved' phase (amounts in filtered acidified water) revealed that only 30% of the TBT and 60–70% of the MBT and DBT were found in the filtered water. For the other samples (filtered prior to acidification), the differences in butyltin concentrations between the bulk and filtered samples appeared hardly significant, due to lower butyltin inputs and lower suspended amounts.

**Variability over a tidal cycle**

Butyltin variability over a tidal cycle was assessed at a fixed station in Rotterdam harbour located at the end of the salt intrusion (no high salinity fluctuations). No significant variations were found in the water phase (Table 4). However, the collection of suspended matter revealed significant variation of butyltin amounts in the particulates over the same tidal cycle, particularly for MBT and TBT (with a maximum of 50%).

**Effects of diffusion**

In Portugal, TBT in water was invariably detected in marinas, harbours and dry docks (samples T1, T2, S1, S4) as well as in the close vicinity of shipyards (samples T6, S5, S6). The highest concentrations were found in the marina of Bélem (sample T1), a dry dock in the Setubal harbour (sample S4) and in a poorly flushed channel in the Sado Estuary (North Channel) receiving wastes from the Setubal's shipyards (samples S5, S6). In well flushed areas TBT was not detected, although some stations are probably subject to a release of this compound from cargo or yacht antifouling paints, i.e. sites of anchorage for

leisure craft (samples S2, S3) or located in the vicinity of the Lisbon shipyards (samples T4, T5). DBT and MBT were detected in these stations at low concentrations only.

Similar patterns were observed in France, where butyltins were mostly in waters from enclosed marinas and harbours (samples A1, O1, G1) whereas lower levels were detected in well flushed areas located close to these sources (samples A2, O2, G2).

In the Netherlands, high butyltin levels were detected in Rotterdam harbour (Rhine Estuary, sample R1) in July 1988, whereas the concentrations were very low in a nearby seaward station (main stream, sample R2). Low butyltin levels were detected in the main flushed channel of the Scheldt Estuary (upstream zone).

Very high TBT levels were found in an enclosed harbour from the Wadden Sea (Den Oever harbour) whereas butyltin amounts were much lower in the flushed outlet.

## Butyltin distribution in sediments

Butyltin concentrations in sediments are listed in Table 4.

### Variability over the same site

The variability of butyltin content over the same site was assessed in the fine sediment fraction to allow comparison of data.

Variation of TBT amounts in the <60-$\mu$m fraction of sediment over a single site in the Sado Estuary (station S5) showed some variations (20–40%), which are above the measured value of the reproducibility of the analytical method (around 20%) and may be considered as significant. The long-term variability in this area clearly demonstrated that direct TBT inputs strongly influenced the distribution of this compound in sediments (<60-$\mu$m fraction) according to the period of collection (respectively 19 ng $g^{-1}$ in March 1986, 520 ng $g^{-1}$ in July 1986[5] and around 300 ng $g^{-1}$ in July 1988).

Long-term variability over a single site was not demonstrated clearly, however, in the enclosed Lazaret Bay (sample M1) where the TBT inputs were likely to be constant (34 ng $g^{-1}$ in June 1987, 63 ng $g^{-1}$ in June 1988 and 76 ng $g^{-1}$ in November 1988).

### Effects of sieving

Effects of sieving (see Table 4) demonstated that the butyltin compounds were mostly in the finest sediment fractions in comparison with the sandy fractions. However, it should be noted that high amounts were detected in coarse detrital fragments contained in sands. This accumulation led to higher butyltin moieties in the sandy bulk fractions of some Dutch samples, which is underlined by the differences observed between the bulk sediment fractions (containing detrital fragments) rich in butyltins and the washed sandy fractions with much lower butyltin concentrations. Electron-scanning observations (JEOL JSM-840A) revealed that the coarse detrital fragments were mostly composed of vegetal and/or algal debris and light mineral particles (e.g. mica). No tin-containing particles (e.g. paint particles) were detected.[17]

### Effects of diffusion

In estuarine sediments (Table 4), the butyltin concentrations were highly variable in the Sado Estuary, sometimes present at high concentrations close to the sources (shipyards) and to a lesser degree in well flushed areas. In the Tejo Estuary, TBT concentrations in sediments located close to the Lisbon shipyards appeared also quite high (sample T6). High butyltin concentrations in sediments were detected in the Rhine and Scheldt Estuaries.

High differences were observed in intertidal sediments between the butyltin concentrations found in the marinas of Arcachon and Boyardville and their adjacent channels. In the case of Arcachon, the TBT levels in the marina were higher by a factor of seven in comparison with levels detected in the adjacent channel. This increasing gradient appeared more marked in the area of the Boyardville marina, where the TBT levels within the channel increased by a factor of nine in the direction of the marina, and by a factor of 20 in the marina.

Butyltin compounds in coastal sediments along the Mediterranean coast were mostly detected in enclosed areas such as Lazaret Bay (sample M1), and to a lesser degree on the continental shelf in front of the marina of Monaco. In the other coastal sites, mono- and di-butyltin compounds were only detected at low concentrations, whereas TBT was not detected.

## DISCUSSION

The assessment of contamination may appear subjective when the samples used are not clearly defined. In order to compare the different concentrations on a common basis, sample collection

**Table 4** Butyltin distribution in sediments from the different areas of collection.

| | | MBT | DBT | TBT | GS (%) |
|---|---|---|---|---|---|
| *Sado Estuary, Portugal* | | | | | |
| S5 (Mar. 1986)[a] | <60 μm | 115 | 23 | 19 | — |
| S5 (Jul. 1986)[d] | <60 μm | 2100 | 9600 | 520 | — |
| S5a (Sept. 1988) | <60 μm | 25 | 24 | 378 | — |
| S5b (Sept. 1988) | >60 μm | 1 | 1 | nd | 97.6 |
| | Coarse detrital fragments | — | — | — | — |
| | <60 μm | 7 | 43 | 294 | 2.4 |
| S5c (Sept. 1988) | >60 μm | nd | nd | nd | 47.7 |
| | Coarse detrital fragements | — | — | — | 0 |
| | <60 μm | 16 | 33 | 290 | 52.3 |
| S5d (Sept. 1988) | <60 μm | 8 | 7 | 231 | — |
| S5e (Sept. 1988) | <60 μm | 5 | 25 | 315 | — |
| S7 (Jul. 1986)[d] | <60 μm | 177 | 14 | 21 | — |
| *Tejo Estuary, Portugal* | | | | | |
| T6 (Nov. 1988) | <60 μm | 9 | 2 | 223 | — |
| *Oléron Island, France* | | | | | |
| O1 (Oct. 1988) | <60 μm | 4931 | 3548 | 9274 | — |
| O3 (Jan. 1989) | >60 μm | 12 | 14 | 118 | 21.4 |
| | Coarse detrital fragments | 103 | 87 | 504 | 10.8 |
| | <60 μm | 18 | 14 | 475 | 67.8 |
| O4 (Dec. 1988) | <60 μm | 32 | 16 | 55 | — |
| *Arcachon Bay, France* | | | | | |
| AO (core) | 0–1 cm (<60 μm) | 100 | 86 | 466 | — |
| | 4–5 cm (<60 μm) | 98 | 90 | 445 | — |
| | 6–7 cm (<60 μm) | 95 | 88 | 487 | — |
| A1 (Nov. 1988) | >60 μm | 48 | 15 | 17 | 73.0 |
| | Coarse detrital fragments | — | — | — | 0 |
| | <60 μm | 868 | 131 | 596 | 27.0 |
| A2 (Dec. 1988) | <60 μm | 99 | 24 | 76 | — |
| *Mediterranean coast, France* | | | | | |
| M1 (Jun. 1987) | <60 μm | 108 | 23 | 34 | — |
| M1 (Jun. 1988) | <60 μm | 188 | 35 | 63 | — |
| M1 (Nov. 1988) | >60 μm | 15 | 16 | 88 | 44.0 |
| | Coarse detrital fragments | 159 | 116 | 302 | 25.3 |
| | <60 μm | 172 | 40 | 76 | 30.7 |
| M2 (Jun. 1988) | <60 μm | nd | 3 | nd | — |
| M3 (Jun. 1988) | <60 μm | 10 | 6 | nd | — |
| M4 (Sept. 1987) | <60 μm | 7 | 5 | nd | — |
| M5 (Sept. 1987) | <60 μm | 5 | 2 | nd | — |
| M6 (Sept. 1987) | <60 μm | 13 | 2 | 25 | — |
| M7 (Sept. 1987) | <60 μm | 7 | 9 | nd | — |
| M8 (Jun. 1988) | <60 μm | nd | nd | nd | — |
| *Rhine Estuary, The Netherlands* | | | | | |
| R1 (Jun. 1988) | >60 μm (bulk) | 43 | 42 | 319 | 76.5 |
| | >60 μm (washed) | 14 | 9 | 17 | 74.0 |
| | Coarse detrital fragments | 54 | 388 | 1117 | 2.5 |
| | <60 μm | 50 | 82 | 139 | 23.5 |
| R1 (Oct. 1988) | >60 μm (bulk) | 27 | 66 | 433 | 40.1 |
| | >60 μm (washed) | 6 | 4 | 88 | 37.3 |
| | Coarse frag. | 364 | 157 | 1247 | 1.8 |
| | <60 μm | 31 | 70 | 118 | 59.9 |
| R2 (Jul. 1988) | >60 μm | 13 | 14 | nd | 95.5 |
| | Coarse detrital fragments | — | — | — | 0 |
| | <60 μm | 25 | 23 | 130 | 4.5 |

**Table 4** (continued)

| | | MBT | DBT | TBT | GS(%) |
|---|---|---|---|---|---|
| *Scheldt Estuary, The Netherlands* | | | | | |
| | <60 μm | 25 | 23 | 130 | 4.5 |
| Sc (Jul. 1988) | >60 μ (bulk) | 21 | 32 | 63 | 74.0 |
| | >60 μm (washed) | 15 | 7 | 63 | 72.0 |
| | Coarse detrital fragments | 37 | 32 | 315 | 2.0 |
| | <60 μm | 104 | 75 | 168 | 16.0 |
| Sc (Oct. 1988) | >60 μm (bulk) | 19 | 15 | 88 | 34.8 |
| | >60 μm (washed) | 1 | 2 | nd | 32.8 |
| | Coarse detrital fragments | 222 | 115 | 235 | 2.0 |
| | >60 μm | 91 | 67 | 67 | 65.2 |
| *Wadden Sea, The Netherlands* | | | | | |
| D2 (Jul. 1988) | <60 μm | 36 | 16 | 67 | — |

[a]MBT, DBT, TBT = mono-, di- and tri-butyltin species: concentrations are reported in ng $g^{-1}$ as Sn (dry weight). [b]GS (%) = Percentages of the different grain size fractions. [c]—, not analysed; nd, not detected. [d]From Ref. 5.

and treatment and its effects as well as areas of collection, along with their physicochemical parameters, have to be carefully designed.

## Possible errors induced during sample collection

The collection of water and sediment samples may lead to losses or contamination of butyltin contents which are the first cause of variability in monitoring.

### Water collection

The collection of water samples may lead to unforeseeable butyltin losses (adsorption) or contamination. To achieve a suitable sampling strategy, the use of close–open–close samplers in coastal environments was found efficient in order to avoid cross-contamination with microlayer waters.

The use of a rubber boat was recommended for monitoring of trace metals[18] and is justified in the case of butyltin monitoring (especially when the hull of the ship is painted with TBT-containing paint!).

The use of acid-prewashed Pyrex glass bottles to collect water in intertidal zones was thought to be suitable, providing that the bottles are opened and closed at 50 cm below the surface. This type of container did not apparently display a strong adsorption capacity for butyltins.

### Sediment collection

Sediment collection does not pose particular problems providing that the first-centimetre layers are sampled. An example is given with the station AO (core).

## Effects of sample pretreatment

The treatment of samples may lead to additional sources of variability for the water and sediment analyses.

### Water

Acidification is commonly used to preserve the stability of diverse pollutants in water samples. As it is also usual to filter the samples to compare the amounts in the same phase (<0.45-μm generally), these procedures may lead in some cases to an underestimation of contamination. Indeed, the effects of filtration of the samples showed that TBT was mostly in the particulate phase, even after acidification. In cases of low suspended load (e.g. sample D1), one may expect that no main differences in butyltin content would be observed between bulk and filtered water. However, the dissolved concentration of TBT would underestimate the contamination if the suspended loads are very high (which was probably the case, e.g. for sample D2).

The release and adsorption of TBT depend on the amount and quality of suspended matter contained in the water samples. Desorption due to sample acidification prior to filtration may be more or less important according to whether the areas of collection display different parameters. The comparison of the 'dissolved' phases (filtration after acidification) between different sites may lead in any case to discrepancies since TBT

will certainly be released differently, and this procedure is therefore not recommended.

Analyses of bulk turbid water revealed much higher TBT concentrations than in the filtered samples. As suspended matter is ingested by organisms, the TBT adsorbed to particles clearly represents a risk of contamination which is not taken into account using an assessment with analysis of filtered samples only. This cause of underestimation could be avoided if the collected samples are left unacidified, filtered immediately in the field, and both phases (dissolved and bulk) acidified for storage. This procedure would allow us to compare the butyltin levels in the dissolved phase between different areas and to obtain a more realistic view of the contamination considering the amounts in the bulk samples.

No significant differences in butyltin concentrations between filtered and bulk samples were found for samples containing low amounts of suspended matter. This suggests that butyltins are mainly associated with the colloidal fraction. However, the detection of high butyltin levels in suspensions collected by centrifugation clearly confirmed that TBT is strongly adsorbed to particles and therefore analyses of water either filtered or containing less than 100 mg $dm^{-3}$ of suspended matter do not allow us to demonstrate the occurrence of a high contamination, as shown in the Rhine Estuary, if the evaluation is made with results of filtered-water analysis only.

**Sediment**

The sieving of sediment samples at 60-$\mu$m mesh is a good procedure to compare the butyltin levels according to the different areas of collection. The sieving procedure was carefully designed to avoid contamination (one polyethylene sieve per sample) and losses (limitation of desorption using water from the area of collection for sieving). However, this method may also lead to over- or under-estimation of a contamination. Indeed, the amount of the silt/clay fraction may widely differ from one sample to another and therefore the total amount of butyltin contained in the sediment will not represent a realistic view of a contamination. As an example, after calculation of the contribution of the TBT amount contained in the <60-$\mu$m fraction relative to the total mass of sediment (TBT amount in ng $g^{-1}$ × %GS/100, where GS is the proportion of each grain size fraction) in the samples R1 and R2, we remark that for approximately the same TBT levels in the <60-$\mu$m fractions (respectively 139 and 130 ng $g^{-1}$), the TBT amounts related to the total mass of sediment are 33 and 6 ng per gram respectively, which may lead to different interpretations. Similar observations may be made within a same site, e.g. in the Sado Estuary where the total concentration of TBT in the fine sediment fractions from the stations S5b and S5c would be respectively 152 and 7 ng owing to large differences in the silt/clay amounts, whereas the TBT concentrations in these fractions are approximately the same (respectively 294 and 290 ng $g^{-1}$). Moreover, the influence of coarse detrital debris mostly located in the sandy fractions is another source of possible discrepancies. The results have shown that the butyltins were strongly trapped in these coarse light fragments, which can be isolated by flotation from the sand grains. This may lead to an overestimation of the butyltin contamination in sands analysed without prewashing. The bulk sands were analysed first and were washed to isolate those fragments by flotation. The analyses of bulk and washed sands revealed high differences in the organotin concentrations that would be explained by very high organotin amounts detected in the coarse light debris. The debris were analysed in the same way as described for sediment. The amounts of these fragments may widely vary from one site to another (2–10%) and the respective butyltin amounts related to the total mass of sediment may in some cases vary consequently (e.g. in sample O3, TBT in debris = 54 ng, and in the <60-$\mu$m fraction = 322 ng), equal (e.g. in sample R1 TBT in debris = 28 ng, and in the <60-$\mu$m fraction = 33 ng), or even higher (e.g. in sample M1, TBT in debris = 76 ng, and in the <60-$\mu$m fraction = 23 ng), in comparison with the levels found in the silt/clay fractions. Furthermore, the debris are likely to be a source of food for many bottom-dwelling organisms and may easily be washed away during dynamic estuarine processes.[17] Thus it appears very difficult to assess accurately the importance of a contamination in terms of toxicological impact and diffusion in the environment. In view of our results, however, we may see that the distribution of the butyltin compounds in the fine sediment fractions gives a realistic approach for the detection of the contaminated areas. Going into more detail, one should at least consider the amount of the <60-$\mu$m fraction (percentage in relation to the total mass of sediment), and relate the butyltin levels in this fraction to the total mass of sediment to compare

more accurately the distribution of the contamination over different sites, as has already been done for the study of other metals.

## Sample storage

Water and sediment storage is an additional cause for unacceptable losses or contamination and therefore sources of discrepancies. Different methods were extensively tested in a study[8] which revealed that the contents of butyltins are stable over four months in filtered water, acidified at pH 2 and stored in the dark at 4 °C in prewashed Pyrex glass bottles. Turbid water, both acidified to pH 2 and non acidified, was more difficult to stabilize as losses of butyltins were observed after two months of storage in the dark at 4 °C. Sediments were shown to be reasonably stable for their organotin contents, either wet-stored at 4 °C or frozen, and no major changes were observed using a drying (50 °C) or a freeze-drying procedure.

## Butyltin variability over a single site

The variability of butyltin concentrations over a single site is also an important source of discrepancies. The variations demonstrated in this paper corresponded to synchronous samples (collected at low tide) and reflected the geographical butyltin variations over a single site only (samples within 50 m of each other). We have shown that this cause of variability was significant both in water and sediments, but not tremendously so. However, if the variations were shown to be relatively unimportant considering a common basis of comparison (respectively, filtered water and sieved sediments), the interpretation may be radically different if the total concentration of TBT (related to bulk volume or mass of sample) is taken into account, since the relative amount of suspended matter in water or the amount of the silt/clay fraction may differ widely within a single sampling area. This clearly poses the problem of the validity of the interpretations in many cases. It should also appear appropriate to perform a seasonal control of butyltin levels, which are highly dependent on direct inputs according to the period of the year (e.g. cleaning and painting of leisure draft, shipyard activities). In this sense, the use of a time-integrated sampler by pumping large amounts of water over $\geq$ one tidal cycle would certainly be the most suitable way to avoid all the possible causes of variability for a butyltin survey in water.[19]

Moreover, long-term recording of butyltins in sediments in enclosed bays should be carefully considered, since dredging activities are frequent in these areas and may represent an important cause of variability.

## Variability over a tidal cycle

The variability over a tidal cycle is an additional parameter to be addressed.[10]

The very low MBT and DBT amounts in water did not allow a demonstration of a role for these compounds during a tidal cycle in the Rhine Estuary (no significant variations). However, we may emphasize that the station was located in the upstream estuarine zone as attested by the slight changes in salinity (0.5–0.8 ‰) which could explain why no major changes were observed. We have pointed out that a high butyltin variability occurred in suspended matter over a tidal cycle which was either due to TBT inputs from more contaminated areas or, on the contrary, to dilution processes.

The TBT variability over a tidal cycle was shown in water from San Diego Bay, USA, with a higher salinity gradient, the maximum concentrations being found at low tide,[12] which allowed us to suppose that dilution processes were the dominant pathways in the Rhine Estuary.

## Diffusion of butyltin contamination

The diffusion of butyltins from contaminated areas is another source of high variability. In most of the cases studied, strong differences appeared between the TBT sources (marinas, harbours, shipyards) generally located in enclosed areas and well flushed channels located in their close vicinity. Factors increasing from 4 to 10 in butyltin levels were also observed in UK coastal waters between well flushed estuarine areas and areas of leisure craft activities.[6] Hydrodynamics is therefore an important parameter to be considered for a butyltin survey in coastal waters.

As for water, very high differences in butyltin concentrations in sediments ($<$60-$\mu$m fraction) appeared between enclosed and well flushed sampling areas. This indicated again the effects of flushing limiting the accumulation of these compounds in sediments, which has been already observed in sediments from San Diego Bay,

California.[20] It is particularly important to note that the accumulation of these compounds seems to be quite rapid in sediments from harbours and marinas, which could explain why low concentrations are detected at only 500 m from TBT inputs. This was well illustrated in the cases of the Arcachon (samples A1 and A2) and Boyardville (samples O1, O3 and O4) marinas. Thus it could be unsurprising to detect low TBT levels in sediments from areas suspected to be highly contaminated, if these areas are in well flushed waterways, and we should consider this pattern as another source of underestimation of a contamination.

### Persistence of butyltins in the environment

Finally, another cause of variability is the persistence of butyltins (i.e. degradation) in the environment. The respective concentrations of the various butyltin species in the different media allowed us to address the persistence of tributyltin in the environments studied. Controversies appeared in relation to the rapidity of TBT degradation in water, and TBT half-lives ranged between 7–15 days[21] and several months.[22] However, strong degradation of TBT in the water samples collected in the different areas was not clearly demonstrated, since in most cases TBT was largely dominant in comparison with its degradation products. Similar patterns were observed in waters from the Crouch Estuary in the UK[6]. This distribution in the order of importance TBT > DBT > MBT in water may signify that a slight stepwise degradation of TBT may occur in natural waters only. However, this pattern could also mean that constant inputs of TBT probably masked the real importance of the degradation. The same remark may be applied to the sediment samples, although the distribution of the butyltin species was generally in the order TBT > MBT > DBT, which suggested that a direct degradation of TBT to MBT could occur in sediments, as shown by Stang and Seligman,[23] or that DBT was less stable in this medium and consequently desorbed.[23]

## CONCLUSIONS

It appears more and more critical to accurately address the long-term variability of butyltins in the marine environment for the monitoring of contamination. Such monitoring programmes are valid if they answer to established strategies. Until now, the control of accuracy in the analytical determination has been only addressed for TBT (e.g. with intercomparison exercises[24]). However, it also appears critical to evaluate and remove all other pitfalls to achieve comparable sets of data. These pitfalls may appear significant at different steps of a monitoring campaign, i.e.

(a) sample collection (careless choice of the sampling site, contamination or losses);
(b) sample pretreatment (acidification of water, sieving of sediment);
(c) sample storage (losses by adsorption and/or degradation of butyltin species);
(d) variability over the same site;
(e) variability over a tidal cycle;
(f) variability due to diffusion from contaminated areas (e.g. due to flushing).

In order to remove the possible bias, accurate strategies have to be designed, involving particularly:

(1) precautions to avoid contamination during sampling, i.e.
  (a) for waters, use of close–open–close samplers or sampling below the surface in order to avoid contamination with microlayer waters;
  (b) for sediments, collection of the 5-cm upper layer with butyltin-free materials (avoiding PVC);
(2) careful pretreatment of the samples, i.e.
  (a) filtration of water with cleaned filtering units (e.g. sterile Nalgene units), analysing separately suspended matter collected by centrifugation to avoid losses due to adsorption on the filters (analyses of turbid waters are difficult to achieve due to the need for extraction steps and, separate analyses of filtered water and solid suspensions will be more accurate);
  (b) sieving of sediment with prewashed sieves using water from the area of collection in order to avoid desorption from particles—washing of sands is recommended if the grain-size partitioning has to be addressed (due to the presence of coarse detrital fragments);
(3) achievement of a suitable storage procedure, e.g. 4 °C at pH 2 in the dark for water samples, and freezing or wet storage of sediments followed by drying or freeze-

drying, in order to avoid losses (adsorption and/or degradation);
(4) assessment of the variability over a single site (synchronous collection of two or three replicates);
(5) assessment of the variations over a tidal cycle both in water and suspended matter in estuarine environments;
(6) assessment of the effects of diffusion from contaminated areas due to flushing influences.

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