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Volatile organotin compounds (butylmethyltin) in three European estuaries (Gironde, Rhine, Scheldt)

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Abstract. The occurrence of volatile organometallic species of tin was evidenced and investigated in three major European estuaries, such as the Gironde (F), the Rhine (NL) and the Scheldt (B/NL), along with the salinity gradient and for all seasons. The most ubiquitous species, observed in surface water, were found to be methylated forms of butyl-tin derivatives (Bu_nSnMe_{4-n}, n = 0–3), with concentrations significantly higher in the Scheldt (ca. 75–2000 fmol l^{-1}) than in the Rhine (ca. 5–125 fmol l^{-1}) and the Gironde (ca. 5–90 fmol l^{-1}). Additionally, estuarine anoxic sediments were found to contain large amount of such volatile tin species.

The presence of volatile organic tin compounds is then supposed to result from natural methylation processes of both inorganic metal and anthropogenic derivatives accumulated in the sediments (i.e. tributyltin released from ship antifouling paintings and waste water discharges). These results suggest that microbial mediated and/or chemical methylation mechanisms are likely to produce volatile organotin species in anoxic estuarine environments. The production of volatile organotin species is also mainly dependent on the direct anthropogenic load of butyltin compounds within the estuary and on the residence time of such compounds in the system. Estuarine profiles along with the salinity gradient demonstrate that all investigated estuaries are continuous sources of volatile tin species, although these estuaries present different anthropogenic organotin discharges. In consequence, significant export of volatile tin species to the adjacent coastal waters were found. Finally, the evaluation of the seasonal fluxes of volatile tin species to the atmosphere establishes that volatilisation is a major sink for such compound in estuaries with long water residence time (i.e. Scheldt, Gironde).

Introduction

The contamination of aquatic environments by organotin compounds (OTs) over the last three decades has led to consider these species as 'global pollutants' (Maguire et al. 1986; Chau et al. 1997). Triorganotin (TOTs) compounds and more specifically tributyltin (TBT), widely used as biocides, are directly introduced into aquatic systems from the leaching of antifouling paints (Hugget et al. 1992; Quevauvillier & Donard 1996). Further, many other anthropogenic tin derivatives, extensively used in industrial processes, can significantly contribute to the contamination of natural waters via waste water and sewage sludge rejections (Carlier-Pinasseau, 1996).

Despite of the fact that the OTs concentrations in marine environments have decreased significantly during the last decade, as a result of their ban in the early nineties, their accumulation and fate in the sediments still remain a most critical issue for current and future risk assessment. Important sediment resuspension through large natural or anthropogenic physical perturbations (e.g. bioturbation, tide, storms, dredging activities) will directly results in desorption of the OTs and their remobilization to the overlaying water column (Berg et al. 2001). At present, we can consider that OTs are ubiquitous in all compartments of the environment and certainly originate from various and new sources especially in fresh water media (Donard et al. 2001).

As a result, the fate of OTs in estuarine systems is of major concern due to their impact on this specific environment (Donard & Weber 1985; Quevauvillier & Donard 1990). Estuaries are indeed important pathways for the transfer of dissolved and particulate material from the continent to the marine ecosystem. They are mostly highly dynamic systems characterised by the presence of strong physico-chemical gradients. They most often see high biological activity and are areas of strong sedimentological turn over via intense sedimentation and resuspension processes. In this highly variable environments, the transformation of OTs and production of volatile metabolites can occur via different chemical and biological mechanisms (Weber 1999). The chemical fate of these species is usually associated with that of the fine fraction (<63 μm) of the sediment (Maguire et al. 1986; Quevauvillier et al. 1990).

The strong physicochemical gradients and high biological turn over of these environments results in competition of natural dealkylation and methylation processes affecting the fate and behaviour of these species (Maguire & Tkacz 1985; Aldeman et al. 1990; Yozenawa et al. 1994). Laboratory studies have demonstrated the occurrence of methyltin derivatives in the aquatic environments and the potential biomethylation of both inorganic and organic tin by sulphate reducing bacteria in sediments (Gilmour et al. 1985; Yozenawa et al. 1994). Different natural methyl donor species, such as iodomethane, methyl-cobalamine or humic substances are also able to methylate tin compounds to yield to mono-, di-, tri- and tetramethyltin (Weber 1999). Such natural derivatization pathways could result in the formation of fully substituted and volatile tin compounds in the aquatic environment.

Tin hydride (H_4Sn) and methyltin hydrides (Me_nSnH_{4-n}; $n = 0–4$) have been indeed detected in algae or microalgae cultures (Jackson et al. 1982; Donard & Weber 1988; Weber 1999). These hydride species were suspected to be formed biologically and are likely to occur naturally in the environment. Craig and Rapsomanikis (1985) 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 sediments have also been reported by Maguire et al. (1984, 1986). Recently, Amouroux et al. (2000) have demonstrated the ubiquitous occurrence of such mixed butylmethyltin compounds (Bu_nSnMe_{4-n}; $n = 1–3$) in estuarine and coastal sediments, waters and atmosphere at femtomole per liter levels. These results indicate that natural alkylation processes can also affect anthropogenic tin derivatives and result in the formation of volatile tin compounds. These fully substituted species are then likely to see significant exchanges between the different environmental compartments such as sediment, water, air and in biota.

In this work, the occurrence of volatile tin compounds, their distribution and their potential sources were investigated in three macrotidal European estuaries. Concentrations profiles along with the salinity gradient were used to apply a simple mixing model to evaluate the biogeochemical fluxes of these volatile tin species in the investigated estuaries. Air-water exchange rates of the volatile tin species were also calculated in order to investigate the significance of their atmospheric fluxes versus their estuarine export to adjacent coastal waters.

Materials and methods

Sampling sites and procedures

Sediment, water and atmospheric samples were collected on board the research vessels *Belgica* (SPPS/FN), *Côte d'Aquitaine* (CNRS/INSU) and *Navicula* (NIOZ), during the EU BIOGEST project cruises on the Gironde (Oct. 1996, June and Sept. 1997, Feb. 1998), the Rhine (Oct. 1996, July and Nov. 1997, March 1998) and the Scheldt (July 1996, Dec. 1997, May and Oct. 1998) estuaries together with the hydrological parameters. These three estuaries are macrotidal systems with very different anthropogenic pressure (Wollast 1988; Kramer & Duinker 1988; IFREMER 1994). The Scheldt and the Rhine estuaries host some of the largest harbours and industrial complexes of Europe and are surrounded by a high population density (Wollast 1988; Kramer & Duinker 1988). On the contrary, most of shipping and industrial activities taking place in the Gironde estuary have stopped more than 10 years ago. The density of population along its banks is also much lower. It is therefore considered to be one of the few large pristine estuarine area of Europe (IFREMER 1994). The hydrodynamic characteristics, biogeochemical properties and OT loads of the estuarine systems studied are displayed in Table 1.

Sediments

Sediments were collected using a box corer in the navigation channel of the Scheldt and the Gironde estuary. Sandy and muddy sediments were sampled in the top 5 cm using a polyethylene cup and were immediately transferred to a gas-tight glass vial (100 ml) without any headspace. The vials were then stored in dark refrigeration at 4 °C and processed on board within less than 2 hours. The water content were respectively about 30% and 15% for the muddy and sandy samples. A vertical fluid mud profile was also performed in the Maximum Turbidity Zone (MTZ) of the Gironde estuary in June 1997, using a specific sampler with a 20-cm vertical resolution. The detailed fluid mud sampling procedure are described elsewhere (Tseng et al. 2001).

Water samples

Surface water samples for each estuary were collected for every 2.5 increase of salinity unit with a total span ranging between 0 and 34 (Practical Salinity Scale, International System of Units). Surface waters were sampled at 3m depth with a PTFE coated Go-Flo non metallic sampler (General Oceanic, U.S.A.) to avoid ship and microlayer surface water contamination. After sampling, the collected water was immediately transferred through a silicone tubing into a gas tight PTFE lined 1 l Pyrex bottle until later ship-board treatment.

Air samples

Air sampling was performed all along the investigated estuaries during the first cruises, using a laboratory-made gas sampler developed by Pécheyran et al. (1998b). Air was pumped upwind from the ship for $^1/_2$ hour at c.a. 800 ml min^{-1} from the top or the bow of the ship to avoid potential contamination from engine exhausts.

Table 1. Hydrodynamic characteristics and biogeochemical properties of the West European estuaries investigated

Characteristics		Gironde	Rhine	Scheldt
Location		SW France (Gulf of Biscay)	SW The Netherlands (North sea)	SW The Netherlands/W Belgium (North sea)
Type		Salt wedge to partially mixed	Modified by human impact	Partially to well mixed
Length (km)		70	30–40	160
Surface (km^2)		600	100	300
Residence time of water/particle		1–3 months/years	Days/days	1–3 months/years
Mean Water temperature (°C)[a]		7–25	7–20	6–20
Oxygen saturation range (%)		60–103	80–110	2–98
DOC(μM C)		159 (116–214)[b]	194 (122–342)	404 (92–857)
POC (%)		1.5 (0.7–7.5)	4.3 (0.5–12.1)	5.0 (1.3–12.3)
Mean seasonal Discharge (m^3/s)	Winter	1164	1068	96
	Spring	506	1714	73
	Summer	498	2756	35
	Fall	288	1468	50
Tidal range (m)		2–5	2–3	2–5
SPM range (mg l^{-1})		280 (14–1700)	16 (2–30)	50 (7–141)
TBT (ng Sn g^{-1})	Sediment	–	109–172[c]	67–168[c]
TBT (ng Sn l^{-1})	Water	nd–16[d]	150[d]	51 ± 48[e]

[a] average value and level ranges of parameters listed according to the investigated cruises from 1996 to 1998.
[b] The average concentration shown by the mean value and concentration range listed in parenthesis.
[c] Qeuvauvllier et al. 1991; [d] Quevauvillier & Donard 1990; [e] Ritsema et al. 1998.
nd, not detected.

Extraction and cryogenic trapping of volatile tin compounds

Sediments

Volatile tin compounds were extracted from the sediments and fluid mud collected using a purge and cryogenic trap set-up described elsewhere (Amouroux et al. 2000). About 10 g of fresh sediment was transferred in a 50 mL purge vessel made of glass with 20 ml of pre-purged milli-Q water (under He flow, 10 minutes at 300 ml min^{-1}). The suspension formed was continuously homogenized with a Teflon magnetic stirrer. The gaseous species were stripped out of the vessel and dried by carrying the gas stream through a moisture trap maintained at –20 °C (mixture of ice and acetone), finally cryofocused in a silanized U-shaped glass trap filled with acid-cleaned silanized glass wool (Supelco) and immersed in liquid nitrogen (–196 °C). Most of the volatile tin compounds extracted from the samples can therefore be concentrated and stabilised in the cryogenic trap. After 30 minutes of purge, the cryotraps were closed with gas tight 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 for quantitative recovery (Amouroux et al. 1998).

Water samples

The purge and cryogenic trapping device developed and optimized for the extraction of volatile metal compounds from water samples is described in detail elsewhere (Amouroux et al. 1998; Pécheyran et al. 1998a). Within less than 30 minutes after sampling, the water collected was directly transferred from its 1 l Pyrex bottle to a 1.5 l purging vessel under He atmosphere. The water samples were continuously stripped for 1 hour with an He flow rate at 700 ml min^{-1}. The volatile compounds were then cryocondensed and stored following the same procedure described above for the sediments.

Air samples

The aerosols and water vapour were removed from the air sample pumped using on-line 0.1 μm quartz filter (Millipore) and moisture trap (–20 °C), respectively. The volatile tin species are cryofocused on-line onto a silanised glass tube packed with silanized glass wool and maintained at –170 °C (Pécheyran et al. 1998b). The cryotraps were closed tightly with Teflon caps and stored in liquid N_2 until analysis as described above.

Standards and reagents

All connections and tubing in contact with the samples were made of Teflon PTFE and PFA. All glass- and plastic-ware 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 pure analytical grade chemicals, unless otherwise stated. Isooctane (FLUKA, 99.8%), methanol (FLUKA, 99.8%), acetic acid (Merck, 100%), sodium tetraethylborate ($NaBEt_4$, Aldrich, 99%), ammonium and acetate buffer solution (Merck) were used for the derivatization reactions and the preparation of the standard compound solutions. Pure tetramethyl-tin (STREM, 99%), tetraethyl-tin (STREM, 99%), tripropyl-tin chloride and butyl-tin chloride species (Bu_nSnCl_{4-n}, $0 \leq n \leq 4$, STREM, 99%) were used as standard compounds for calibration and identification.

Determination of organotin compounds

The standard settings and methodologies used for both the GC-ICP/MS and CGC-ICP/MS are discussed in detail by Pécheyran et al. (1998b) and Rodriguez et al. (1999), respectively. These techniques present two different chromatographic resolutions with the same detection device. The approach was used to determine non volatile organotin compounds accumulated in sediments and fluid mud.

Cryogenic Trapping-Gas Chromatography-Inductively Coupled Mass Spectrometry (CT-GC-ICP/MS)

Most of the analytical setup and methodology are discussed in detail elsewhere (Amouroux et al. 1998; Pécheyran et al. 1998b). For most of the samples analyzed, we used a direct injection of the cryotraps and standards solutions into the cryotrapping – gas chromatography and ICP/MS (Elan 5000/6000, Perkin-Elmer) system (Amouroux et al. 1998). The high sensitivity and selectivity of the ICP/MS detector coupled to the cryofocusing technique allows to yield method detection limits (DL) below 1 fmol l^{-1} for tin in water samples. The identification of the volatile tin compounds observed in sediment, water and air samples is discussed in detail elsewhere by Amouroux et al. (2000) and Pécheyran et al. (1998b). Tetramethyltin (Me_4Sn), trimethylbutyltin ($BuSnMe_3$), dimethyldibutyltin (Bu_2SnMe_2) and methyltributyltin (Bu_3SnMe) were the major species identified. Hydride forms of butyltin compounds ($BuSnH_3$ and Bu_2SnH_2) were also observed by

Amouroux et al. (2000) in some of the samples. These species only account for a small fraction of the total volatile tin species and will not be further discussed in this paper. The purge and cryogenic trapping method, used for this work allowed to perform a physical trapping of all the gaseous tin species present in the sample. The volatile tin compounds trapped and identified can then be defined as the Total Volatile Tin fraction (TVT: total sum of tetramethyltin and methyl-butyltin compounds, Bu_nSnMe_{4-n}, $n = 0, \ldots, 3$)).

Ethylation-Capillary Gas Chromatography- Inductively Coupled Mass Spectrometry (Et-CGC-ICP/MS)

To evaluate the contamination level by total organotin compounds in the sediments of the investigated areas, a second analytical technique was used. The different steps of this analytical procedure are detailed elsewhere (Rodriguez et al. 1999). The analytes are first extracted from the natural matrix and then derivatized using a $NaBEt_4$ solution, prior to the separation by capillary gas chromatography, which allows a high separation efficiency. Finally, the detection by ICP/MS (HP 4500, Yokogawa) offers high sensitivity with a method detection limit below 1 ng g^{-1} for tin in sediments.

Results

Distribution of volatile tin compounds in the different estuarine environments

Sediments

Total organotin concentrations have been determined in both Scheldt and Gironde sediments. The Scheldt sediments were found to be more contaminated by butyltin compounds than in the Gironde with total butyltin concentrations (i.e. total sum of mono- di- and tributyltin concentrations) averaging 38 ng Sn g^{-1} and 12 ng Sn g^{-1} (dry weight), respectively. In a pristine area such as the Gironde estuary, the major organotin compound observed in the sediments was the monobutyltin (MBT, 8.0 ± 0.4 ng g^{-1} dry weight) suggesting the efficient degradation of the TBT stored in these sediments, in dibutyltin (DBT) and then MBT. On the other hand, the distribution of the tin species, in the sediments of the Scheldt (Antwerpen Harbour) is characterised by significant amounts of TBT, DBT and MBT with values ranging around 20.2 ± 0.3, 21.7 ± 1.5, 19.7 ± 1.5 ng g^{-1} dry weight respectively. The occurrence of butylated tin compounds mainly originating from ship antifouling paints and industrial effluents (De Mora & Phillips 1997; Bueno 1999) seems then directly related to the anthropogenic load of the investigated area. These values are in the same range than those reported by Ritsema et al. (1998) for the Scheldt estuary.

Table 2. Average volatile organotin compounds concentrations in estuarine sediments

Estuary	*n*	Me_4Sn	$BuSnMe_3$	Bu_2SnMe_2	Bu_3SnMe
		pg g^{-1} dw			
Gironde					
muddy	6	n.d.	n.d.	n.d.	0.005 ± 0.002
Scheldt					
Sandy	3	0.1–23.3	0.1–59.8	0.6–45.2	13.6–58.8
muddy	3	0.1–4.3	0.1–2.5	0.8–9.2	14.4–79.8

n.d. not detected.

The average concentrations obtained for volatile tin compounds in both sediments and fluid mud are presented in Table 2. The concentrations measured were also found to be higher in the Scheldt compared to the results of the Gironde estuary. For the volatile tin content, the methylated forms of butyltin compounds are the major contributors to the total fraction determined. TVT concentrations ranged from 15 to 188 pg g^{-1} and from not detected to 8 fg g^{-1} of dry weight in the Scheldt sediments and the Gironde fluid mud profile respectively. Bu_3SnMe was only observed in the fluid mud profile, with higher values in the bottom of the sampling core. Volatile tin compounds account, nevertheless for only a very small proportion of the total butyltin concentrations recorded in the same samples (c.a. 0.2% and 0.00004% for the Scheldt and the Gironde, respectively).

Water & air samples

The average concentrations of the volatile tin species in estuarine surface waters and their seasonal variations are presented in Table 3. The average TVT concentrations are much higher in the Scheldt than in the Rhine and the Gironde and range respectively from 443 to 1120 fmol l^{-1}, 28 to 71 fmol l^{-1} and 11 to 49 fmol l^{-1}. No significant seasonal trend was observed between the different cruises on the different estuaries. This distribution of TVT concentrations between the three estuaries was expected. Both the Scheldt and Rhine estuaries receive similar organotin contamination loads (Table 1) but the Rhine presents a very different hydrodynamic regime with high river discharge and hence short water residence time (few days). Therefore, the concentrations observed in the water of the Rhine were found to be in the same range than in the Gironde estuary, despite of the fact that this last hydrodynamic system is potentially less exposed to contamination sources. On the contrary, the hydrodynamic regime of the Scheldt and the Gironde estuaries

Table 3. Average volatile tin compounds concentrations in water along European estuaries

Estuary	*n*	Me_4Sn fmol l^{-1}	Range	$BuSnMe_3$ fmol l^{-1}	Range	Bu_2SnMe_2 fmol l^{-1}	Range	Bu_3SnMe fmol l^{-1}	Range	TVT fmol l^{-1}	Range
Scheldt											
Dec. 1996	*13*	**20**	1–50	**3**	< DL[a]–6	**32**	5–81	**495**	117–1174	**550**	131–1262
May 1998	*12*	**90**	19–140	**7**	2–17	**43**	2–28	**843**	254–1983	**983**	307–2214
July 1996	*14*	**19**	7–28	**3**	1–5	**16**	4–61	**405**	75–989	**443**	80–1074
Oct. 1998	*15*	**67**	1–145	**12**	2–31	**90**	19–141	**951**	88–2162	**1120**	190–2416
Gironde											
Feb. 1998	*12*	**2**	2–4	n.d.		n.d.		**36**	13–48	**38**	2–76
June 1997	*7*	n.d.		n.d.		n.d.		**11**	3–19	**11**	3–19
Sept. 1997	*11*	**3**	2–5	**5**	2–7	n.d.		**41**	10–87	**49**	10–90
Oct. 1996	*17*	**1**	< DL–4	n.d.		**1**	1–2	**26**	2–50	**28**	3–53
Rhine											
Nov. 1997	*15*	**3**	1–7	**1**	1–2	**2**	< DL–5	**38**	5–67	**44**	5–65
March 1998	*13*	**5**	2–11	**2**	1–4	**3**	1–5	**61**	22–125	**71**	24–133
Oct. 1996	*9*	**1**	1–2	**1**	< DL–1	**1**	< DL–2	**25**	8–45	**28**	8–50

[a] DL: 0.4 fmol l^{-1} (Amouroux et al. 1998); nd, not detected.

present similar characteristics with long water and particle residence times, which certainly favour the production of volatile tin species via methylation pathways. Nevertheless, due to the high industrialisation and urbanisation of the Scheldt watershed, TVT water concentrations were found more than ten times higher in the Scheldt estuary than in the Gironde. Moreover, these volatile tin species are ubiquitous in all areas studied, even in a pristine estuarine system such as the Gironde.

In the atmosphere above, volatile organotin compounds were determined for at least two season in each estuaries. Only Me_4Sn was detectable in overlying atmosphere of the Scheldt, the Gironde and the Rhine estuaries with concentrations ranging between 1 pg m^{-3} and 20 pg m^{-3}. This result demonstrates however that a net transfer of the volatile organotin species to the atmosphere can be observed, at least for the most volatile and probably most stable compounds. This is also a second confirmation of the occurrence of volatile organotin compounds in the natural atmosphere, after the observations made by Pécheyran et al (1998b) in the Gironde estuary.

Distribution of volatile tin compounds in surface waters along the salinity gradient

Bu_3SnMe was found to be the major species for volatile tin in all water samples. This ubiquitous compound represents up to 85% of the TVT concentrations. The distribution of Bu_3SnMe for both winter and spring cruises in the Scheldt and Rhine estuaries and winter and summer cruises in the Gironde estuary was plotted against salinity in Figures 1, 2 and 3. The Bu_3SnMe distribution in all seasons displays the same pattern, for the Scheldt and Rhine estuaries, with concentration maxima between salinity 5 and 20 which then decrease at both end-members of the system (lowest and highest salinity). In the Gironde estuary, the Bu_3SnMe concentrations also decrease seaward but without significant trend. Indeed, no significant concentration maxima could be observed in the upper and middle estuary.

These non-conservative distributions demonstrate that volatile organotin compounds are produced and released in the estuary within the intermediate salinity range at the estuarine maximum turbidity zone (MTZ). Below salinity 5, the Bu_3SnMe concentrations decrease upstream but exhibit significant values in the river end-member of the Scheldt (100–300 fmol l^{-1}), the Rhine (5–25 fmol l^{-1}) and the Gironde (10–20 fmol l^{-1}) estuaries. For salinity levels higher than 20, the Bu_3SnMe concentrations decrease seaward following traditional estuarine mixing processes. The average downstream concentrations of Bu_3SnMe (marine end-member) are approximately 180 fmol l^{-1}, 10 fmol l^{-1} for the Scheldt and the Rhine, respectively, and below the detection limit for the Gironde. The high SPM load measured in the Gironde and tidal

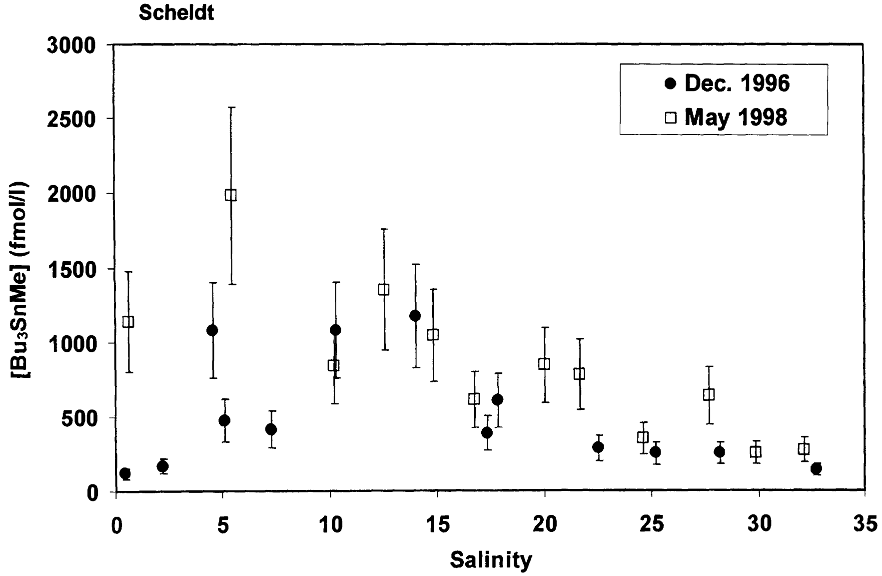

Figure 1. Distribution of tributylmethyltin (Bu_3SnMe) in surface waters of the Scheldt estuary as a function of salinity in December 1996 and May 1998. Error bars represent a relative standard deviation of 25% obtained from duplicate analysis.

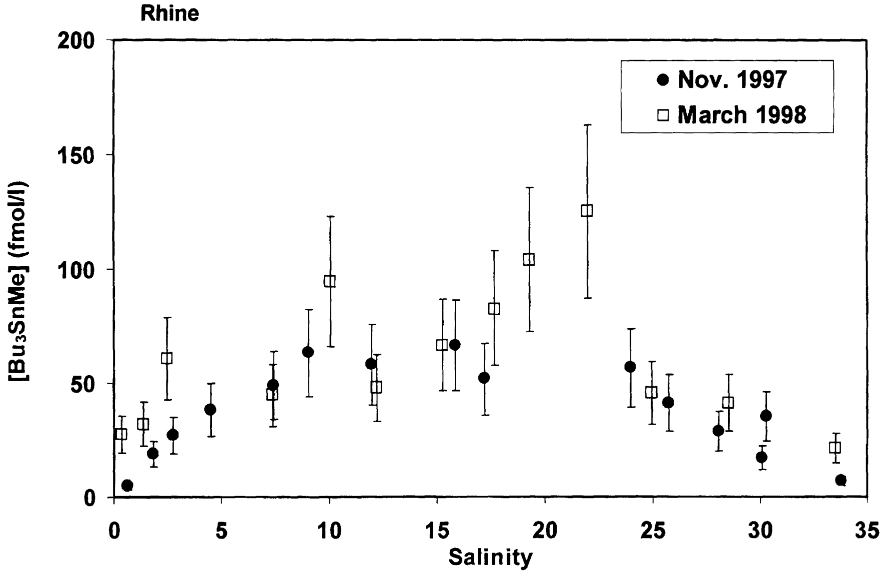

Figure 2. Distribution of tributylmethyltin (Bu_3SnMe) in surface waters of the Rhine estuary as a function of salinity in November 1997 and March 1998. Error bars represent a relative standard deviation of 25% obtained from duplicate analysis.

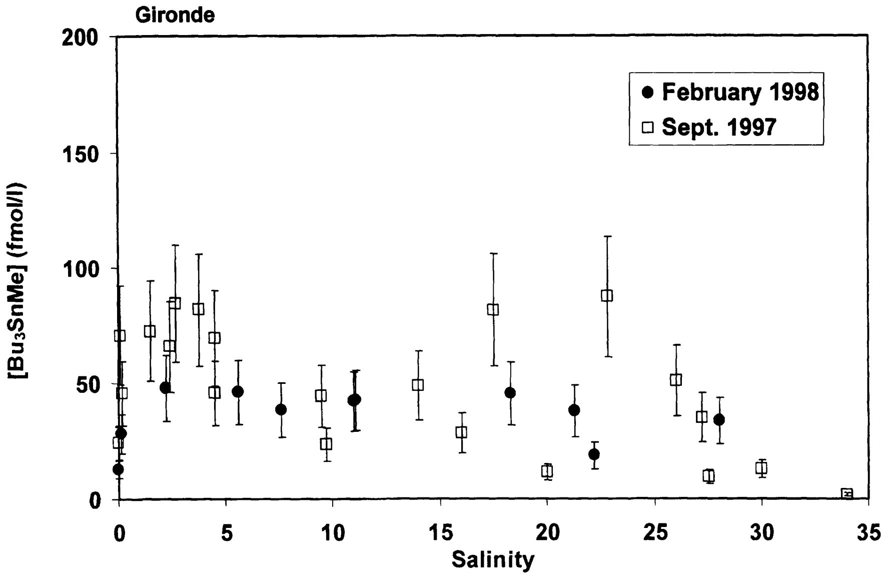

Figure 3. Distribution of tributylmethyltin (Bu_3SnMe) in surface waters of the Gironde estuary as a function of salinity in September 1997 and February 1998. Error bars represent a relative standard deviation of 25% obtained from duplicate analysis.

cycling could interfere in the Bu_3SnMe distribution in the water column, by trapping and releasing successively volatile organotin compounds (Tseng et al. 2001). A fraction of the volatile tin compounds produced and released in the estuary can then be transported to coastal waters and also be transferred to the atmosphere.

Discussion

Sources and formation of volatile tin compounds in estuarine environments

Formation of volatile tin compounds in estuarine environments
Tetramethyltin and three methylated and volatile forms of butyltin compounds were observed in both sediment and water column, with high concentrations in the underlying sediments. These results suggest that the volatile tin species can be produced in anoxic sediments from previously accumulated organotins and then passively diffuse to the water column (Amouroux et al. 2000). The presence of these species demonstrates that natural chemical or biological methylation processes do not only involve inorganic tin but also anthropogenic butyltin derivatives released in estuarine environments mainly by ship antifouling paintings and other urban and

industrial wastes (Carlier-Pinasseau 1996; Bueno 1999; Donard et al. 2001). Indeed, the methylation of trialkyltin species via chemical or biological pathways has been demonstrated during incubations of natural sediments (Guard et al. 1981; Craig et al. 1984). Yozenawa et al. (1994) also evidenced that such mixed methylbutyltin compounds could be produced under sulphate-reducing activity in incubated sediments. Therefore these mixed species could result from the degradation of anthropogenic tributyltin compounds via successive losses of butyl group in the sediment. Its degradation products can then be involved in biological and/or chemical methylation mechanisms (Amouroux et al. 2000).

The relative distribution of the volatile tin compounds observed in estuarine environments could then be derived from the presence of Bu_3SnMe. In the Rhine estuary, the extremely short residence time of the water and particles generates a conservative estuarine mixing of chemicals (i.e. dilution). Significant correlation concentrations were therefore found between the different volatile species (c.a. Me_4Sn vs Bu_3SnMe: $R^2 = 0.62$; $BuSnMe_3$ vs Bu_3SnMe: $R^2 = 0.58$ and Bu_2SnMe_2 vs Bu_3SnMe: $R^2 = 0.54$). In more complex estuarine systems, with a long water and particles residence time such as the Scheldt and the Gironde, the same trend was observed, but was not statistically significant.

Significant correlation between the average Bu_3SnMe concentrations and several biogeochemical parameters were also found and are presented in Table 1. The Bu_3SnMe average concentrations were found to be anti correlated with the oxygen saturation ($R^2 = -0.76$) and correlated with particulate organic carbon ($R^2 = 0.53$), CO_2 partial pressure ($R^2 = 0.87$) and phaeopigments concentrations ($R^2 = 0.88$). These correlation suggest that the formation or the distribution of volatile tin compounds is potentially linked to the biogeochemistry of carbon in the estuary (e.g. respiration and/or degradation) and to the related microbial activities. Inputs of fresh organic carbon from the river and the watershed contribute to the heterotrophy of the estuarine system. Organic matter oxidation occurring in the MTZ leads then to reducing conditions in the surface sediments and in the water column which in turn enhance chemical and microbial mediated methylation mechanisms.

Riverine inputs and production of volatile tin compounds

In order to discuss the nature of the biogeochemical processes taking place in the the estuarine Bu_3SnMe profiles, presented in Figures 1–3, a simple direct estuarine mixing model has been applied to the concentrations obtained on the three estuaries. This approach allows us to determine the apparent production and/or consumption of dissolved Bu_3SnMe within the estuary. These calculations were performed assuming that the estuarine system is

Table 4. Seasonal river and estuarine Bu_3SnMe fluxes

Estuary	F_{River} mmol d^{-1}	$F_{Estuary}$ mmol d^{-1}	$F_{Estuary} - F_{River}$ mmol d^{-1}	$F_{Volatilisation}$ mmol d^{-1}
Scheldt				
Dec. 1996	0.4	5.0	4.6	143.2
May 1998	6.5	10.9	4.4	240.3
July 1996	0.6	2.8	2.2	170.6
Oct. 1998	0.6	16.9	16.3	305.5
Gironde				
Feb. 1998	2.0	5.7	3.7	15.7
Sept. 1997	1.9	7.1	5.2	29.0
Oct. 1996	0.5	1.6	1.1	37.9
Rhine				
Nov. 1997	0.6	15.2	14.6	14.9
March 1998	4.4	18.0	13.6	7.7
Oct. 1996	1.5	10.5	9.0	2.2

in a steady state during the sampling period, and that lifetimes of dissolved gaseous tin compounds are in the order of their estuarine residence time. The shapes of estuarine profiles are then indicative of the behaviour of conservative mixing, removal or input and allow to provide estimates of internal production/consumption and export fluxes of dissolved constituents from the estuary (Boyle et al. 1974). In this part, volatilisation fluxes to the atmosphere are not considered and will be discussed in the following part.

In order to make these calculations, we have considered the fluvial flux into the estuary (river flux, F_{river}) which is given by $R \times C_o$ and where R = river water discharge and C_o = river end-member concentration. The flux expelled out of the estuary into the ocean (estuarine flux, $F_{estuary}$) is given by $R \times C_{*s}$, where C_{*s} is the apparent river water concentration extrapolated from the Bu_3SnMe concentration *vs.* salinity relationship at the seawater end-member. Under these considerations, the difference between river and estuarine flux would represent the net flux balance (removal or input) of Bu_3SnMe in the estuary. The flux calculations from the mixing model are presented in Table 4.

The seasonal river fluxes obtained were found to be in the range of 1 mmol Sn d^{-1}, for the three estuaries investigated except in spring. During this period, the high river discharge generates elevated concentrations of suspended particulate matter and could results in large riverine inputs of Bu_3SnMe into the estuary as it can be observed (ca. 6.5 mmol Sn d^{-1} and 4.4 mmol Sn d^{-1} for the Scheldt and the Rhine, respectively). Therefore, the Bu_3SnMe brought by the river inputs can not explain the differences in the water concentrations observed between the 3 estuaries (Table 3). Water column concentrations are indeed 10 times higher in the Scheldt estuary than in the Rhine and the Gironde estuaries despite of the fact that the fresh water fluxes are of the same magnitude.

The yields of seasonal estuarine fluxes were always found to be higher than river fluxes with similar values and are in the range of 1–20 mmol d^{-1} for all estuaries and all seasons. These calculations suggest that estuarine systems are continuous sources of Bu_3SnMe to the ocean, and besides that Bu_3SnMe is also produced continuously within the estuary.

The water and particle residence times seem to influence significantly the concentration of volatile tin derivatives in each estuary. The water residence time varies from a few days for the Rhine estuary to several months to years for the Gironde and the Scheldt (Paucot & Wollast 1997; Irigoien & Castel 1997). For the three estuaries studied here, a decreasing trend of the overall average concentration of Bu_3SnMe against increasing river discharge can be observed. The highest TVT concentrations were recorded in the estuary presenting the longest water residence time and with an important particulate material load. Factors such as industrial inputs, residence time and the total organotin concentration level in the sediment appear to simultaneously affect the TVT concentrations in these estuaries. These conditions certainly favour the formation (methylation) and transfer (diffusion) processes involved in the remobilization of volatile tin species in the water column. These reactions may take place on the bacteria associated on the particles of the estuarine system.

These suggestions are consistent with the overall distribution of Bu_3SnMe concentrations against salinity and indicates that these compounds are formed within the MTZ in both the Scheldt and the Gironde estuaries. These estuarine systems display both a strong sedimentation rate and high potential remobilization of the particulate material (Figures 1 & 3) via various resuspension modes. The sediment-water exchanges affecting directly the concentration of volatile organotin compounds are certainly strongly enhanced by the resuspension of the surface sediments.

The three estuaries studied are indeed macrotidal systems with high turbulent mixing processes. The high tidal current friction on the surface sediments certainly contributes to the remobilization of the volatile tin species to the upper water column (Middelburg et al. 1995; Berg et al. 2001).

Volatilisation fluxes of total volatile tin from European estuaries

The method used for the saturation ratio and flux calculations is exposed in detail elsewhere (Amouroux et al. 2000).

The relative distribution of the volatile organotin species in the different compartments investigated indicate that they can be transferred to the atmosphere under passive or turbulent diffusion processes. Therefore, air and water measurements of volatile tin species allowed us to calculate fluxes of the TVT at the air-water interface. First, the saturation ratio (SR) estimation is necessary to validate the transfer of volatile species at natural interfaces. For the water to air exchange the saturation ratio (SR) is expressed as the water to air concentration ratio multiplied by the Henry's law constant of each volatile compounds. The Henry's law constants were derived from literature data and molecular properties (Amouroux et al. 2000). If the SR is above 1, volatile organotin compounds are supersaturated in water and are likely to diffuse to the atmosphere. Flux calculations are then based on the Fick's first law of diffusion with the assumption that the concentrations of the studied compounds in the water column are in steady state compared to their transfer velocities at the interface (Liss PS & Merlivat L, 1986). A model developed in an estuarine tidal environment was used in order to calculate accurately the transfer velocities (K) at the air-water interface. K is expressed as a function of the Schmidt number of the studied compounds and the wind speed (Clark et al. 1995). Sc was calculated and corrected for the temperature and salinity as explained by Amouroux et al. (2000). *In situ* wind speed values recorded during each cruise were then implemented to the Clark's model.

Seasonal fluxes of Bu_3SnMe and average flux densities of Bu_3SnMe are presented for each cruise in Table 4 and Table 5. The different volatile tin compounds were found largely supersaturated in all seasons for all estuaries. The flux density of Bu_3SnMe follows the same overall distribution than the water concentrations and exhibits much higher values in the Scheldt estuary than the Rhine and the Gironde estuary. Estimated fluxes are then strongly dependent on the contamination levels of the estuaries and range from 4 to 416 nmol m^{-2} y^{-1} (as Sn). Annual water to atmosphere TVT flux is thus higher for the Scheldt (78 mol Sn y^{-1}) than for the Gironde (9 mol Sn y^{-1}) and the Rhine (3 mol Sn y^{-1}) estuary.

The seasonal Bu_3SnMe volatilisation fluxes for the Rhine estuary are in the same range of order than the previous export flux estimates obtained from the mixing model. The production within the Rhine estuary seems then to be balanced between volatilisation processes and estuarine export to the coastal environment. On the contrary, for the Scheldt and Gironde estuary, the seasonal volatilisation fluxes are 20–80 and 4–30 times higher than the export of Bu_3SnMe to the ocean. In such estuaries with long water residence time,

Table 5. Average water to atmosphere saturation ratios and flux densities of volatile organotin compounds in European estuaries

Estuary	Saturation ratio				Bu$_3$SnMe Flux Density
	Me$_4$Sn	BuSnMe$_3$	Bu$_2$SnMe$_2$	Bu$_3$SnMe	(nmol m^{-2} y^{-1})
Scheldt					
Dec. 1996	8260	2250	20460	232290	195
May 1998	54430	8660	6850	586070	327
July 1996	9930	4000	14850	310320	232
Oct. 1998	38060	14350	91160	606530	416
Gironde					
Feb. 1998	1070	4475	2980	17000	21
June 1997				9300	6
Sept. 1997	2330	5730	2140	43880	16
Oct. 1996	650	548	1180	18050	9
Rhine					
Nov. 1997	1390	1020	1620	19183	28
March 1998	2522	2290	2110	32473	14
Oct. 1996	830	770	1100	16916	4

the evasion of Bu$_3$SnMe to the atmosphere appears then to be the preferential elimination pathway of volatile tin species.

Conclusion

Although their anthropogenic OT loads was significantly different, all investigated estuaries were found to be continuous sources of volatile organotin compounds to the water and atmosphere. The estuarine mixing model used did not allowed us to establish the effective production of such compounds in the estuaries and probably has led to underestimate the potential sources strengths. On the other hand, it seems that volatilisation pathways are major sink for volatile organotin compounds in estuaries, at least for those having long water residence time. In summary, production of volatile organotin compounds within the estuaries seems therefore mainly driven by the residence time of water and particles, the sediment contamination level and the *in situ* microbial activity related to the anoxic conditions occurring in the sediment. Further investigations are now necessary to describe the production sources and pathways of volatile organotin compounds in estuaries, but also their potential sinks within the system, especially their transfer to the biota.

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