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Volatilization of Organotin Compounds from Estuarine and Coastal Environments

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The occurrence and speciation of volatile tin compounds (Sn) have been investigated in a contaminated area of the Arcachon Bay (SW France) and in the water column of the Scheldt (Belgium/Netherlands) and Gironde (SW France) estuaries. This paper describes the application of a multi-isotope analytical method, using gas chromatography and inductively coupled plasma-mass spectrometry. Analytes were collected by cryogenic trapping of the gaseous species. This trapping has allowed us to probe volatile tin compounds by detecting both ^{118}Sn and ^{120}Sn isotopes. Volatile organic tin compounds have been determined in both sediment and water. They could result from both natural methylation and hydridization processes of inorganic tin ($R_nR'_{4-n}Sn$; $R = Me$, $R' = H$, $n = 0-4$) and from anthropogenic butyltin derivatives released from ship antifouling paintings which have accumulated in sediments ($R_nR'_{4-n}$ Sn; $R = Bu$, $R' = H$ or Me, $n = 0-3$). The most ubiquitous species were found to be the methylated forms of butyltin derivatives (Bu_nSnMe_{4-n}, $n = 0-3$). These results suggest that biological and/or chemical methylation mechanisms are likely to occur in sediments and to lead to remobilization of tin species into the water column and subsequently to the atmosphere. Finally, sediment−water and water−atmosphere fluxes have been calculated to assess the potential impact of these processes on the fate of organotin compounds in coastal environments.

Introduction

The increasing production and release of organotin compounds to the environment over the last three decades has led to consider these species as "global pollutants" (*1*, *2*). The contamination generated by the direct introduction of biocides, mainly triorganotins, and more specifically of tributyltin (TBT) into the aquatic environment from the leaching of antifouling paints, is well established (*3*, *4*). Despite various degradation pathways and the evidence of decreasing concentrations in water column in some places around the world, TBT contamination is still considered to be one of the most important ecotoxicological problem of the last 2 decades (*5−7*).

Understanding the fate of tin compounds is of primary importance due to their impact on the environment (*8−14*). Organotin compounds are usually associated with the fine fraction (<63 μm) of the sediments (*1*, *15*). Transformation of organotin compounds can occur via different chemical and biological routes. The chemical fate of these compounds is known to be mainly driven by dealkylation processes in oxic or anoxic conditions (*7*, *9*, *16*). The dealkylation processes can be offset to some extent by competing reaction pathways involving natural methylation (*17−21*). Studies have indicated the occurrence of methyltin derivatives in the aquatic environments (*22*, *23*). Different natural methyl donor species, such as iodomethane, methyl-cobalamine or humic substances are indeed able to methylate tin compounds to yield mono-, di-, tri-, and tetramethyltin (*21*). In anoxic sediments, sulfate reducing bacteria can actively promote the methylation of inorganic or organic tin compounds (*16*, *24*). Such natural derivatization pathways may lead to the formation of fully substituted and volatile tin compounds in the aquatic environment (*18*, *23*, *25*). These results suggest that tin could be volatilized to the atmosphere from the marine environment (*19*). More recently Adelman et al. (*7*) came to the same conclusion after they studied the fate of TBT in laboratory experiments. They observed the degradation of radiolabeled TBT (^{14}C) during batch incubations in an enclosed marine ecosystem. At the end of the experiment, they were unable to recover all the ^{14}C activity from the TBT introduced in the system. The authors related this loss in the radioactivity budget to the exchange of butyltin compounds at the air/water interface.

To date, there is no significant evidence of losses of organotin compounds to the atmosphere. Results reported for volatile tin compounds mainly suggest the occurrence of hydride forms of tin compounds. Tin hydride (H_4Sn) and methyltin hydrides (Me_nSnH_{4-n}, $n = 0-4$) have been detected in algae or microbial cultures (*21*, *22*, *26*). These hydride species were suspected to be formed biologically and are likely to occur naturally in the environment. Craig and Rapsomanikis (*20*) suggested that chemical methylation could also take place in the environment and explain the formation of tetramethyltin. The occurrence of methylated butyltin compounds, such as tributylmethyltin (Bu_3SnMe) and dibutyldimethyltin (Bu_2SnMe_2), in the surface of contaminated harbor sediments at concentrations below 50 ng/g (dry weight) have also been reported by Maguire et al. (*1*, *11*). Critical discussion has highlighted the care needed in the identification of such compounds when using atomic spectrometric detection methods, due to the lack of molecular information provided by such analytical techniques (*27*). Bu_3SnMe was finally identified by GC/MS at concentrations up to 400 ng/g from incubated anoxic sediments spiked with TBT (*16*). Its formation was related to the specific activity of sulfate reducing bacteria.

While it is generally agreed that butyltin compounds inputs in coastal waters have been reduced, a major question remains, however, with regard to their accumulation and fate in sediments. It is now of major concern for risk assessment of butyltin contamination to know whether these compounds will be degraded or could be remobilized in the water column through natural diffusion, bioturbation processes, or by turbulent mixing due to the action of water.

The results presented in this paper report on the ubiquitous occurrence of volatile tin compounds in coastal areas. These results were obtained with highly sensitive and selective analytical methods. Several volatile tin species have been identified in all environments studied.

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Materials and Methods

Sampling Sites and Procedures. Determination of the concentrations of total organotin compounds in the dissolved or suspended solid phase of the samples was not the objective of the present work.

Sediment. Sediments were collected at low tide or using a box corer in the main basin of the Arcachon harbor (France) and in the navigation channel of the Scheldt estuary (Belgium/Netherlands), respectively, where the organotin contamination from antifouling paints has been extensively reported (*12–15*). Sediments were sampled in the top 5 cm using a polyethylene cup and were immediately transferred to a gastight glass vial (100 mL) without any headspace. The vials were then stored in the dark at 4 °C and processed within 24 h. Sediment samples from the Arcachon harbor and the Scheldt estuary were from quasi anoxic conditions (black color). Sediment samples were further analyzed for butyltin compounds (*28*), total organic carbon and sulfur (LECO CS-125 analyzer), and water content.

Water. In the Arcachon harbor, water samples were directly collected into 1 L Pyrex bottles with gastight Teflon-lined caps and were processed like the sediments. Estuarine water samples were collected in two European estuaries selected for their different anthropogenic pressure during the EU BIOGEST (biogas transfer in estuaries) project cruises. Both the Scheldt and the Gironde estuaries are both macrotidal systems with long residence times for both water and suspended matter and very different anthropogenic contributions (*29, 30*). The Scheldt estuary contains one of the largest harbors and industrial complexes in Europe and is bordered by a high population density (*29*). On the contrary, most of harbor and industrial activities in the Gironde estuary stopped more than 10 years ago, and the density of population along its banks is much lower (*30*). It is therefore considered to be one of the few large pristine estuarine area of Europe. In both estuaries, water samples were collected during four cruises on board the research vessels *Belgica* (SPPS/FN) and *Côte d'Aquitaine* (CNRS/INSU). These cruises took place in July 1996 and December 1996 for the Scheldt estuary and in November 1996 and June 1997 for the Gironde estuary. All samples were collected at 3 m depth, below the ship draught, using an acid-cleaned Teflon-coated Go-Flo sampler (GO, Miami, U.S.A.) or a custom 1 L ultra clean sampler (*4*). Both sampling devices gave the same results. Immediately after collection, the samples were transferred to a Teflon-lined capped 1 L Pyrex bottle for ship-board treatment within 30 min. Water samples were collected over a salinity gradient of 0–34 units (Practical Salinity Scale, International System of Units) during each cruise in both estuaries.

Stripping Volatile Tin Compounds from Samples. Sediment. Volatile tin compounds were extracted from the sediments collected using a purge and cryogenic trap setup. About 10 g of fresh sediment was transferred and weighed in a 50 mL purge glass vessel. A volume of 20 mL of milli-Q water prepurged with He (10 min at 300 mL/min) was added to the purging vessel. The suspension formed was continuously homogenized with a Teflon-coated magnetic stirrer. Gaseous species were stripped out the vessel and dried by passing them through a water trap at −20 °C (mixture of ice and acetone), finally cryofocused in a silanized glass trap (U-shaped, 6 mm i.d.) filled with acid-cleaned silanized glass wool (Supelco), and immersed in liquid nitrogen (−196 °C). After a 30-min purge, the cryotraps were closed with gastight Teflon caps and immediately transferred to a dry atmosphere cryogenic container (cooled with liquid nitrogen) for a maximum storage period of 1 week before analysis (*31*).

Water. Volatile tin compounds were extracted from water samples in the field using a purge and cryogenic trap setup described elsewhere (*31*). Within less than 30 min after sampling, the water sample was transferred directly from its 1 L Pyrex bottle to a 1.5 L purging vessel under He atmosphere. Water samples were continuously stripped for 1 h with a He flow rate of 700 mL/min to yield optimal extraction efficiency (*31*). The volatile compounds were then trapped and stored following the procedure described above for sediment.

Chemicals and Standards. All connections and tubing in contact with the samples were made of Teflon PTFE and PFA, respectively. All glass- and plasticware were previously cleaned with a biocide detergent and soaked with concentrated nitric acid (10%, Prolabo, France) for 3 days. Millipore milli-Q water was used for rinsing and preparing aqueous solutions. Reagents and standards were prepared with analytical grade chemicals, unless stated. Hexane (Fluka, 99.8%), methanol (Fluka, 99.8%), dichloromethane (Fluka, 99.8%), tropolone (Fluka, 99%), methylmagnesium chloride (Aldrich, 99%), sodium borohydride (Aldrich, 99%), and sodium sulfate (Prolabo, 99%) were used for the derivatization reactions and standard compound solution preparations. Tetramethyltin (Strem, 99%), tetraethyltin (Strem, 99%) and butyltin chloride species (Bu_nSnCl_{4-n}, $0 \le n \le 4$, Strem, 99%) were used as standard compounds for calibration and identification. Different volatile organotin compounds were synthesized for the identification of unknown species present in natural samples. Hydride forms of butyltin compounds were obtained from stock solutions of butyltin chloride compounds mixed with milli-Q water acidified to pH 2 with pure HCl (Prolabo) and 100 μL of 5% $NaBH_4$ (Merck) aqueous solution (*32*). Mixed methylated forms of butyltin compounds were obtained by dilution and extraction of the butyltin chloride stock solution by tropolone in hexane. The extract was dried over anhydrous Na_2SO_4 followed by classical Grignard derivatization reaction with MeMgCl (*33*). The volatile tin compounds, extracted into the organic phase, were dried with anhydrous Na_2SO_4 prior to injection into both analytical systems. Although recoveries of the volatile organotin species synthesis were less than 100%, these compounds were only extracted for qualitative identification in the natural samples.

Determination of Volatile Tin Compounds. The standard settings and methodologies used for both the ICP/MS and MIP/AED are discussed in details by Pécheyran et al. (*34*) and Szpunar et al. (*28*), respectively. Both techniques are independent of each other in both the chromatographic and detection aspects and are complementary for the identification of volatile tin compounds.

Cryogenic Trapping−Gas Chromatography−Inductively Coupled Mass Spectrometry (CT-GC−ICP/MS). Most of the methodology is discussed in detail elsewhere (*31, 34*). For most of the samples analyzed, direct injection was used for both the cryotraps and standards solutions into a cryotrapping−gas chromatography and ICP/MS (Elan 5000, Perkin-Elmer) system (*34*). This analytical procedure allows the samples to be trapped on inert materials, thus preventing chemical alteration. The high sensitivity and selectivity of the ICP/MS detector coupled with the cryofocusing technique permit operations which deliver detection limits lower than 50 femtogram for tin (as Sn).

Capillary Gas Chromatography−Microwave Induced Plasma−Atomic Emission Detection (CGC-MIP/AED). To confirm and identify some of the unknown volatile compounds detected by CT-GC-ICP/MS, a second analytical technique was employed to take advantage of its high sensitivity of the overall system, the high separation efficiency provided by the capillary columns and the selectivity of the detector (CGC-MIP/AED, Hewlet-Packard Model 5921A) (*28*). With this approach, volatile species trapped in the field were also desorbed at 300 °C over 12 min under a helium flow rate at 10 mL/min. Volatile tin compounds were trapped in 10 mL Teflon-lined headspace vials filled with prepurged hexane.
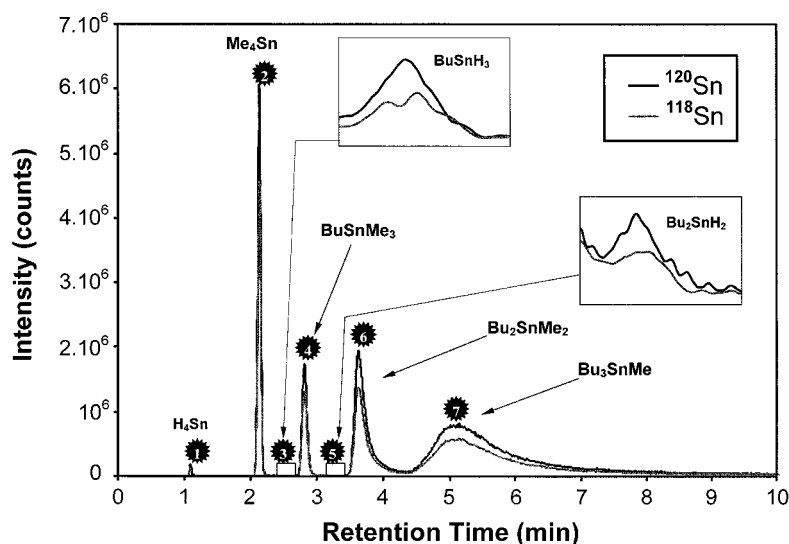
FIGURE 1. Chromatogram of volatile tin compounds in a surface sediment sample from the harbor of Arcachon, obtained by purge, cryogenic trapping, gas chromatography, and ICP/MS detection (CT-GC-ICP/MS).
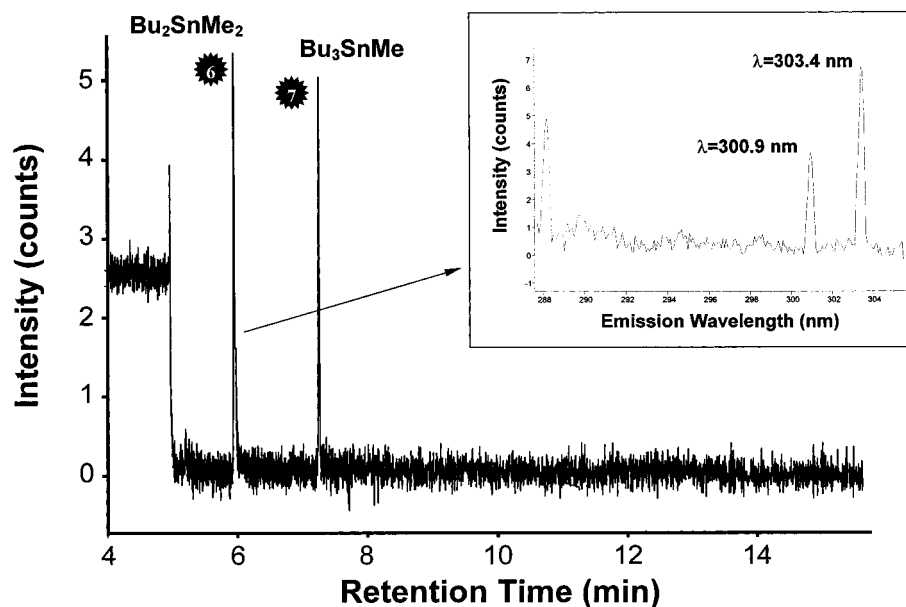

FIGURE 2. Chromatogram of volatile tin compounds in a surface sediment sample from the harbor of Arcachon, obtained by cryogenic trapping followed by capillary gas chromatography and MIP/AES detection (CGC-MIP/AED).

These solutions were then evaporated at room temperature under nitrogen flow (10 mL/min) to preconcentrate the less volatile species before their direct injection into the CGC using an automated sample injector (HP Model 7673A). This technique offers a detection limit below 1 pg as Sn.

Results and Discussion

Identification of Volatile Tin Compounds in Coastal Environments. All analyses performed by CT-GC-ICP/MS on sediment and water samples from the Arcachon harbor and the Scheldt and Gironde estuaries presented similar chromatographic profiles. A typical CT-GC-ICP/MS chromatogram obtained for a contaminated sediment of Arcachon (silt) is presented in Figure 1 and is used as reference sample for the identification procedure applied in this work. On this chromatogram, seven peaks can be seen. The isotopic ratio $^{120}Sn/^{118}Sn$ (=1.35) for each peak was verified and confirmed the presence of tin-containing compounds (31). Peak identification for lower boiling point compounds was first based on a comparison of the retention times obtained with the

CT-GC-ICP/MS system. Peaks corresponding to higher boiling points compounds underwent a complementary identification of retention time and detection using both CT-GC-ICP/MS and CGC-MIP/AED apparatus.

The peaks labeled from 1 to 5 (Figure 1) were accurately attributed to (1) stannane (H_4Sn), (2) tetramethyltin (Me_4Sn), (3) monobutyltin trihydride ($BuSnH_3$), (4) monobutyltrimethyltin ($BuSnMe_3$), and (5) dibutyltin dihydride (Bu_2SnH_2). Peaks 6 and 7 could not be identified by this approach, due to the large uncertainties of their retention time (RSD > 3%). The cryofocusing technique has low resolving separation capabilities for high boiling point compounds (31), and several organotin compounds could account for these peaks. Therefore, the same sediment sample was analyzed by CGC-MIP/AED; the chromatogram is shown in Figure 2. Only two peaks are present in both samples as a result of the poor recovery of light volatile species during the desorption step into the organic solvent. The spectral emission lines of these two peaks at 300.9 and 303.4 nm also confirmed the detection of tin-containing compounds. The precision of the retention
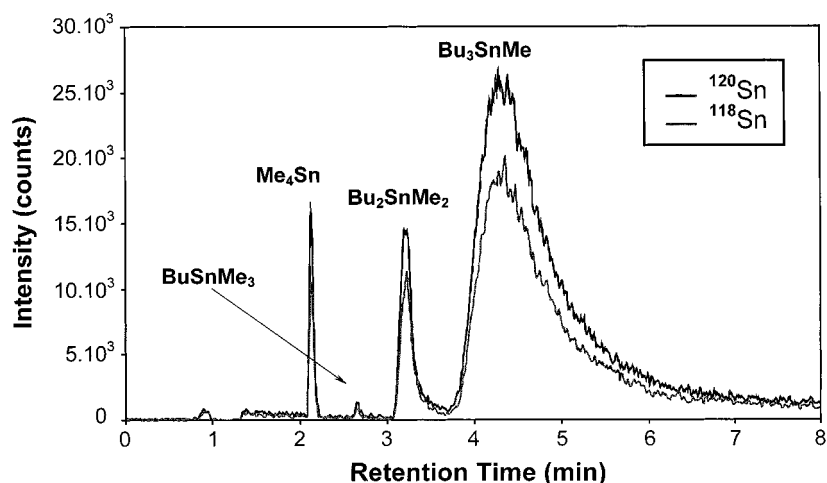
FIGURE 3. Typical chromatogram of volatile organotin compounds in surface water samples from the Scheldt estuary and obtained by purge, cryogenic trapping, gas chromatography, and ICP/MS detection (CT-GC-ICP/MS). Elution conditions have been slightly changed by using faster heating programs than use for Figure 1 to improve the chromatographic elution.

TABLE 1: Organotin Compounds, Total Organic Carbon (TOC), Total Sulfur (TS), and Water Content in Different Sediments, Collected from Arcachon Harbor and Scheldt Estuary

	type	Sn inorg[a] (ng/g dw)[b]	MBT (ng/g dw)	DBT (ng/g dw)	TBT (ng/g dw)	ΣSn (ng/g dw)	TOC (%)	TS (%)	water (%)
Arcachon harbor (April 1997)	silt	390	2460	530	600	3980	2.20	1.17	30
Arcachon harbor (April 1997)	sand	380	2720	2030	3340	8470	0.88	0.45	17
Scheldt estuary (May 1998)	silt	3	20	22	20	65	1.86	0.29	27
Scheldt estuary (May 1998)	sand	1	5	1	9	16	0.2	0.07	17

[a] Acid leachable inorganic tin. [b] Concentration in nanogram of tin per gram of sediment dry weight.

TABLE 2: Volatile Tin Compounds Concentrations in Two Different Types of Surface Sediments in Arcachon Harbor and Scheldt Estuary

		H_4Sn	Me_4Sn	$BuSnH_3$	$BuSnMe_3$	Bu_2SnH_2	Bu_2SnMe_2	Bu_3SnMe	TVT[a]
Arcachon harbor silt	Sn (pg/g dw)[b]	0.5	19.3	n.d.[e]	8.5	n.d.[e]	21.2	51.4	100.9
	TVT (%)[c]	0.5	19.1		8.4		21.0	50.9	100.0
	MR (%)[d]		0.0049		0.0003		0.0040	0.0086	0.0025
Arcachon harbor sand	Sn (pg/g dw)	n.d.[e]	10.0	0.1	24.9	0.4	19.1	38.1	92.6
	TVT (%)		10.8	0.1	26.9	0.4	20.6	41.1	100.0
	MR (%)		0.0026		0.0009		0.0009	0.0011	0.0011
Scheldt estuary silt	Sn (pg/g dw)	n.d.[e]	0.3	n.d.[e]	0.4	0.1	2.7	18.8	22.4
	TVT (%)		1.4		1.8	0.5	12.0	84.3	100.0
	MR (%)		0.0105		0.0020		0.0124	0.0938	0.0347
Scheldt estuary sand	Sn (pg/g dw)	n.d.[e]	0.5	n.d.[e]	0.02	0.1	0.6	13.6	14.9
	TVT (%)		3.6		0.1	0.8	3.9	91.5	100.0
	MR (%)		0.0871		0.0004		0.0584	0.1601	0.1012

[a] Total volatile tin. [b] Concentration in picogram of tin per gram of sediment dry weight. [c] $[Bu_nSnR_{4-n}]100/[TVT]$, R = Me or H. [d] Methylation ratio: $[Bu_nSnMe_{4-n}]100/[Bu_nSnX_{4-n}]$, $n = 0-3$. [e] Not detected.

time allows much better possibilities for the identification of high molecular weight organotin compounds (boiling point > 200 °C). The retention times obtained for peaks 6 and 7 corresponded exactly to Bu_2SnMe_2 and Bu_3SnMe species, respectively. Bu_3SnH could coelute with Bu_3SnMe in the samples investigated, but to date, except for extreme anoxic condition (26), methylation processes appear to override natural hydridization processes. The chromatographic peaks observed in sediments, corresponding to Me_4Sn, $BuSnMe_3$, Bu_2SnMe_2, and Bu_3SnMe, are present in most of the water samples collected. A typical sample chromatogram is shown in Figure 3.

Distribution of Volatile Tin Compounds in Coastal Sediments and Waters. Sediment. Total organotin concentrations and other characteristics have been determined in both Arcachon and Scheldt sediments as shown in Table 1. Arcachon sediments were found to be heavily contaminated

with butyltin compounds when compared to Scheldt estuary samples. This difference can be partially explained not only by the enrichment of Arcachon samples in organic carbon and sulfur but also by the fact that Arcachon sediments were collected in the vicinity of a shipyard. The average values obtained for volatile tin compounds in the sediments are presented in Table 2. Most of the seven compounds used in this study were identified in the contaminated sediments investigated. Methylated forms are the major contributors to the total volatile tin (TVT) content. The hydride forms are found to account for only a small fraction of TVT (0.5−0.8%) and will not be discussed further. All the samples analyzed contained concentrations of TVT ranging from 15 to 100 pg/g (125−840 fmol/g) of dry sediment (Table 2). Concentrations in sediments represent therefore a very small proportion of the total organotin concentrations measured in the same samples and are highly variable, ranging between 0.001 and

		n	Me_4Sn (fmol/L)[a]	$BuSnMe_3$ (fmol/L)	Bu_2SnMe_2 (fmol/L)	Bu_3SnMe (fmol/L)	TVT (fmol/L)
Arcachon harbor	(April 97)	2	32.4 ± 3.2	11.0 ± 1.1	12.4 ± 2.5	63.1 ± 12.6	118.9 ± 19.4
Scheldt estuary	(July 96)	21	18.2 ± 10.2	1.6 ± 2.4	53.1 ± 87.1	470.0 ± 302.9	542.9 ± 402.6
Scheldt estuary	(Dec 96)	15	19.6 ± 3.2	3.4 ± 2.5	45.5 ± 38.8	526.2 ± 422.2	594.7 ± 479.5
Gironde estuary	(Oct 96)	17	0.5 ± 1.1	0.1 ± 0.1	0.6 ± 1.1	28.6 ± 15.8	29.8 ± 18.1
Gironde estuary	(June 97)	15	n.d.[b]	n.d.[b]	n.d.[b]	4.3 ± 5.6	4.3 ± 5.6

[a] Concentration in femtomole of tin per liter of water. [b] Not detected. [c] Mean $\pm$ SD; n is the number of samples.
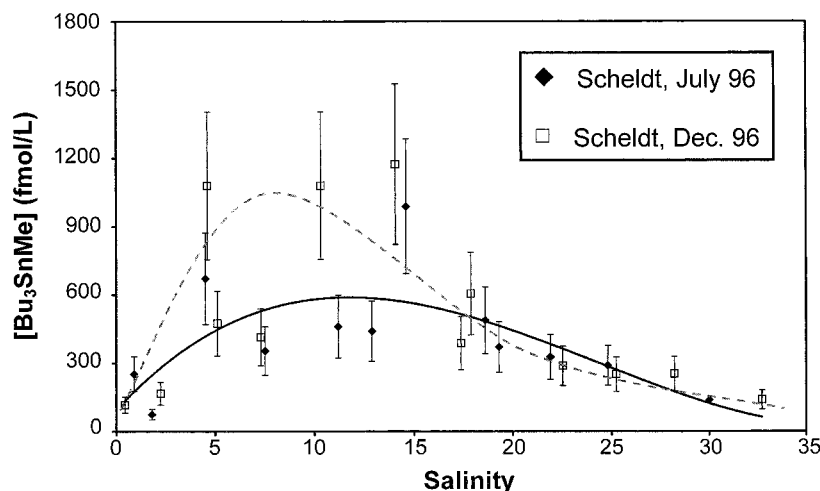

FIGURE 4. Distribution of tributylmethyltin (Bu₃MeSn) in surface waters of the Scheldt estuary as a function of salinity in July and December 1996. Error bars represent a relative standard deviation of 25% obtained from duplicate analysis.

0.003 to 0.03−0.1% dry weight in the Arcachon and Scheldt sediments, respectively (Table 2). The relative distribution of the volatile methylated tin species differs significantly between Arcachon and Scheldt samples. Bu_3SnMe represents 41−51% of the TVT in Arcachon sediments and up to 84−92% in Scheldt sediments (Table 2).

Water. The average concentrations of the volatile tin species in surface waters obtained from different sampling campaigns are presented in Table 3. Concentrations recorded range from nondetect to 600 fmol/L for TVT. These concentrations are very low and could only be detected due to the sensitivity of the analytical method. However, they clearly demonstrate that these compounds are ubiquitous in all of the areas studied. Average TVT concentrations in Arcachon surface waters are higher than in the Gironde estuary with 120 and 4 to 30 fmol/L, respectively. They are however much lower than in the Scheldt estuary, which ranges from 540 to 600 fmol/L. No significant variations could be observed between the seasonal cruises on both estuaries. The fact that TVT concentrations in the Scheldt estuary are 50−100 times higher than in the Gironde estuary was expected. Both estuarine systems have a similar water residence times (a few weeks to some months) but present contrasting contamination patterns (29, 30).

The ubiquitous and major species in all sample is Bu_3-$SnMe$. It represents 50−100% of the TVT concentration in the samples. The distribution of Bu_3SnMe for each cruise in both estuaries was plotted against salinity in Figures 4 and 5. Other volatile organotin compounds were present at much lower concentrations, and we could not find significant variability in either estuary. In both the Scheldt (Figure 4) and the Gironde (Figure 5) estuaries, the Bu_3SnMe concentrations present a similar distribution and exhibit a maximum between salinity 5 and 15 at ca. 1200 and 40 fmol/L, respectively. This nonconservative distribution with maximum concentrations at intermediate salinity demonstrates

that both estuaries are a continuous source of Bu_3SnMe to the water column. Below salinity 5, Bu_3SnMe concentrations decrease upstream but present significant concentrations in the river end-member of the Scheldt (100−250 fmol/L) and Gironde (10−20 fmol/L) estuaries. River inputs can thus partially contribute to the budget of volatile tin compounds in both estuaries. Above salinity 15, Bu_3SnMe concentrations decrease seaward following a pseudolinear dilution curve showing a marine end-member concentration around 100 fmol/L and below the detection limit for the Scheldt and the Gironde estuaries, respectively. A fraction of the volatile tin compounds released in the estuary can thus be transported to coastal waters. A budget for volatile organotin compounds in the investigated estuaries will be discussed in detail elsewhere by Tessier et al. (manuscript in preparation).

Formation of Volatile Organotin Compounds in Coastal Environments. Tetramethyltin and three methylated and volatile forms of butyltin compounds in sediment and water are reported here for the first time. These findings demonstrate that natural chemical or biological methylation processes do not only involve inorganic species but also anthropogenic butyltin compounds. In the investigated sediments, the apparent methylation yield can be derived from the concentration ratio or "methylation ratio" (MR), between each methylated volatile tin compound and a potential precursor which has the same number of butyl groups (Bu_nSn, $n = 0-3$). The MR presented in Table 2 suggest that the apparent methylation yield of tin compounds is generally higher in the Scheldt than in Arcachon sediments, with global values ranging from 0.001 to 0.003 and 0.035−0.100%, respectively. No significant trend was observed, however, between silt- and sand-type sediments in terms of volatile tin species distribution and for the MR. In each sediment, the MR for Bu_3SnMe is also generally higher than for the other tin species. These results indicate that the methylation of tributyltin is more efficient or that Bu_3SnMe
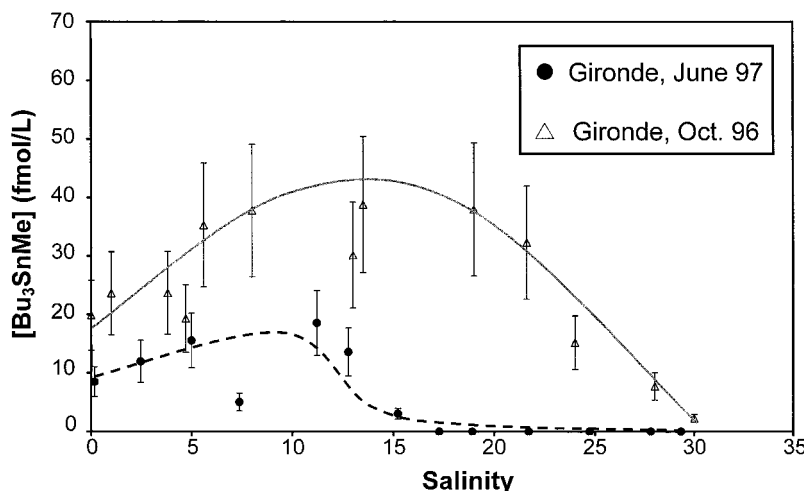
FIGURE 5. Distribution of tributylmethyltin (Bu₃MeSn) in surface waters of the Gironde estuary as a function of salinity in October 1996 and June 1997. Error bars represent a relative standard deviation of 25% obtained from duplicate analysis.

lifetime is longer than for other species for all type of sediments and contaminated sites. Moreover, previous investigations have demonstrated that trialkyltin species, such as trimethyltin, can be easily converted into tetramethyltin via chemical and biological pathways during incubations of natural sediments (18, 23).

For water samples, the correlation coefficients were calculated between the concentrations of Bu₃SnMe as a function of Bu₂SnMe₂ and Me₄Sn during the four cruises performed on the Gironde and Scheldt estuaries. The two regression lines obtained with both Bu₂SnMe₂ and Me₄Sn gave good correlation coefficients ($R^2 = 0.78$ and 0.72, respectively) and suggest that the occurrence of these compounds could be derived from the presence of Bu₃SnMe. The slopes of both regression curves indicate that Bu₃SnMe concentrations are about 6 and 12 times higher than Bu₂-SnMe₂ and Me₄Sn concentrations, respectively. This ratio is in agreement with the relative distribution of total and volatile tin compounds observed in the sediments collected in the Scheldt (see Tables 1 and 2). The relative distribution is also similar between the Arcachon surface waters and total and volatile butyltin compounds observed in the collected sediments (see Tables 1 and 2). This result suggests that the various butyltin and inorganic tin species present in sediments follow identical methylation pathways in anoxic sediments and diffuse into the water column with similar transfer rates.

The degradation of butyltin compounds via sequential losses of butyl groups is therefore not the only route for butyltin removal in coastal sediments. Tributyltin and its degradation products can be involved in biological and/or chemical methylation pathways which lead to fully volatile substituted organic tin species. Yozenawa et al. (16) demonstrated that such mixed methylbutyltin species could be produced under sulfate-reducing activity during incubations with spiked sediments in the laboratory. However, it is not clear whether this process is due to intracellular mechanisms or to the reductive chemical conditions generated in the medium. The reaction pathway could follow either a reductive or an oxidative route for methyl group transfer from a carbanion or a carbocation donor, respectively (21). This result allows us to propose some hypotheses for the processes regulating the transformation and the transfer of tin in the coastal environment. It also demonstrates the overlap and interaction of natural and anthropogenic tin biogeochemical cycles in these environments.

Figure 6 presents a model of organotin cycling in coastal environments developed from this work. It demonstrates

that volatile tin compounds occupy a central part of the chemical cycling of organotin compounds in estuarine and coastal environments. Butylmethyltin species result from both degradation of anthropogenic tributyltin biocide and natural methylation of tin species. Both processes contribute to the formation of volatile and mobile compounds. It is also reasonable that the formation of butylmethyltin species takes place when butyltin compounds disproportionate under reducing conditions in sediments. The relative distribution of the volatile organotin species in the different compartments also indicate that they can be transferred to the atmosphere under passive or turbulent diffusion processes.

Transfer of Volatile Organotin Compounds to the Atmosphere. A more detailed description of the saturation ratio and flux calculation method is found in the Supplementary Information. Prior to the determination of the transfer of volatile tin, the saturation ratio (SR) of these compounds must be determined by comparing their concentrations in sediment or water to water or atmosphere, respectively. At the sediment–water interface, the concentrations obtained by extracting the volatile compounds after stripping a sediment slurry may have led to an overestimate of the "real" porewater concentrations. This overestimation was assumed to be up to 10 times the "real" porewater concentration considering an identical dilution factor. For the water–atmosphere interface, the Henry's law constant for each volatile organotin compounds was required to calculate the SRs and was derived from literature data and molecular properties. If the SR is above 1, volatile compounds are then supersaturated in sediment or water and diffuse to the water or atmosphere, respectively. The different average SR, displayed in Table 4, demonstrate that volatile organotin compounds will systematically diffuse from surface sediment to the atmosphere.

Sediment to Water Fluxes. In a contaminated area such as the Arcachon harbor and the Scheldt estuary, total volatile tin compound concentrations in surface sediment per volume of pore water are from 80 to 30 000 times higher than in the overlying water. A simple modified diffusion model approach was used to evaluate fluxes of the compounds from surface sediments to the water column (35). For sediment to water exchanges, it was assumed that all volatile tin species were produced by chemical or biological mechanisms in bulk sediments and were passively released to pore waters. Volatile forms, extracted by stripping a sediment slurry, also strictly represent the water exchangeable fraction of the volatile tin compounds, which correspond to one to 10 times the "real" porewater concentrations. A large range of flux densities can
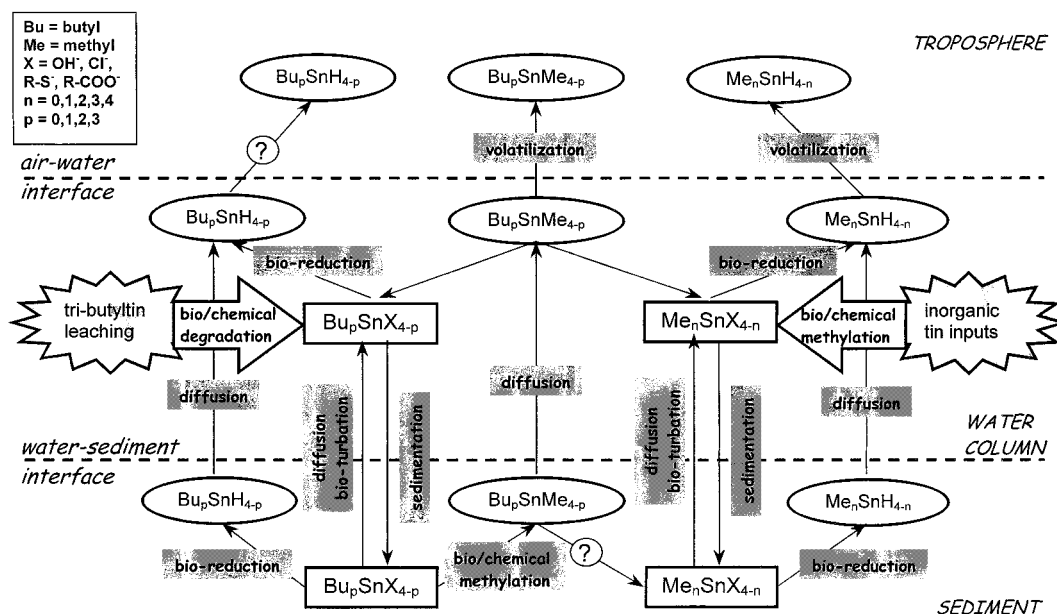
FIGURE 6. Schematic diagram of organotin compounds chemical cycling in coastal and estuarine environments.

TABLE 4: Average Calculated Sediment to Water and Water to Sediment Saturation Ratios and Flux Densities of Volatile Organotin Compounds in the Coastal and Estuarine Environments Investigated[c]

	saturation ratio				total volatile tin (TVT) flux density (nmol/m^2.yr)
	Me_4Sn	$BuSnMe_3$	Bu_2SnMe_2	Bu_3SnMe	
Sediment to Water[a]					
Arcachon harbor	850−8520	2860−28590	3060−30600	1340−13360	50−470
Scheldt estuary	80−790	200−2010	90−880	100−1010	80−790
Water to Air[b]					
Arcachon harbor	22810	16080	9730	49520	90
Scheldt estuary	9190	3120	25660	262250	510
Gironde estuary	30	550	1180	13680	20

[a] SR sediment−water: $[Bu_nSnMe_{4-n}]_{pore\,water}/[Bu_nSnMe_{4-n}]_{water}$, $n = 0−3$, flux model adapted from ref 35. [b] SR water−air: $[Bu_nSnMe_{4-n}]_{water} \times H/[Bu_nSnMe_{4-n}]_{air}$, $n = 0−3$, flux model adapted from ref 36. [c] Methods and calculations are described in detail in the Supporting Information. The range obtained at the sediment−water interface corresponds to the potential overestimate in the porewater concentrations ("real") considering water exchangeable concentrations ("measured") to be 1−10 times higher.

be obtained but, by taking into account the hydrodynamic characteristic of the sites investigated, a better estimate can be determined. The Arcachon harbor is a tidal bay with low turbulent mixing, suggesting that mainly bioturbation will enhance sediment−water exchanges (37). On the other hand, the Scheldt estuary is a macrotidal channel with high turbulent mixing, where sediment resuspension and tidal current friction can strongly enhance the sediment−water exchanges (35). Flux calculations of the total volatile tin compounds at the sediment−water interfaces in the Arcachon harbor and Scheldt estuary are presented in Table 4. In Arcachon harbor, calculated flux densities range from 50 to 470 nmol/m^2.yr, considering low turbulent mixing. In the Scheldt estuary, flux densities obtained are higher and range from 80 to 790 nmol/m^2.yr, considering high turbulent mixing.

Water to Air Fluxes. During the two first cruises on the Gironde and the Scheldt, atmospheric samples were collected (34). Only Me$_4$Sn was detected (detection limit ca. 20 fmol/m^3) in a few samples, demonstrating that total volatile tin compounds were supersaturated in surface waters. To obtain accurate flux estimations, transfer velocities at the air−water interface were calculated using a model developed in an estuarine tidal environment (36). The turbulence at the interface is mainly driven by the wind speed in aquatic ecosystems, and it is difficult to predict average flux densities over a period of time within the range evaluated (35, 36).

However, in turbulent systems, due to high tidal current velocity, such as the Scheldt and the Gironde estuaries, wind speed has a less dominant influence and measured transfer velocities are generally high in any conditions (38). Atmospheric fluxes calculated for the different surface water samples collected in the Arcachon harbor and the Scheldt and Gironde estuaries are displayed in Table 4. The previous assumption led to TVT water to air fluxes at about 510 and 20 nmol/m^2.yr for the Scheldt and the Gironde estuaries, respectively, and 90 nmol/m^2.yr in the Arcachon harbor.

Mass Balance of Volatile Organotin Compounds in the Water Column. The TVT fluxes obtained in this work may allow the determination of the contribution of volatile organotin transfer to the total organotin budget in the respective environments (Arcachon, Scheldt). Such estimation remain very complex in the case of the Scheldt estuary and will be discussed elsewhere (Tessier et al., in preparation). For the Arcachon harbor, a large fraction of the TVT present in the sediment can reach the atmosphere. An average TVT flux of 10 g Sn/yr is emitted into the water column, from which about 50% enters the atmosphere. For a standing inventory of butyltin compounds in surface sediments, estimated to range from 1 to 10 kg as Sn (13−15), such a process would then require 100−1000 years to remove this toxic substances from the harbor sediments.

These results have further global implications for the fate of organotin compounds trapped in sediments. In turbulent

systems such as estuaries, diffusion processes of volatile organotin species to the water column and to the atmosphere may be a significant pathway to efficiently remove organotin compounds from coastal environments. Sediments have long been considered to be a sink for these highly toxic constituents. In the case of minimal external inputs resulting from increasingly efficient regulation, sediments should now be considered as a significant source of organotin compounds to overlying waters and a potential source to the atmosphere.

Acknowledgments

Supporting Information Available

Flux calculation methods for volatile organotin species at the water−air and sediment−water interface. This material is available free of charge via the Internet at http://pubs.acs.org.

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