Grain-size partitioning of butyltins in estuarine and coastal sediments

Philippe QUEVAUVILLER [a] [*], Henri ETCHEBER [b], Christophe RAOUX [a] and Olivier DONARD [a]

[a] Laboratoire de Photophysique et Photochimie Moléculaire, Université Bordeaux I, 351, Cours de la Libération, 33405 Talence, France.

[b] Centre de Recherches sur l'Environnement Sédimentaire et Structural des Domaines Marins, CNRS UA 197, Université Bordeaux I, 351 Cours de la Libération, 33405 Talence, France.

[*] *Present address:* Commission of the European Communities, Community Bureau of Reference (BCR), 200 rue de la Loi, 1049 Brussels, Belgium.

ABSTRACT

Grain-size partitioning of tributyltin (TBT) and its degradation products di- and monobutyltin (DBT and MBT) in coastal sediments revealed a strong tendency on the part of these compounds to adsorb on to detrital fragments (algal and leaf debris mixed with light mineral particles). Butyltins have been weakly detected in sands washed from these debris, a finding which underlined the need to separate both fractions (sands and debris) for an accurate assessment of the grain size partitioning. In debris-free sediments, butyltins were mostly detected in the silt/clay fraction. It was found necessary to consider the total amount of butyltins in each fraction, and hence the relative proportion of each fraction, in order accurately to assess the grain-size partitioning of these compounds. At this stage however, it was difficult to determine whether butyltins were only adsorbed on the surface of particles (high adsorption capacities in organic debris and silt/clays) or strongly bound to organic matter. Further investigation of the butyltin bounding state is consequently necessary.

Oceanologica Acta, **1991**. Proceedings og the International Colloquium on the environment of epicontinental seas, Lille, 20-22 March, 1990, **vol. sp. n° 11**, 247-255.

RÉSUMÉ

Distribution granulométrique des composés butylés de l'étain dans les sédiments estuariens et côtiers

La distribution granulométrique du tributyl-étain (TBT) et de ses produits de dégradation di- et monobutyl-étain (DBT et MBT) dans les sédiments côtiers a révélé une forte affinité d'adsorption de ces composés sur des fragments détritiques (débris d'algues et de feuilles mélangés à des particules minérales légères). Les butyl-étains ont été faiblement détectés dans les sables lavés de ces débris, ce qui a souligné la nécessité de séparer les deux fractions (sables et débris) pour une évaluation précise de leur distribution granulométrique. Dans les sédiments ne contenant pas de débris, les butyl-étains ont été surtout détectés dans la fraction silto/argileuse. Il s'est avéré nécessaire de considérer la quantité totale de butyl-étains dans chaque fraction, et donc la proportion relative de chaque fraction, pour évaluer précisément la distribution granulométrique de ces

composés. A ce stage, il n'a toutefois pas été possible de distinguer si les butyl-étains étaient seulement adsorbés sur la surface des particules (forte capacité d'adsorption des débris organiques et des silts et argiles) ou fortement liés chimiquement à la matière organique. Des recherches sont nécessaires dans ce domaine pour clarifier l'état d'adsorption des butyl-étains.

INTRODUCTION

The past ten years have seen a growing interest in several classes of hydrophobic contaminants such as polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and - more lately - organometallic compounds (e.g. organotins). Tributyltin (TBT) is a very efficient biocide and is directly introduced into the marine environment *via* antifouling paints. Effects induced by the release of this chemical on a wide variety of marine organisms have been largely documented and shown to occur at the ng.l^{-1} range (Maguire, 1987; Waldock *et al.*, 1987). Little attention has been paid so far to the matter of the organotin concentrations measured in sediments. This compartment of the ecosystem is, however, known to be a major sink of contaminants in the biosphere. The grain-size partitioning and effects of particulate organic carbon content on the total trace metal distribution in sediment have been well documented in the past (Förstner and Wittman, 1983). However, little is known in this field about the biogeochemical behaviour of butyltin compounds (tributyltin and its degradation products mono- and dibutyltin). This knowledge is of paramount importance, since sediments play a major role in the storage and biogeochemical history of contaminants. In this paper, therefore, we address the grain-size partitioning of butyltins in estuarine and coastal sediments, with special attention to light fragments (algal and leaf debris) present in the samples.

MATERIAL AND METHODS

Sample collection

The collection of a total of nineteen sediment samples was performed in different European estuarine and coastal areas during several sampling campaigns in 1988 and 1989 (Fig. 1, Table). Sampling sites were located in Portugal (Sado and Tejo estuaries), France (Arcachon and Boyardville marinas and Mediterranean coast) and the Netherlands (estuarine sections of the Rhine and Scheldt rivers). More details on the sample location are given in the literature (Donard *et al.*, 1989; Quevauviller *et al.*, 1989; Quevauviller and Donard, 1990).
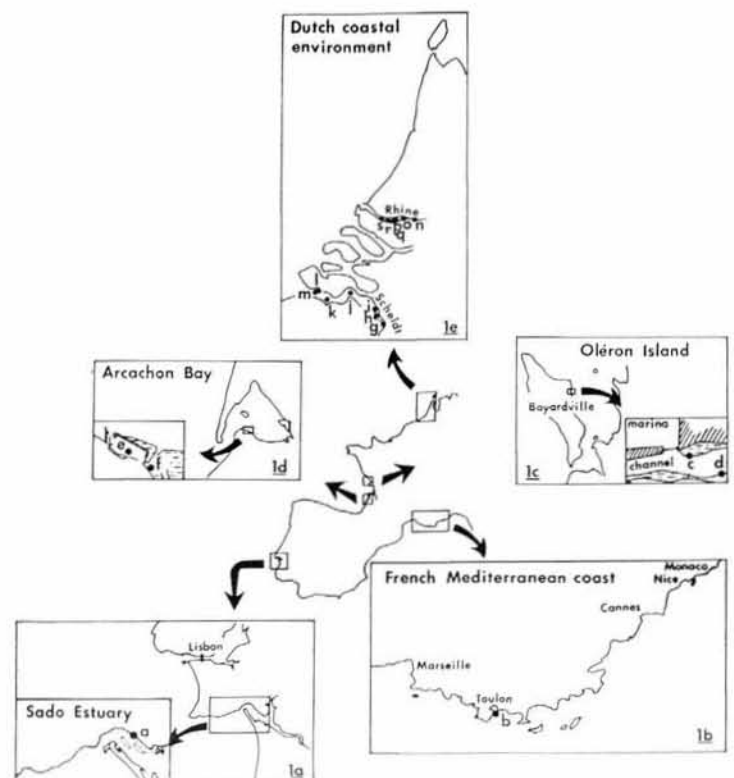

Figure 1

Sampling locations: 1 a: Sado estuary (Portugal), sample a; 1 b: Lazaret bay (Toulon, France), sample b; 1 c: Oléron island (France), samples c and d; 1 d: Arcachon bay (France), samples e and f; 1 e: Scheldt estuary, samples g to m; Rhine estuary, samples n to s.

Figure 2

Butyltin distribution in three grain size fractions (sandy, coarse detrital and silt/clay) from samples of the Scheldt and Rhine estuaries (samples i and q), and the Lazaret bay (sample b) and Oléron island (sample e). 2 a = butyltins in ng/g; 2 b = butyltins in relation to the total mass of sediment (%).

a   b
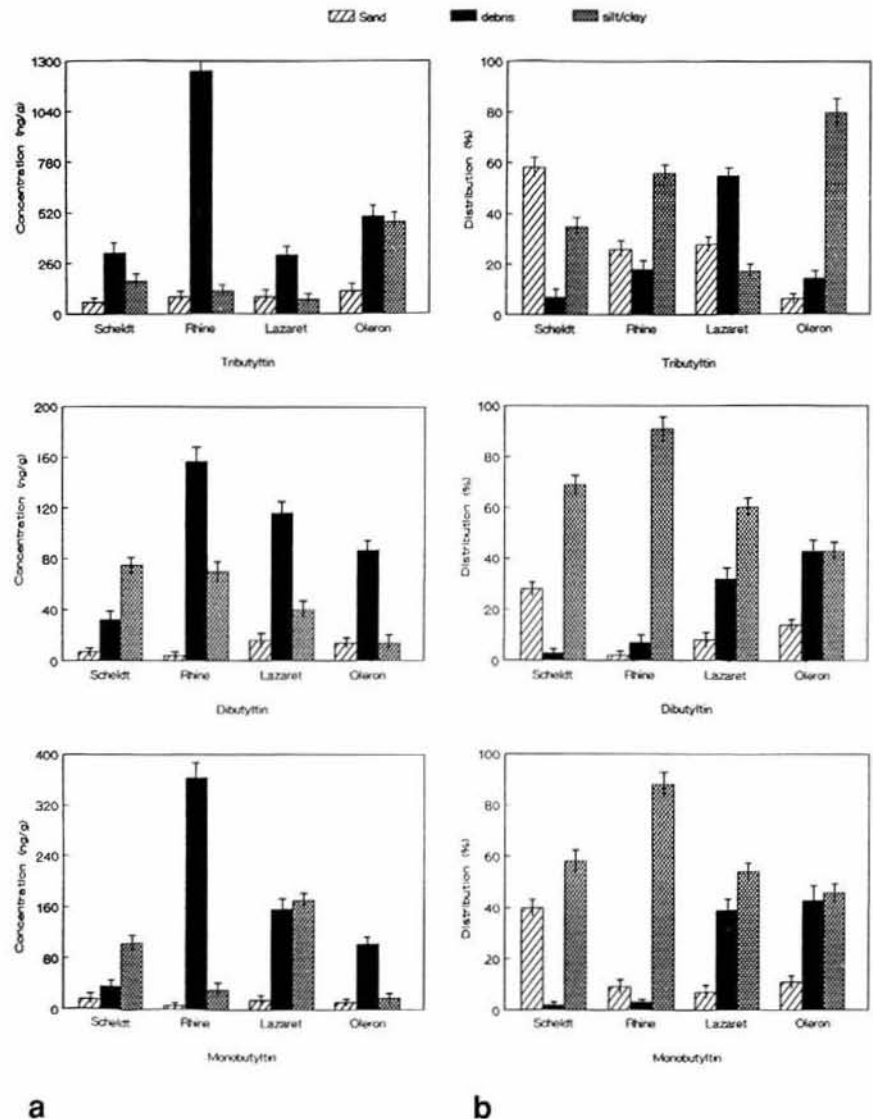
Intertidal samples were collected from the shore at low tide whereas estuarine and coastal sediments were sampled with a Reyneck box core or a Petersen grab. The 2 cm top layer of the collected sediments was scraped with a *Teflon spatula* and the samples immediately sieved and frozen prior to analysis.

Sample fractionation

All samples were wet sieved at 60 µm, using disposable pre-washed polyethylene sieves which were replaced for each sample to avoid cross-contamination. Sediments were divided into three subfractions : inferior to 60 µm, superior to 60 µm ; and the "debris" fraction described below.

Wet-sieving was performed using whenever possible overlaying water collected at the same site to avoid potential desorption. The < 60 µm fraction will be referred to later in the text as the silt/clay, and the > 60 µm fraction as the sand or sandy fraction. Most of the sediment samples contained light particles mostly comprising detrital fragments of plants (*e. g.* algae and leaf debris) and light mineral particles (*e. g.* mica). Since this sediment fraction is associated with very high organic content, special care was taken to

measure the organotin concentrations, the fraction being isolated either from the sandy fraction (*e. g.* Fig. 2) or from the different grain size fractions (*e. g.* Fig. 4). Sediment samples were gently agitated by hand for 30 minutes in large beakers filled with natural water from the area when possible or with organotin-free tap water (MilliQ water is considered to be too acid for this purpose). Floating particles collected at the surface of the water from each subfraction were gently collected after settling of sediment particles, dried and weighed. The material from each subfraction was then pooled for each sediment and will be referred later in the text as "debris". A more complete sieving scheme was undertaken on some samples (Table) using a greater number of sieves (30, 60, 300 and 500 µm). A general distinction in organotin content was also made between samples or subfractions investigated without removal of the light fraction (referred to later as "bulk") and after washing away of the light debris (referred later as "washed").

After size fractionation, samples were dried at 40-50 °C or freeze-dried. Neither procedure modifies the organotin nor the organic matter contents (Quevauviller and Donard, 1991). The weight of each subfraction of the

sediment was carefully measured to estimate the relative contribution of each fraction to the total mass of the sediment (referred as % GS). Finally all samples were ground with an agate pestle and mortar prior to analysis.

Analysis

The determination of mono-, di- and tributyltin (MBT, DBT and TBT) was performed in duplicate by hydride generation, separation after cryogenic trapping and detection by atomic absorption spectrometry on a Perkin
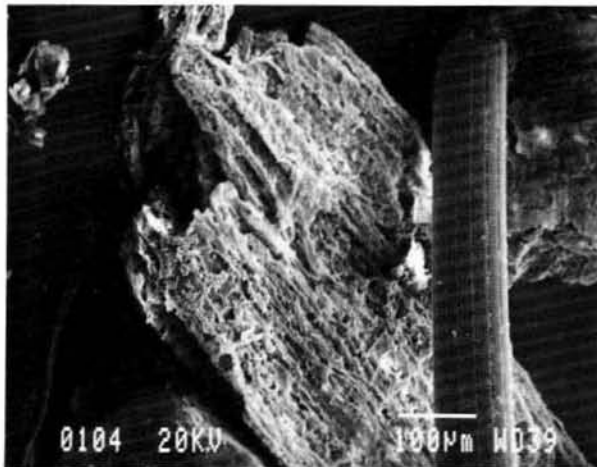
Coarse detrital fragments : Rhine Estuary
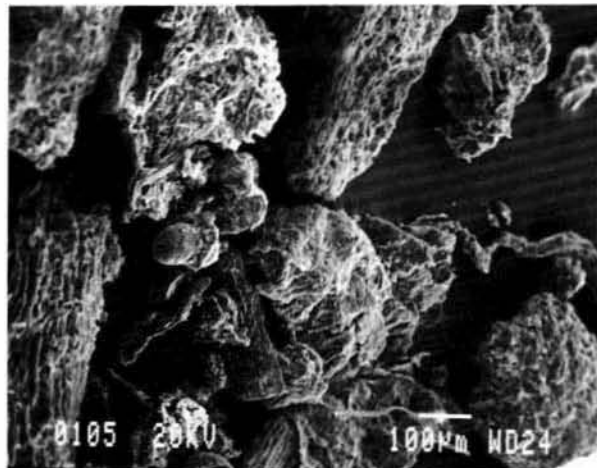
Coarse detrital fragments : Scheldt Estuary

Figure 3

Electron probe microanalysis of coarse detrital fragments in sample collected in the Scheldt and Rhine estuaries (sample i and q).
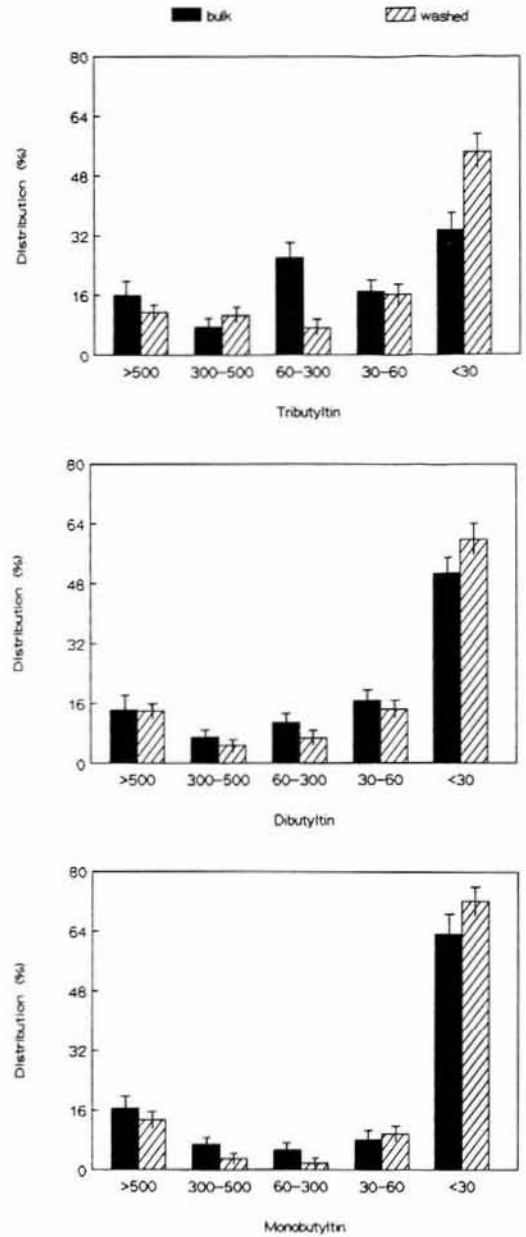

Figure 4

Grain-size distribution of butyltins in sub-fractions of a sample from the Rhine estuary, without washing (bulk subsamples) and after washing.

Elmer 5000. Organotin compounds were leached from the different samples (0,2 to 1 g) overnight at room temperature with 20 ml of pure glacial acetic acid. After extraction, samples were centrifuged and 1 to 2 ml of the leachate was used for analysis. This method makes it possible to separate and detect the different organotin species with detection limits ranging from 0.5 to 2 ng/g as Sn. The repeatability of the method was less than 15 %. Complete details of the analytical method have been given elsewhere (Donard, 1989; Quevauviller and Donard, 1990). Particulate organic carbon (POC) analysis was performed according to the Strickland and Parsons method modified by Etcheber (1981).

RESULTS AND DISCUSSION

Grain-size partitioning of butyltin compounds

The grain-size distribution of butyltins is presented for four samples (Table) which were selected because their different grain-size distributions were considered to be representative of estuarine (Scheldt and Rhine estuaries, samples i and q), coastal (Lazaret Bay, sample b) and intertidal (Oléron Island, sample e) sediments.

Butyltin concentrations are presented in the different grain-size fraction (Fig. 2). In Figure 2 *a*, the organotin concentrations are plotted for each sub-fraction. In Figure 2 *b*, the contribution of each subfraction (i) to the total mass of organotins is presented. The calculations were

done as follows (on the basis of 1 g of total sediment):

$$Xi \ (ng) = \frac{Ci \times GSi}{Ci \times GSi} \quad \text{and } Xi \ (\%) = \frac{xi}{Sxi} \times 100$$

where Ci is the organotin concentration in each subfraction and GSi is the relative proportion of each subfraction (in %).

From Figure 2 *a*, it appears that the debris fraction is a preferential sink for all the butyltin compounds in all the samples studied. Similar observations have been reported by Quevauviller (1988) and Raoux (1988) studying respectively PCB and PAH distribution in sediments. This fact is certainly to be related to the high hydrophobicity and liposolubility of the three classes of chemicals mentioned. The total contribution of the debris fraction (Fig. 2 *b*) is
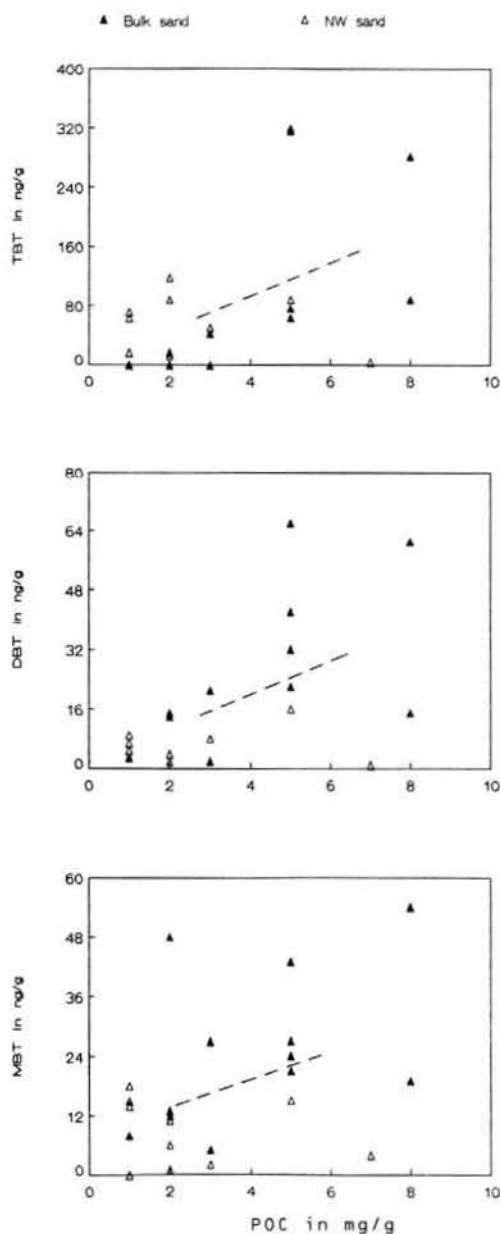

Figure 5

Plotting of butyltin concentrations (ng/g as Sn) against POC contents (mg/g) in sand fractions.
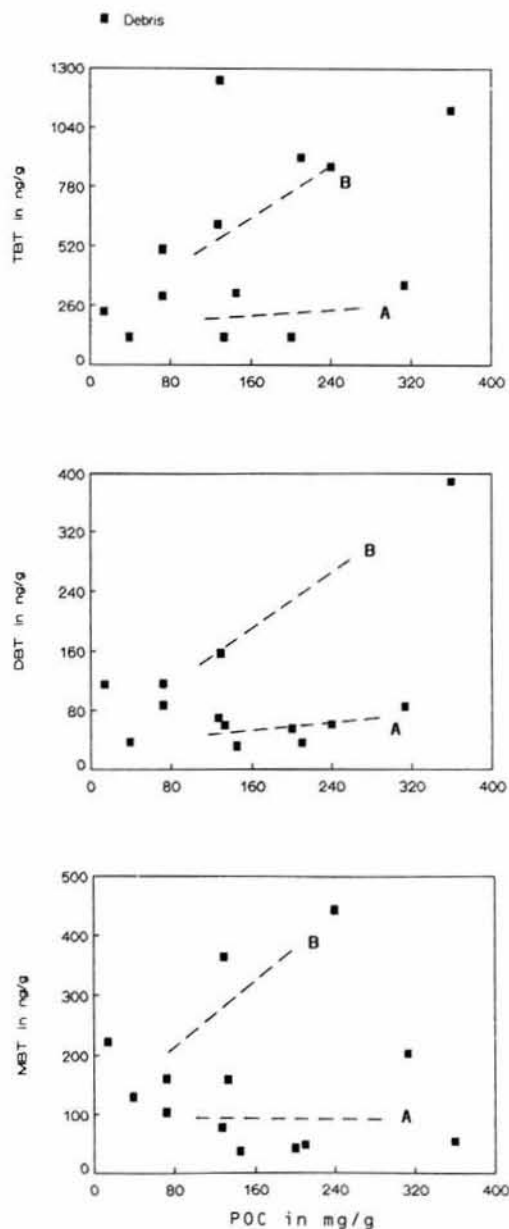

Figure 6

Plotting of butyltin concentrations (ng/g as Sn) against POC (mg/g) in debris.

Table

Butyltin concentrations in subfractions of sediments from the different areas studied. * = bulk fraction; + = washed fraction; MBT, DBT, TBT = mono-, di- and tri-butyltin species in ng/g as Sn (dry weight); nd = not detected; POC = Particulate organic carbon (mg/g); % GS = Percentages of the different grain size fractions

Concentrations des butyl-étains dans les fractions granulométriques des sédiments considérés. ∗ = fraction brute ; + = fraction lavée ; MBT, DBT, TBT = mono-, di- et tri-butylétain en ng/g (Sn) de matière sèche ; nd = non détecté ; POC = carbone organique particulaire (mg/g) ; % GS = pourcentages des différentes fractions granulométriques.

Locations		MBT	DBT	TBT	POC	% GS
Sado Estuary (P)						
a	> 60 µm*	nd	nd	nd	0.7	47.7
	Debris	—	—	—	—	0
	< 60 µm	16	33	290	7.6	52.3
Lazaret Bay (F)						
b	> 60 µm+	15	16	88	0.5	44.0
	Debris	159	116	302	7.2	25.3
	< 60 µm	172	40	76	3.1	30.7
Oléron Island (F)						
c	>60 µm+	12	14	118	0.2	21.4
	Debris	103	87	504	7.2	10.8
	< 60 µm	18	14	475	1.4	67.8
d	> 300 µm*	54	61	281	0.8	61.7
	60-300 µm*	27	21	42	0.3	28.2
	< 60 µm	26	19	71	1.6	10.1
Arcachon Bay (F)						
e	> 60 µm*	48	15	17	0.2	73.0
	Debris	—	—	—	—	0
	< 60 µm	868	131	596	4.1	27.0
f	> 60 µm*	24	22	76	0.5	87.0
	Debris	—	—	—	—	0
	< 60 µm	99	24	76	2.8	13.0
Scheldt Est. (NL)						
g	> 60 µm+	4	1	4	0.7	17.4
	Debris	158	60	122	13.3	2.0
	< 60 µm	5	12	76	3.1	80.6
h	> 60 µm*	19	15	88	0.8	34.8
	> 60 µm+	1	2	nd	0.2	32.8
	Debris	222	115	235	1.4	2.0
	< 60 µm	91	67	67	3.4	65.2
i	> 60 µm*	21	32	63	0.5	74.0
	> 60 µm+	15	7	63	0.1	72.0
	Debris	37	32	315	14.5	2.0
	< 60 µm	104	75	168	3.4	16.0
j	> 60 µm*	8	3	nd	0.1	92.5
	Debris	—	—	—	—	0
	< 60 µm	88	10	147	1.6	7.5
k	> 60 µm+	nd	5	71	0.1	54.0
	Debris	77	70	613	12.7	0.7
	< 60 µm	42	8	nd	2.0	45.3
l	> 60 µm*	5	2	nd	0.3	68.0
	Debris	—	—	—	—	0
	< 60 µm	81	14	118	2.2	32.0
m	> 60 µm*	18	9	17	0.1	79.6
	Debris	—	—	—	—	0
	< 60 µm	91	14	504	1.4	20.4

Table *(continuation)*

Rhine Est. (NL)

n	> 500 μm*	31	35	315	19.0	10.0
	Debris	48	36	907	21.0	1.8
	300-500 μm*	9	12	109	3.7	14.3
	Debris	129	37	122	3.9	1.8
	60-300 μm*	5	14	265	2.2	19.6
	60-300 μm+	2	8	50	0.3	17.4
	Debris	201	85	349	31.3	2.2
	30-60 μm*	15	40	336	3.9	10.2
	Debris	444	61	865	24.0	0.3
	< 30 μm	26	27	147	5.4	45.9
o	> 60 μm*	13	14	nd	0.2	95.5
	Debris	—	—	—	—	0
	< 60 μm	25	23	130	2.3	4.5
p	> 60 μm*	31	35	315	0.5	76.5
	> 60 μm+	14	9	17	0.1	74.0
	Debris	54	388	1117	36.0	2.5
	< 60 μm	50	82	139	3.7	23.5
q	> 60 μm*	27	66	433	0.8	40.1
	> 60 μm+	6	4	88	0.2	38.3
	Debris	364	157	1247	12.9	1.8
	< 60 μm	31	70	118	3.9	59.9
r	> 60 μm+	11	4	13	0.2	82.6
	< 60 μm	13	17	109	2.7	17.4
s	> 60 μm+	nd	nd	nd	0.1	24.3
	Debris	42	55	122	20.0	0.5
	< 60 μm	6	11	172	1.7	75.2

all the more significant as its relative percentage is high (Lazaret and Oléron). However, the dominant feature of Figure 2 *b* is that the major amount of butyltin compounds is associated with the silt/clay fraction. This general trend may be related with the classical trilogy demonstrated earlier for trace metals (Förstner and Wittman, 1983): small grain-size = high surface area = absorption of organic matter. In our case, the high absorptive affinity for the silt/clay fraction seems to be better demonstrated for mono- and dibutyltin compounds than for tributyltin which could be related to their higher ionic character. Nevertheless, since it is clearly shown in Figure 2 *a* that the detrital fragment is a preferential sink for TBT, part of this trend could be explained by the difficulty in always achieving a complete separation of the debris from sandy fractions.

The debris fractions of sediment samples from the Rhine and Scheldt estuaries (samples i and q) were examined by scanning electron microscope coupled with JEOL JSM - 84OA electron probe microanalysis. Pictures of the fragments are presented in Figure 3. Most of this fraction was composed of coarse vegetal detrital fragments from higher plants. No tin-rich particles (*e. g.* from antifouling paint chips) could be detected, which suggested that the high levels of organotin measured on these fragments were likely due to the high diffused adsorption capacity of this material.

A detailed examination of the grain-size effects was made

on some sediments. Figure 4 presents results obtained after sieving of a sample collected in the Rotterdam harbour (sample n, Table) in five subfractions (fractions < 30 μm, 30-60 μm, 60-300 μm, 300-500 μm and > 500 μm and debris collected in each subfraction).

High butyltin concentrations were systematically detected in the debris collected in each subfraction (*see* Table). This leads to several important conclusions which are presented in Figure 4: firstly, more than 25 % of the organotin concentration may be found in the coarse fraction of the sediment (> 300 μm). Secondly, comparison between analyses performed on bulk (containing debris) and washed samples from sandy fractions indicated again the important contribution of the vegetal fragments. The relative abundance of this light and organotin-rich component in the coarse fraction of the sediment may be mistaken with regard to the potential affinity of the sandy fraction of sediment to organotin. This is particularly so in the case of TBT which was shown to be dominant in the <30 μm in the washed sediment (free from debris) whereas this compound was demonstrated to be dominant in sands in the bulk fractions due to the presence of debris. These fragments are difficult to remove from the sediment matrix and may represent a source of overestimation of TBT concentrations in sands. However, special attention should be paid to this light component of the sediment matrix since its low density will confer on it a very different hydrodynamic behaviour in comparison to the silicate constituents of the sediment. It could also represent, along
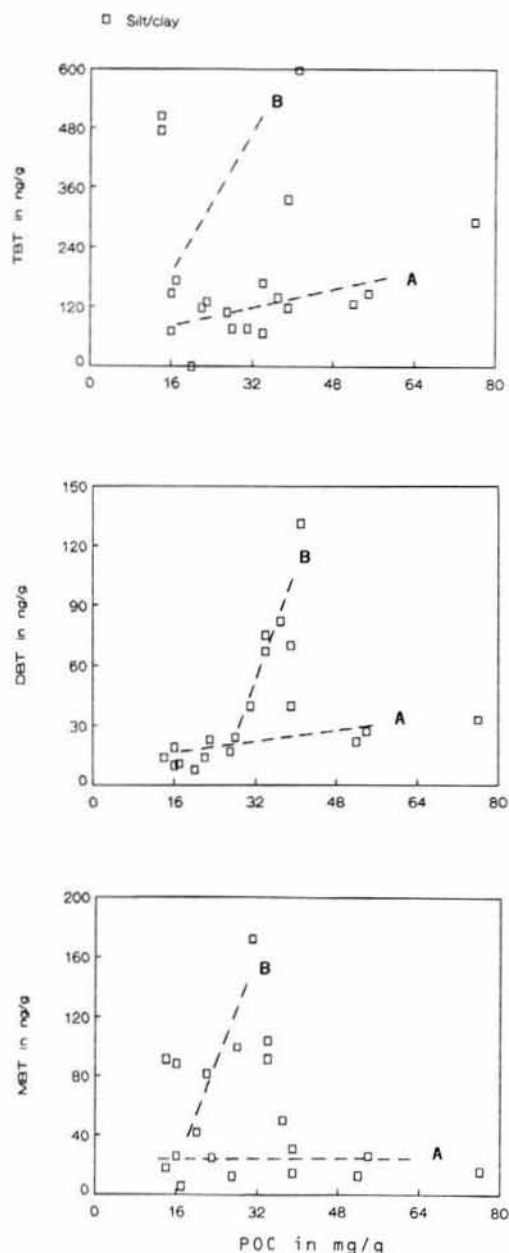
Figure 7

Plotting of butyltin concentrations (ng/g as Sn) against POC (mg/g) in silt/clay fractions.

with the silt/clay fraction, a potential food source for bottom-dwelling and filter-feeding organisms.

Butyltin and total organic carbon relationships

It has already been well established that the particulate organic carbon (POC fraction) of the sediment constitutes one of the preferential supports for trace metals (Förstner and Wittman, 1983). A graph plotting butyltin concentrations against POC content for all the subfractions did not reveal any strong correlation; this was already observed by Randall and Weber (1986). However, we have detailed the study of these possible relationships by

plotting in Figures 5, 6 and 7 the organotin and POC contents present in each subfraction of sediment analysed. The results revealed possible associations that could not be detected with the analysis of bulk samples.

It must be underlined as an introduction that the possible relationship existing between POC and butyltins will probably be influenced by the different hydrodynamic conditions of the sampling locations (and therefore the sediment grain size) and local anthropogenic inputs (*e. g.* harbours).

A close examination of the diagrams reveals that general relationships could be highlighted in the different fractions :

In Figure 5, the scatter of data shows a general trend which is mostly due to the presence of debris in the bulk sands displaying higher butyltin concentrations. The high scatter of data could be due to an inhomogeneity of some samples. In some cases, it was suspected that the debris was not totally removed during the washing of the sands, which could explain high butyltin amounts in some washed sand samples. This could not be detected by a strong increase in the POC content as the amount of debris was always very weak.

Figure 6 shows that the apparent scatter of data could be regulated by two modes of association between butyltin and POC content in debris. The trend line "A" shows that butyltin contens is not at all or only weakly influenced by POC amounts in situation involving low organotin inputs. However, a relationship may exist (trend line "B") in situations of high butyltin inputs (*i. e.* in areas of higher anthropogenic inputs). This relationship may be mediated by a higher adsorption capacity of butyltins on to organic matter. However, this trend may also be partly due to a synchronous release and sinking of organotin and POC in sediment, as may be expected in contaminated areas (*e. g.* harbours).

Similar observations could be done with the distribution observed in the silt/clay fraction (Fig. 7).

A general trend was systematically observed in the different sub-fractions when looking at the levels of concentrations of the three butyltin species: TBT showed a higher affinity in comparison with DBT and MBT. This could be a consequence of the higher hydrophobic properties of this compound and its preferential support for organic carbon.

CONCLUSIONS

This study illustrates the preferential accumulation of butyltins in the coarse detrital fraction of estuarine and coastal sediments. Due to its relatively low density, this fraction of the sediment may have very different hydrodynamic behaviour and may be easily washed away. This fraction induced a very wide heterogeneity in the content of butyltin concentration in sediment. Butyltin/POC relationships suggested the occurrence of two different modes of association of the organotins : one related to high butyltin amounts in both silt/clay and

coarse detrital fractions; and the other associated with low butyltin content (diffused contamination) for which no strong influence of POC was demonstrated. These results clearly point to the need for a clear definition of sample pretreatment prior to butyltin determination in sediments.

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