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Formation and volatilisation of alkyl-iodides and -selenides in macrotidal estuaries

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Abstract. The occurrence of alkylated volatile iodide and selenide species was evidenced and investigated in water, sediments and overlying atmosphere of three major European estuaries, such as the Gironde (F), the Rhine (NL) and the Scheldt (B/NL), along with the salinity gradient. For iodine, up to eight volatile species were observed as alkyl-iodides in estuarine waters. The major one (ca. 40%) was methyl-iodide (MeI) with average seasonal concentrations ranging from 1 to 100 pmol l^{-1}. Other species observed were found to correspond to several halomethane derivatives and light alkyl-iodide species. For selenium, dimethyl selenide (Me_2Se) was the main compound (ca. 90%) over three methyl-selenides encountered in estuarine waters. Me_2Se average seasonal concentrations were found to range between 0.2 and 100 pmol l^{-1} in the water column. The occurrence of methylated iodides and selenides seems to be mainly related to the algae's biomass turnover as indicated by photosynthetic pigment tracers (i.e. chlorophyll a and phaeopigments) and seasonal variation of surface water concentrations. The production and release of gaseous iodide and selenide compounds may then result from natural biological pathways leading to the methylation of their inorganic form. Finally, significant volatilisation rates were evaluated leading to average seasonal flux rates for total volatile iodide and selenide compounds ranging from 4 to 100 and from 1 to 75 nmol m^{-2} d^{-1}, respectively. Estuarine mass balance estimated from MeI and Me_2Se distributions indicates that volatilisation to the atmosphere represents a primary sink for MeI and Me_2Se from estuarine surface waters.

Introduction

Iodine (I) and selenium (Se) are known to be essential micronutrients for the biological development of many living species such as plants, animals and human beings (Kirk 1991; Frieden 1991; Rayman 2000; Sadtman 1990). Their distribution in the biosphere is heterogeneous and some areas of the

Earth's surface are depleted with I and Se, leading to serious health problems for both animals and humans. The occurrence of gaseous I and Se species in the marine environment is thus of major interest as their potential volatilisation to the atmosphere is now considered as a major pathway in their respective global biogeochemical cycles (Lovelock et al. 1973; Liss 1986; Mosher & Duce 1986; Amouroux et al. 2001).

Anthropogenic and natural production of volatile halogenated organic compounds, including methyl-iodide (MeI), play an important role in atmospheric chemical processes and are involved in stratospheric ozone depletion (Gribble 1992; Keppler et al. 2000). Further, MeI was recently proposed for the direct replacement for methyl-bromide (MeBr), the most widely used soil fumigant. This compound will be banned by the year 2001 in the U.S.A. and later in most developed countries (Ohr et al. 1996; Gan et al. 1997). Naturally occurring MeI is also known to be a strong methylating agent able to potentially remobilize and alkylate numerous heavy metals to their more toxic forms in the environment (Thayer et al. 1984). The occurrence and distribution of MeI and other alkyl-iodide compounds, such as ethyl-, propyl-iodide, chloroiodomethane, in seawater and atmosphere is well documented (Edmonds & Morita 1998). MeI presents a mean concentration of 3 pmol l^{-1} in seawater (Moore & Groszko 1999) but little is known on the production and fate of this compound in estuarine waters. MeI and several alkyl-iodides are known to be produced by marine algae (Edmonds & Morita 1998; Moore & Groszko 1999). Manley and Dastoor (1987, 1988) observed the direct formation and release of MeI in seawater, from macrophyte incubation experiments. These authors also speculated that bacterial decay of kelp could potentially increase this source of MeI. Laboratory experiments conducted on phytoplankton cultures also reported its formation via biological mediated methylation processes (Moore et al. 1996; Manley & de la Cuesta 1997). Production of MeI via aqueous photochemistry has also been reported (Moore & Zafiriou 1994; Happell & Wallace 1996). However, direct abiotic photochemical mechanisms leading to its formation have not been clearly evidenced. In contrast, Moore and Groszko (1999) measured MeI maxima in the Eastern Atlantic, at depths up to 65 m, demonstrating potential *in situ* production at low light levels. Recently, Keppler et al. (2000) suggested a new pathway of methyl halides production, via abiotic chemical reactions, involving the organic matter oxidation in sediments and soils. MeI production, from biological mediated reactions is none the less probably the most significant source from global oceans to the atmosphere and the fluxes can be estimated to range between 2 and 5 10^{11} g yr^{-1} (Liss 1986; Moore & Groszko 1999).

Different volatile forms of reduced Se (-II), such as dimethyl selenide (Me_2Se), dimethyl selenyl sulphide (Me_2SSe) and dimethyl diselenide (Me_2Se_2) have been observed in the environment and play an important role with regard to potential Se remobilization and bioavailability (Chasteen 1998). In natural waters, organic selenide compounds, such as organic and amino acids (i.e. selenomethionine, selenocysteine), can be formed after assimilation of inorganic selenium by bacteria or plankton species (Cutter & Bruland 1984; Cooke & Bruland 1987). These compounds can then be released in water as methylated selenium molecules and may potentially lead to the formation of volatile selenium species, such as Me_2Se, Me_2SSe and Me_2Se_2 (Cooke & Bruland 1987; Karlson & Frankenberger 1993; Amouroux et al. 2000a). To better understand and describe these potential dynamic transformation and transfer pathways, further investigations focused on Se biogeochemical cycling in aquatic environments are now necessary. For instance, the production of volatile selenium species in contaminated aquatic systems via biological mediated processes and their evasion to the atmosphere may be understood as a detoxification pathway (Karlson & Frankenberger 1993). On a larger scale, gaseous Se emission from oceanic environments has been estimated to range from 5 to 29 10^9 g Se yr^{-1} (Mosher & Duce 1987; Amouroux & Donard 1996). Thus, the formation of volatile selenium species definitely contributes to a major part of the atmospheric transfer and global cycle of selenium (Amouroux et al. 2001).

Iodine and selenium cycling in estuarine and coastal ecosystems may play an important role along the continent-ocean transfer of these elements. In such specific ecosystems, characterised by strong physico-chemical gradients, enhanced biological activity and intense sedimentation and resuspension, the formation and volatilisation of alkyl-iodides and -selenides may represent major processes for the removal of these elements from surface waters. The data presented in this paper report on the ubiquitous occurrence of volatile iodine and selenium compounds in macrotidal European estuaries and their distribution along with the salinity gradient. Results obtained are integrated with the main biogeochemical parameters in order to estimate the role of the major factors controlling iodine and selenium bio-volatilisation pathways and leading to a net flux of these elements to the atmosphere.

Material and methods

Sampling and sample treatment in macrotidal estuaries

Surface sediment, surface water and atmospheric samples were collected in the Gironde, the Rhine and the Scheldt estuaries from October 1996 to

October 1998 (Frankignoulle & Middelburg 2002). Sampling was performed on board the research vessels *Belgica* (SPPS/FN), *Côte d'Aquitaine* (CNRS/INSU) and *Navicula* (NIOZ), during the EU BIOGEST project cruises, covering various seasonal and hydrographic conditions. These three estuaries are macrotidal systems characterised by very different hydrodynamics, physicochemical gradients and contamination levels (Kramer & Duinker 1988; Wollast 1988; IFREMER 1994). The Scheldt and the Rhine estuaries contains among the largest harbours and industrial complexes in Europe and are bordered by a high population density. In contrast, most of shipping and industrial activities in the Gironde estuary stopped more than 10 years ago, and the density of population along its banks is much lower. It is therefore considered to be one of the few large pristine estuarine area of Europe.

Sediment, water and air sampling procedures and samples treatment are discussed in details elsewhere (Amouroux et al. 1998, 2000b; Pécheyran et al. 1998b; Tessier et al. 2002). Sandy and muddy sediments were sampled in the top 5 cm and were immediately transferred to a gas-tight glass vial (100 ml) without any headspace and stored in a refrigerator at 4 °C. About 10 g of fresh sediment was subsequently transferred in a 50 ml purge vessel with 20 ml of milli-Q water. The slurry formed was then purged during 30 minutes under Helium flow (c.a. 800 ml min^{-1}). The gaseous species were stripped out of the vessel and dried by carrying the gas stream through a moisture trap maintained at –20 °C. Finally the analytes were cryofocused in a U-shaped glass trap filled with acid-cleaned silanized glass wool (Supelco) and immersed in liquid nitrogen (–196 °C). Most of the volatile species extracted from the samples can therefore be concentrated and stabilised into the cryogenic trap. Following the purge, the cryotraps were tightened 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). At this stage, it is important to mention that the concentrations obtained from the sediment samples are not total pore-waters concentrations and can not therefore be used for mass balance calculation. They can also be underestimated due to potential loss of the gaseous species during sample handling (i.e. light compounds). Finally, they can be overestimated due to the fact that sediment slurry dilutes pore-waters and may lead to release some of the water exchangeable fraction of the volatile organic compounds into the aqueous phase (Amouroux et al. 2000b). We therefore assume that the labile and volatile fraction measured in our samples represents the potential fraction of the compounds investigated that may diffuse or be remobilized at the sediment-water interface.

On each estuary, surface waters were sampled between 1 and 3 m depth at every 2.5 salinity unit with salinity ranging between 0 and 34 (Practical Salinity Scale, International System of Units). Samples were always collected within the well mixed surface layer observed in all estuaries from salinity-temperature cast measurements. A PTFE coated Go-Flo non metallic sampler (General Oceanic, U.S.A.) was used for this purpose in order to avoid ship contamination and microlayer surface water contamination. Volatile iodine and selenium compounds were then extracted from the water samples using a purge and cryogenic trapping device described in details elsewhere (Pécheyran et al. 1998a; Amouroux et al. 1998). Within less than 30 minutes after sampling, the water collected was directly transferred to a purging vessel under He atmosphere. 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 sediment. No filtration was performed on the water samples prior to the purging step. Various experiments have shown that without filtration good accuracy can be obtained for DMSe in estuarine waters as validated by standard additions (Pécheyran et al. 1998a), and for MeI by comparison with continuous water-gas equilibration device (Groszko & Moore 1998).

Air sampling was performed all along the investigated estuaries, using a laboratory-made gas sampler developed and optimised by Pécheyran et al. (1998b). Air was pumped upwind from the top or the bow of the ship to avoid potential contamination from engine exhausts. The aerosols and water vapour were removed from the sample pumped using on-line quartz fiber filter (0.1 μm, Whatmann) and moisture trap (–20 °C), respectively. The volatile species are cryofocused on-line onto a glass tube packed with silanised glass wool and maintained at –170 °C (Pécheyran et al. 1998b). The cryotraps were then tightened with Teflon caps and stored until analysis as described above for the sediment.

Determination of alkyl-iodides and -selenides in estuarine samples

The standard settings and methodologies used for the Cryogenic Trapping-Gas Chromatography-Inductively Coupled Mass Spectrometry (CT-GC-ICP/MS) technique are discussed in detail by Pécheyran et al. (1998b) and Amouroux et al. (1998). Cryotraps and standards solutions are directly injected into the CT-GC-ICP/MS system (Elan 5000/6000, Perkin-Elmer) for subsequent multielemental speciation analysis. This analytical technique allows separation of several gaseous I and Se species and simultaneous detection of I and Se isotopes. The high sensitivity and selectivity of the ICP/MS detector coupled to the cryofocusing technique permit operations which deliver absolute detection limits lower than 130 femtogram and 1 pico-

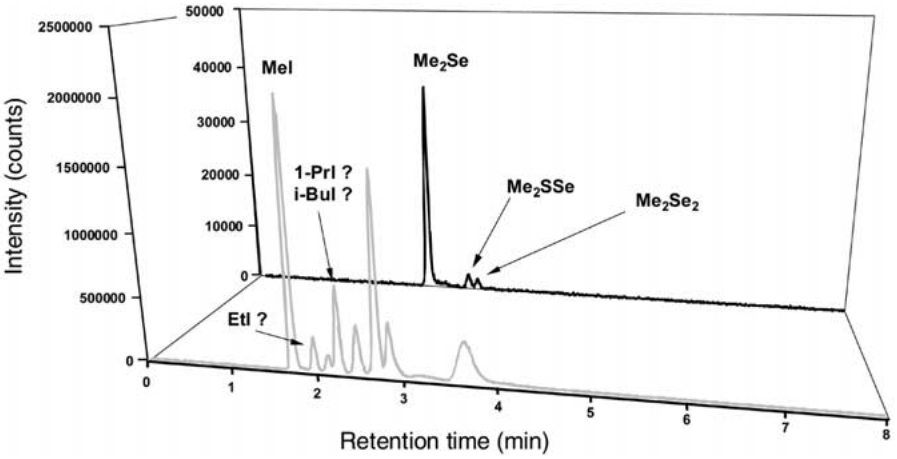

Figure 1. Typical chromatogram of volatile alkyl-iodide and -selenide compounds in surface water sample from the Scheldt estuary, obtained by purge, cryogenic trapping, gas chromatography and ICP/MS detection (CT-GC-ICP/MS).

gram for iodides and selenides, respectively, and method detection limits of 1 fmol l^{-1} and 15 fmol l^{-1} for MeI and DMSe, respectively.

Results and discussion

Identification of volatile iodine and selenium compounds

A typical CT-GC-ICP/MS chromatogram obtained for surface water samples of the Scheldt estuary is presented in Figure 1. All analyses on sediment and water samples from the three estuaries investigated exhibited similar chromatographic profiles. On such chromatograms 8 and 3 peaks were usually distinguished for I and Se, respectively. For atmospheric samples, the heavier volatile I and Se compounds, with a retention time over 3 min were not observed. The potential molecular species were identified by comparison with the retention time obtained for standards solutions of commercially available compounds such as Me_2Se, Me_2Se_2, MeI (Amouroux et al. 1998). The other compounds were identified using the linear relationship between their boiling point and the chromatographic retention time (Amouroux et al. 1998), and comparing those results with previous GC/MS investigations (Edmonds & Morita 1988; Chasteen 1993).

For I, the first peak was the only one clearly identified as methyl iodide (MeI or CH_3I). The second and fourth peaks can be attributed to ethyl iodide (EtI: C_2H_5I), 1-propyl iodide (1-PrI: C_3H_7I) or iso-butyl iodide (i-BuI:

$(CH_3)_3CI$), respectively (Figure 1). The other peaks are probably related to alkyl-iodides or mixed alkyl-halides such as chloro-iodo- and bromo-iodo-alkanes. Despite of the fact that further investigations are needed to fairly identified the less abundant iodide derivatives, MeI was found to be the most ubiquitous volatile iodine compound and the major contributor to the total volatile iodide content (TVI: total sum of the volatile iodide concentrations) in all the samples. MeI concentrations represent on average 40% and up to 50% of the TVI measured in water and sediment samples, and from 50% to 70% of the TVI content in the atmospheric samples, respectively. Only MeI and TVI results will be further presented and discussed in this paper.

For Se, the main volatile selenium compound detected in estuarine sediments, waters and atmosphere was Me_2Se. The ICP/MS technique allowed also simultaneous detection of several Se isotopes (^{82}Se, ^{78}Se, ^{77}Se). The isotopic ratio $^{78}Se/^{82}Se$ was verified for each chromatographic peak at ca. 5% standard deviation from the theoretical value (2.56), and thus confirmed the occurrence of three selenium containing compounds (Figure 1). Amounts of Me_2SSe and Me_2Se_2 have also been observed, in most of the sediment and water samples, in the three estuaries investigated. In air samples, only Me_2Se was detected with concentrations close to the method detection limit (ca. 2.5 pmol m^{-3}) (Pécheyran et al. 1998b). Me_2Se concentrations generally represent more than 90% of the total volatile selenium (TVSe: total sum of the Me_2Se, Me_2SSe and Me_2Se_2 concentrations) in the water samples. However a different distribution was observed in the sediments. Me_2Se was still the major contributor to TVSe, but larger amounts of Me_2SSe and Me_2Se_2 were measured in muddy sediments. Only Me_2Se and TVSe results will be further presented and discussed in this paper.

Distribution of volatile alkyl-iodides and -selenides among and within estuaries

The average concentrations of the volatile I and Se derivatives in estuarine surface waters and their seasonal variations are presented in Table 1. TVI and TVSe concentrations in surface waters follow the same distribution between the three estuaries studied. Average concentrations are much higher in the Scheldt than in the Rhine and the Gironde estuary, ranging from 7 to 68 pmol l^{-1}, 5 to 10 pmol l^{-1} and 3 to 8 pmol l^{-1} for TVI and from 6 to 41 pmol l^{-1},1 to 10 pmol $l^{-1}$and 1 to 5 pmol l^{-1} for TVSe, respectively. These measurements clearly demonstrate that volatile I and Se species are ubiquitous in all of the investigated areas, even in the Gironde estuary which exhibits less anthropogenic load and lower biological turnover (IFREMER 1994). They also confirmed the TVSe values measured by Amouroux and Donard (1997) and Pécheyran et al (1998a) in the Gironde estuary. Moreover, significant seasonal variations in TVI and TVSe levels were observed in the three estuarine systems, with higher TVI and TVSe concentrations generally occurring during the spring-summer period (Table 1).

In surface sediments, the relative distribution of the volatile I and Se species is slightly different than in surface water, with larger amounts of Me_2SSe and Me_2Se_2 (c.a. 19% and 24% of TVSe). In the Scheldt estuary, TVI and TVSe concentrations in muddy and sandy surface sediments average 203 and 207 pg g^{-1} dry weight, respectively. In the Gironde estuary, fluid mud sediments were collected in the maximum turbidity zone (MTZ) in June 1997 (Tseng et al. 2001; Tessier et al. 2002). MeI and Me_2Se were the major contributors detected in these samples, with concentrations ranging from 0.9 to 3.4 pg g^{-1} and from 0.4 to 2.4 pg g^{-1} of dry weight, respectively.

MeI and other light alkyl-iodides were also detectable in the overlying atmosphere of the three investigated estuaries. However, MeI represents approximately 60% of the TVI, with concentrations ranging between 0.3 to 18 ng m^{-3}, 0.2 to 15 ng m^{-3} and 0.8 to 8.3 ng m^{-3} for the Scheldt, the Rhine and the Gironde, respectively.

The distribution of MeI and Me_2Se concentrations against salinity for both spring and fall cruises in the three estuaries is presented Figures 2, 3 and 4 together with important biogeochemical ancillary parameters such as dissolved oxygen, chlorophyll a and phaeopigments concentrations.

The MeI overall distribution displays roughly the same pattern in each estuaries, despite of the fact that the concentration levels are significantly different. Water concentrations increase along the salinity gradient and peak at high salinity 20–35 (Figures 2–4). Higher concentrations are obtained seaward during the warmer seasons, especially in spring for the three estuaries. These high concentrations are observed seaward and within the high primary productivity zone occurring during the spring-summer bloom period (Lemaire et al. 2002; Frankignoulle & Middelburg 2002). The pigments data exhibited in Figures 2–4 do not show any phytoplanktonic biomass maximum at higher salinity. However, it has been shown that in such macrotidal and relatively turbid estuaries, primary productivity is mainly occurring at high salinity where sunlight penetration is not limited by suspended particles (Lemaire et al. 2002). A significant spike of MeI was for example observed in spring at the mouth of the Scheldt estuary during an intense phytoplanktonic bloom event (Lemaire et al. 2002), suggesting that primary productivity is directly or indirectly involved in MeI production (Figure 2). These profiles have been also confirmed for dimethylsulfide (DMS), another biogenic gas produced by phytoplankton, on samples collected during the same cruises (Sciare et al. 2002). MeI concentrations decrease upstream but exhibit significant values in the river end-member, averaging 3.5 pmol l^{-1}, 3.1 pmol l^{-1}

Table 1. Average volatile iodine and selenium compounds concentrations in surface waters along European estuaries

Estuary	*n*	MeI (pmol l^{-1})	Range	TVI (pmol l^{-1})	Range	Me_2Se (pmol l^{-1})	Range	Me_2SSe (pmol l^{-1})	Range	Me_2Se_2 (pmol l^{-1})	Range	TVSe (pmol l^{-1})	Range
Scheldt													
Dec. 96	13	**3.2**	0.5–5.9	**9**	1–17	**7.7**	0.2–27.7	*n.d.		n.d.		**7.7**	0.2–27.7
May 98	13	**24.0**	3.5–104.4	**68**	10–294	**14.8**	2.4–50.1	**2.4**	0.7–4.3	**0.4**	<DL–1.8	**17.6**	3.7–53.0
July 96	14	**2.4**	0.4–5.2	**7**	1–15	**4.7**	0.2–12.0	**1.1**	0.0–2.6	**0.7**	<DL–1.4	**6.5**	0.2–15.3
Oct. 98	15	**9.2**	3.4–23.9	**26**	10–67	**39.1**	3.6–99.5	**1.1**	0.5–1.6	**1.0**	0.2–1.7	**41.2**	4.3–102.2
Gironde													
Feb. 98	12	**1.4**	0.9–2.1	**3**	2–5	**1.3**	0.3–2.0	n.d.		**0.1**	<DL–0.4	**1.3**	0.1–2.3
June 97	13	**3.6**	2.0–5.6	**8**	5–13	**0.3**	0.1–1.0	**0.2**	<DL–0.4	**0.1**	<DL–0.2	**0.6**	0.1–1.1
Sept. 97	25	**3.5**	1.2–11.5	**8**	3–19	**5.6**	0.6–16.9	n.d.		**0.4**	<DL–1.9	**6.0**	2.2–8.7
Oct. 96	17	**1.3**	0.8–2.3	**3**	2–5	**0.6**	0.3–1.2	**0.2**	0.1–0.3	n.d.		**0.8**	0.4–1.3
Rhine													
Nov. 97	16	**2.7**	1.0–4.8	**5**	2–9	**9.8**	2.1–15.5	**1.0**	<DL–1.7	**0.2**	<DL–0.4	**11.0**	2.1–16.9
March 98	13	**5.6**	1.9–9.6	**10**	4–18	**10.2**	0.5–24.2	**3.7**	0.5–8.2	n.d.		**13.9**	1.1– 30.7
July 97	15					**1.2**	0.4–3.6	**0.7**	0.2–1.5	**0.2**	<DL–0.5	**2.1**	0.6–5.2
Oct. 96	12	**2.9**	0.4–4.8	**5**	3–9	**3.7**	0.3–9.3	**0.6**	0.1–1.5	**0.1**	<DL–0.3	**4.7**	0.4–10.3

∗not detected.

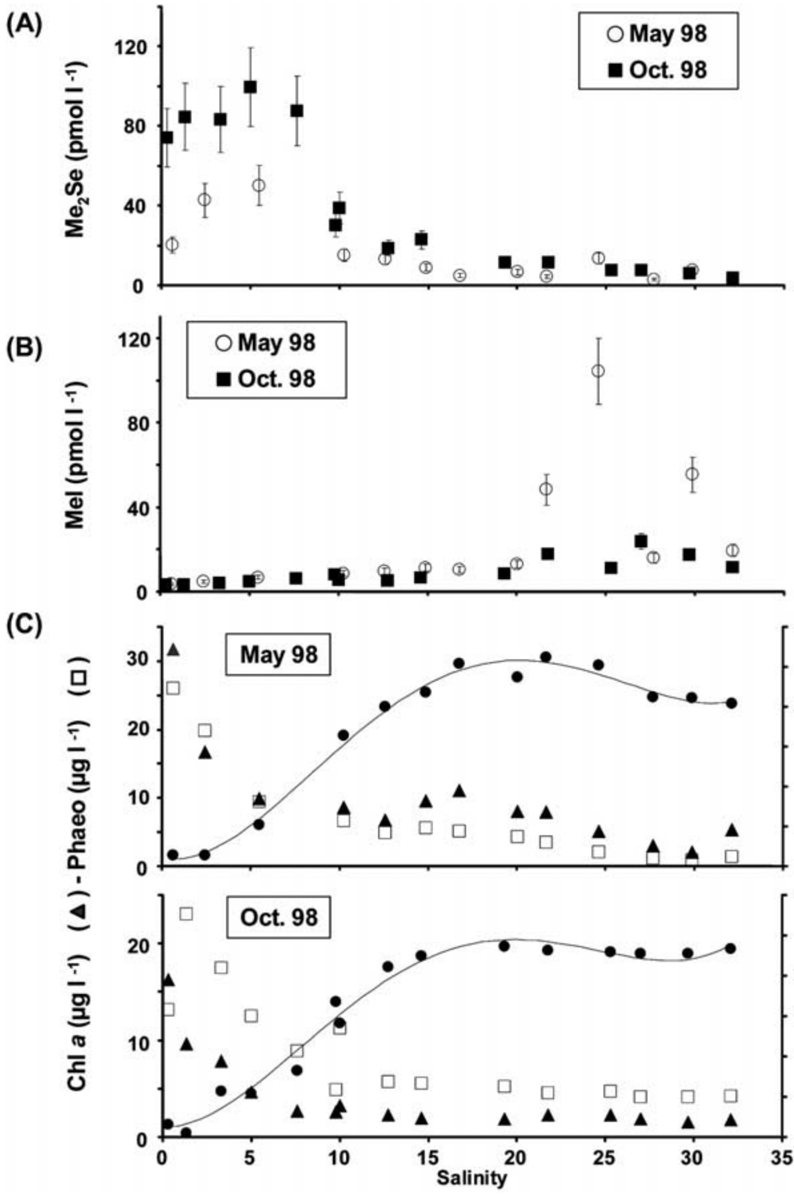

Figure 2. Distribution of dimethylselenide (Me_2Se) (A), iodomethane (MeI) (B) and some biogeochemical parameters (C) in surface waters of the Scheldt estuary as a function of salinity in spring and fall season. Error bars represent a relative standard deviation of 15% and 20% for MeI and Me_2Se, respectively, obtained from duplicate analysis.

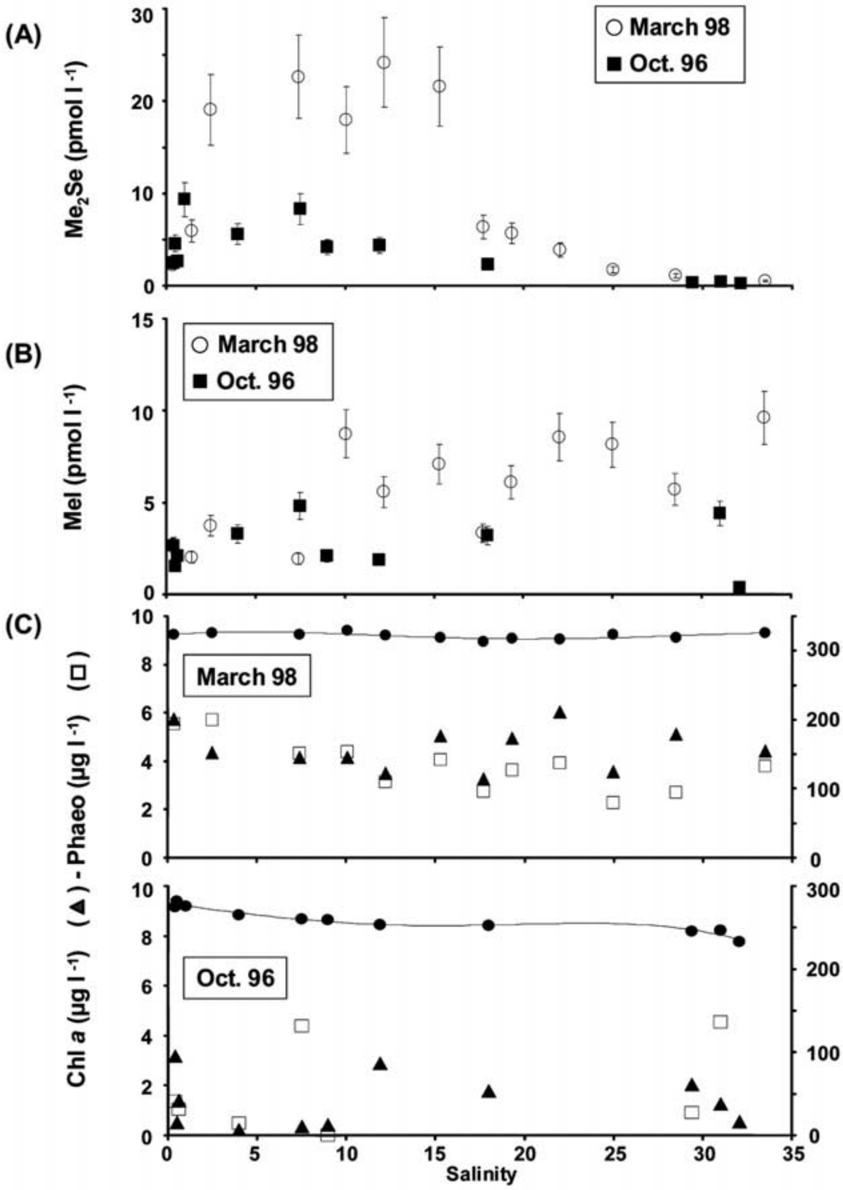

Figure 3. Distribution of dimethylselenide (Me_2Se) (A), iodomethane (MeI) (B) and some biogeochemical parameters (C) in surface waters of the Rhine estuary as a function of salinity in spring and fall season. Error bars represent a relative standard deviation of 15% and 20% for MeI and Me_2Se, respectively, obtained from duplicate analysis.

and 2.2 pmol l^{-1} for the Scheldt, the Gironde and the Rhine estuaries, respectively. River inputs can therefore partially contribute to the budget of volatile I compounds in estuaries. These species, widely distributed in the biosphere, are likely to enter the aquatic environments through waste waters and other anthropogenic effluents (Edmonds & Morita 1998).

Me_2Se concentrations exhibit an overall similar distribution in the different estuaries and for the seasons investigated. Water concentrations decrease along with the salinity gradient and present a maximum in the upper estuary, between salinity 0 and 10 (Figures 2–4). This area generally corresponds to the maximum turbitdity and/or low oxygen estuarine area (Frankignoulle & Middelburg 2002). Maximum gaseous selenide concentrations are for example observed in the Scheldt estuary at low salinity. This area directly represents the estuarine zone where riverine phytoplankton biomass accumulates and enhanced heterothrophic activity generates oxygen depletion (Figure 2). A similar trend is also found in the Gironde estuaries during the September cruise (Figure 4). This non conservative distribution demonstrates that volatile alkyl-selenide compounds could be released in the estuary at low salinity and then transferred along with estuarine mixing processes (Amouroux & Donard 1997). The concentration levels obtained are however much higher in the Scheldt than in the Rhine and the Gironde estuary. They are also elevated during the warmer seasons and for low river discharge period. For the Scheldt estuary, the Me_2Se concentrations measured in fall were comparable to those of spring suggesting that riverine inputs are an important and continuous source. Significant Me_2Se concentrations were measured in the river end-member of the Scheldt (2–74 pmol l^{-1}), the Rhine (2–6 pmol l^{-1}) and the Gironde (1–8 pmol l^{-1}) estuaries. River inputs, including waste waters or anthropogenic effluents, can therefore partially contribute to the budget of volatile Se compounds. The production and volatilisation of methylated Se compounds (i.e. Me_2Se, Me_2SSe and Me_2Se_2) from sulphur-rich environments, such as smelters, sewage sludge or sewage plants, has already been well evidenced (Reamer & Zoller 1980; Chasteen 1998).

Formation of volatile alkyl-iodides and -selenides in macrotidal estuaries

MeI and Me_2Se average concentrations for all cruises in each estuaries are plotted in Figure 5 and 6 against average chlorophyll a, phaeopigments and dissolved organic carbon (DOC) concentrations measured on the same water samples. MeI and Me_2Se average concentrations appear to follow a positive linear correlation with both type of phytoplankton pigments and with DOC among estuaries. Such correlation are not observed when comparing single water samples analysis obtained in a specific cruise. Average concentrations

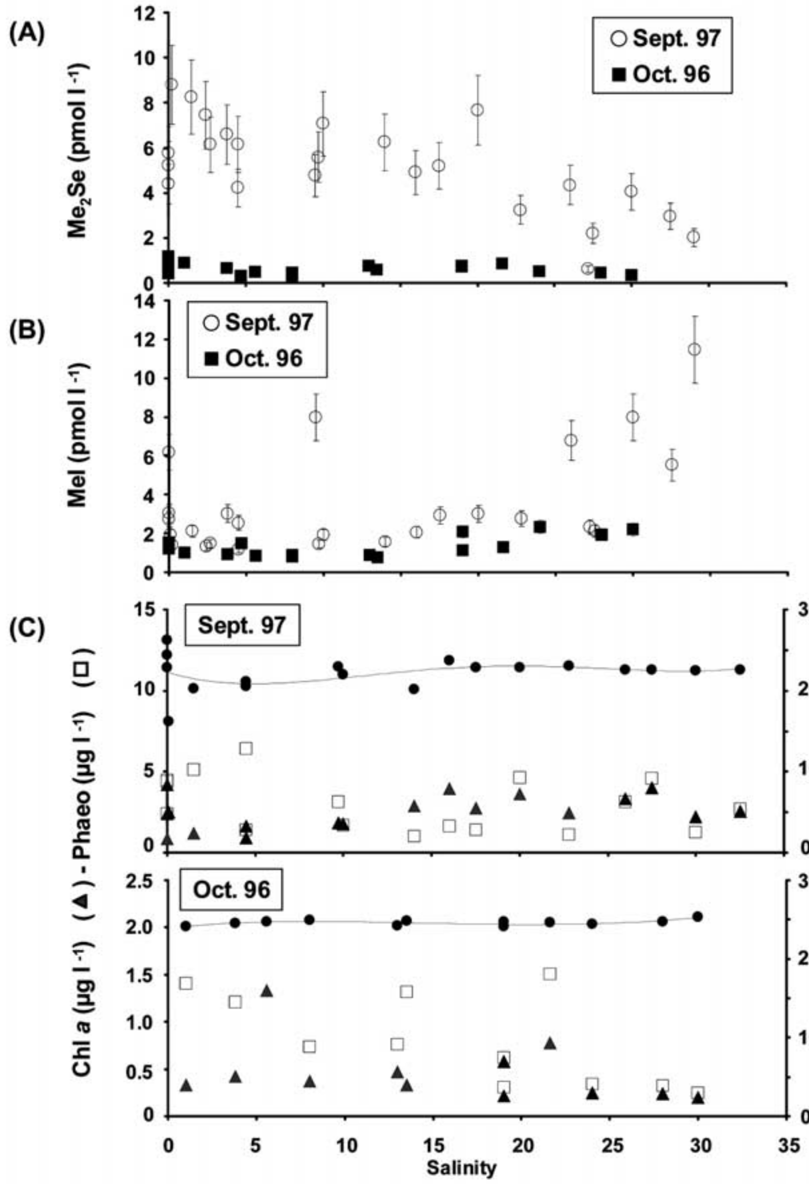

Figure 4. Distribution of dimethylselenide (Me_2Se) (A), iodomethane (MeI) (B) and some biogeochemical parameters (C) in surface waters of the Gironde estuary as a function of salinity in summer and fall season. Error bars represent a relative standard deviation of 15% and 20% for MeI and Me_2Se, respectively, obtained from duplicate analysis.

determined from samples collected along the salinity gradient, correspond almost to the global inventories of the volatile species investigated, the phytoplankton biomass and the dissolved organic matter. The relationship obtained are thus more related to biogeochemical and hydrodynamic characteristics among estuaries and seasons. They may also indicate that water residence time, anthropogenic pressure and seasonal biological turnover potentially control the occurrence of alkyl-iodides and -selenides in estuarine waters.

For MeI, significant positive correlation coefficients are obtained after the linear regression with phytoplankton pigments (Figure 5). Such relationship has been obtained removing from the regression single stations in the Scheldt estuary corresponding to highly eutrophicated freshwater samples (Lemaire et al. 2002). A positive trend is also found with DOC, but do not correspond to any significant biogeochemical behaviour between these two parameters. These results suggest that plankton biomass turnover following seasonal variation controls MeI production in estuarine waters via biological formation pathways. The production of MeI by marine seaweed and also probably by the associated bacterial decay has been evidenced by Manley and Dastoor (1987, 1988). Further, significant amounts of MeI have been detected in marine phytoplankton laboratory cultures (Moore et al. 1996; Manley & de la Cuesta 1997). Finally, photochemical mechanisms may also be involved and enhance the production of volatile iodine compounds in clear estuarine waters (Moore & Zafiriou 1994; Happell & Wallace 1996). However, it has to be demonstrated whether the light intensity plays a role through photosynthetic pathways rather than direct photochemical reactions.

MeI and other light alkyl-iodides were also observed in both surface sediments of the Scheldt estuary and fluid mud of the Gironde estuary. These results suggest the occurrence of a secondary production pathway of alkyl iodides in sediments of the maximum turbidity zone (MTZ). Recently, laboratory experiments conducted by Keppler et al. (2000) highlighted the formation of halocarbons, such as MeI, from halide ions in organic-rich sediments, during an abiotic sequence of oxidation-reduction reactions. Methyl halides formed represent degradation products of oxidised organic matter, by an electron acceptor such as Fe(III).

For Me_2Se, Figure 6 shows that a very significant positive correlation is obtained for the linear regression with phaeopigments concentrations among the different cruises in all estuaries. Additionally, significant correlation coefficient are also observed with chlorophyll a and DOC concentrations. These results indicate Me_2Se formation may also be related to the plankton biomass turnover. Maximum Me_2Se concentrations were observed during lower river discharge period, at low salinity, which corresponds to the maximum turbidity zone, especially in the Scheldt and the Gironde estuary (Figures 2–4). During

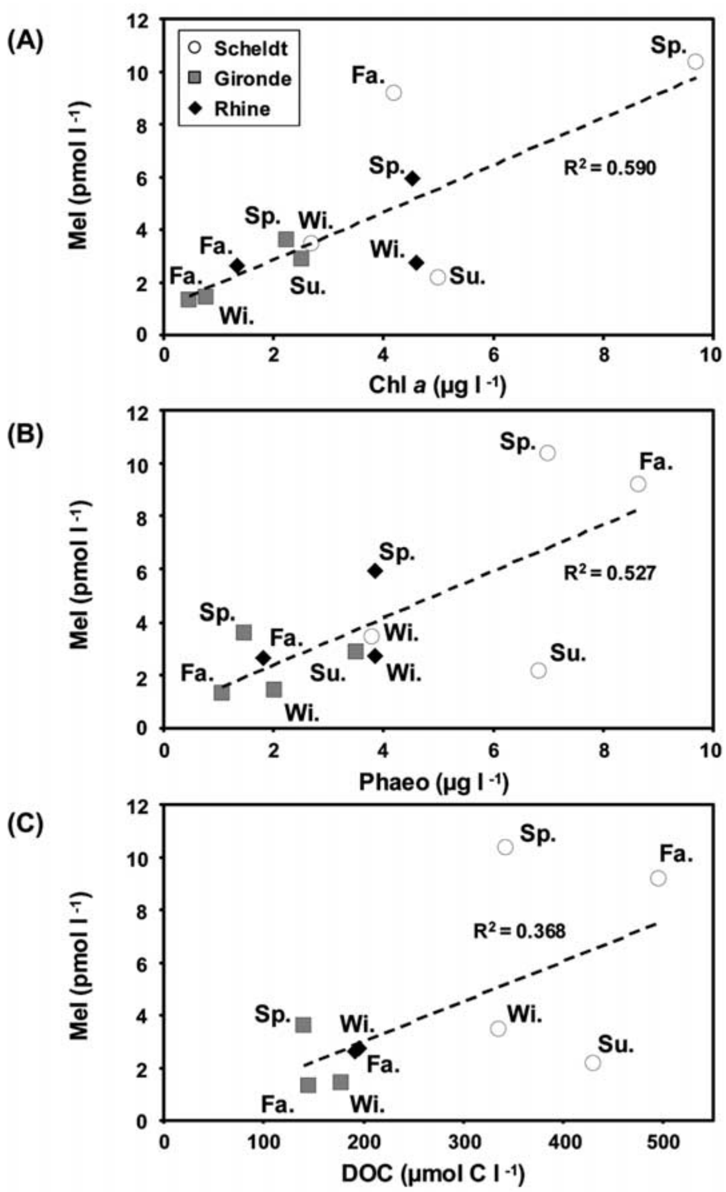

Figure 5. Average MeI concentrations obtained for each cruises in each estuaries: relationship with chlorophyll pigments concentrations (A), and phaeopigments concentrations (B) and dissolved organic carbon concentrations (C). Wi: Winter; Sp: Spring; Su: Summer; Fa: Fall.

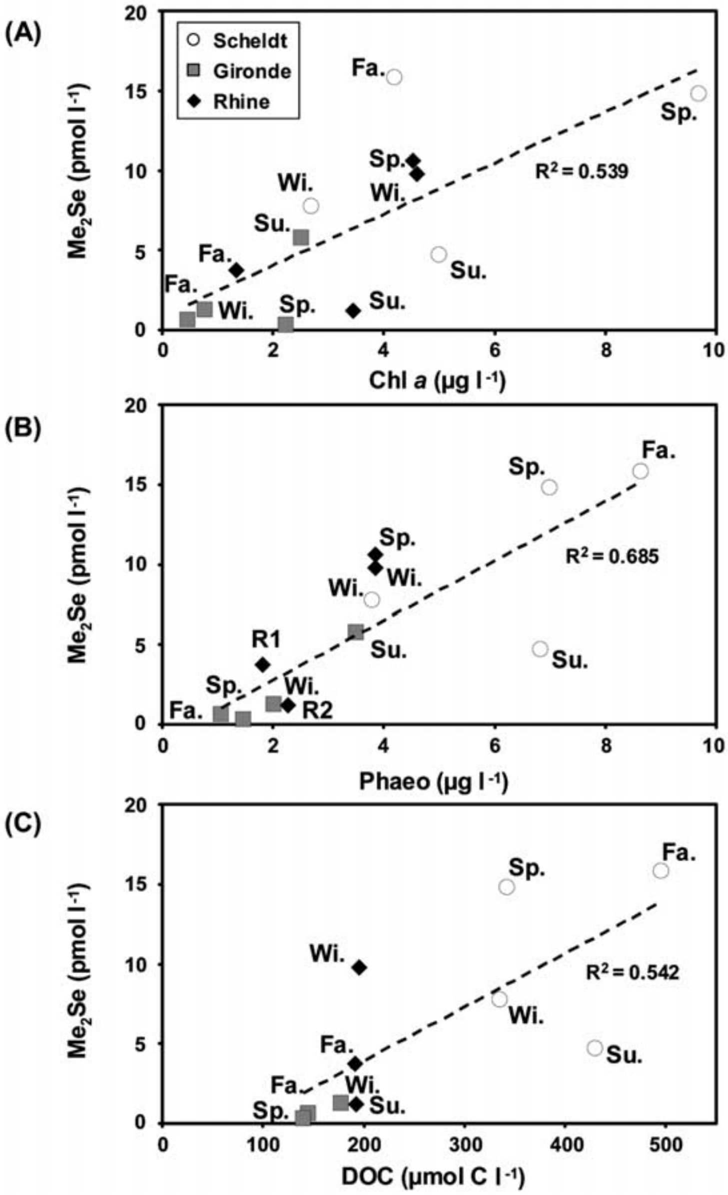

Figure 6. Average Me_2Se concentrations obtained for each cruises in each estuaries: relationship with chlorophyll pigments concentrations (A), and phaeopigments concentrations (B) and dissolved organic carbon concentrations (C). Wi: Winter; Sp: Spring; Su: Summer; Fa: Fall.

warmer seasons, the high biological productivity in river and estuarine waters lead to the transport and accumulation of fresh organic matter in the MTZ (Lemaire et al. 2002). These conditions are likely to enhance the production of volatile selenium compounds via the organic matter degradation released by phytoplankton biomass.

Me_2Se production in aquatic environments can be strongly stimulated by addition of amino acids and proteins (Thompson-Eagle & Frankenberger 1990, 1991; Frankenberger & Karlson 1994). The estuarine mixing processes and the lower productivity of marine waters lead to a decreasing gradient of Me_2Se concentrations seaward. Formation pathways of volatile Se compounds would then be mainly due to riverine and marine phytoplankton inputs associated with the intense microbial activity within the MTZ (Amouroux & Donard 1997). Several mechanisms for Se biomethylation have been proposed from laboratory experiments, involving the contribution of living cells such as micro-organisms and algae species (Karlson & Frankenberger 1993).

Alkyl selenides, such as Me_2Se, Me_2SSe and Me_2Se_2, were also measured in surface sediments and fluid mud samples, with significant amounts of Me_2SSe and Me_2Se_2 in the muddy sediments. Further, the microbial activity is well developed in such anoxic sediments and could be another source for biomethylation of inorganic Se species (Reamer & Zoller 1980; Chasteen 1993; Karlson & Frankenberger 1993; Oremland 1994). The release of alkyl selenides in surface waters from microbial anaerobic processes in the sediment, may be then enhanced by the estuarine sedimentation and resuspension cycles within the MTZ (Tseng et al. 2001).

Volatilisation fluxes of alkyl-iodides and -selenides from estuarine waters

From the measured concentrations of the gaseous I and Se species, in both air and water samples, and together with meteorological data, we have estimated the flux rates to the atmosphere for MeI and Me_2Se using the Clark's model for air-water exchanges (Clark et al. 1995) adapted for gaseous iodine and selenium compounds. Flux rates were then extrapolated to TVI and TVSe. The flux model and calculations used in this paper are exposed in details elsewhere (Amouroux et al. 2000b; Tessier et al. 2002). Clark's model was developed in an estuarine tidal environment and allows to properly calculate the transfer velocities of the gaseous species studied at the air-water interface. Flux calculations are based on the Fick's first law of diffusion, where the flux is express as a function of the mass transfer coefficient (transfer velocity) and the concentration gradient of the diffusing compound between the two phases (Liss & Merlivat 1986). Table 2 gives the seasonal average flux values obtained in the three estuaries. The different volatile iodine and selenium compounds were found to be largely supersaturated in estuarine surface waters, in all seasons and for all estuaries, confirming that these gaseous species are likely to diffuse from the surface water mixing layer to the atmosphere. TVI and TVSe flux densities exhibit therefore much higher values in the Scheldt, compared to the Rhine and the Gironde estuary. Estimated fluxes average 16.7 and 11.7 μmol m^{-2} y^{-1} in the Scheldt, 3.8 and 4.8 μmol m^{-2} y^{-1} in the Rhine and 4.2 and 1.1 μmol m^{-2} y^{-1} in the Gironde for TVI and TVSe, respectively. These results suggest that the concentrations and volatilisation rates of such species are strongly related to the anthropogenic load in each estuary (Kramer & Duinker 1988; Wollast 1988; IFREMER 1994). In fact, anthropogenic pressure in estuaries stimulates both the biological turnover and the trace elements discharge. The variability of the MeI, TVI, Me_2Se and TVSe fluxes among seasons follows the distribution of the concentrations in water, with higher flux density in the warmer seasons. For the Rhine estuary, winter fluxes were found higher than in the spring period for both I and Se volatile species. Indeed, the high wind speeds, recorded during this cruise, significantly enhanced the turbulent diffusion processes and thus the volatilisation of the dissolved gaseous I and Se compounds.

Estuarine mass balance of volatile iodine and selenium compounds: significance of volatilisation pathways

The estimated average annual fluxes of both Volatile I and Se compounds at the air-water interface are mainly related to the net production of such species in the estuarine environment. In order to discuss the nature of the biogeochemical processes taking place, a simple estuarine reaction/mixing model has been implemented to the concentrations obtained on the three estuaries, using the estuarine profiles of MeI and Me_2Se shown in Figures 2–4. The shapes of the estuarine profiles are then indicative of the behaviour of the dissolved constituents such as conservative mixing, removal or input and allow to provide estimates of internal production/consumption and export fluxes from the estuary (Boyle et al. 1974; Kaul & Froelich 1984; Tessier et al. 2002). River and estuarine fluxes of the investigated species (i.e. MeI, Me_2Se) can then be estimated and their difference would represent the net flux balance (removal or input) of these species within the estuary. The flux calculations from the mixing model are presented in Table 3.

The fresh water flux of MeI (Riverine flux: F_{River}), derived from the mixing model, is directly dependent to the river discharge, and exhibit highest values for the Rhine (428 mmol d^{-1} in March 98 and 297 mmol d^{-1} in October 96) compared to the Gironde (97 mmol d^{-1} in September 97 and 30 mmol d^{-1} in October 96) and to the Scheldt (24 mmol d^{-1} in May 98 and 15 mmol d^{-1} in October 98). The estuarine MeI flux ($F_{Estuary}$) was found to be

Table 2. Average water to atmosphere flux densities of volatile iodine and selenium compounds in European estuaries

Estuary	Flux density (μmol m^{-2} y^{-1})			
	MeI	TVI	Me_2Se	TVSe
Scheldt				
Dec. 96	1.7	5.1	4.5	4.5
May 98	14.4	40.6	8.1	9.7
July 96	1.8	5.1	3.9	5.3
Oct. 98	5.6	16.0	23.0	27.4
Gironde				
Feb. 98	1.3	3.2	1.2	1.2
June 97	3.2	7.7	0.4	0.5
Sept. 97	1.7	4.1	2.8	2.5
Oct. 96	0.7	1.6	0.3	0.4
Rhine				
Nov. 97	2.7	5.0	10.6	11.6
March 98	2.1	3.8	3.5	4.8
July 97			0.4	0.7
Oct. 96	1.4	2.6	1.7	2.0

equivalent to the riverine flux for the Gironde and Rhine estuaries, in both spring and fall season. Here MeI profiles present a conservative behavior without apparent removal or production (Figures 3(B) & 4(B)). The MeI concentration increases with salinity, likely to inorganic iodine concentrations previously observed in various estuaries (Takayanagi & Cossa 1985; Wong & Cheng 1998). The net fluxes of MeI in the Rhine and the Gironde estuaries are then equal to zero, although the seasonal volatilisation fluxes (F_{Vol}) are higher than 30 times the export fluxes of MeI to the ocean ($F_{Estuary}$). This difference suggests that concentrations of MeI are controlled by the balance of rapid transient production and removal, via volatilisation within the estuary, rather than by the marine or fluvial inputs.

In spring and fall, in the Scheldt, MeI profiles display a broad production maximum at the mouth of the estuary (salinity 20 to 30) and thus $F_{Estuary}$ was found to be much greater than F_{River} (Figure 2(B)). These calculations suggest that the Scheldt estuary is a significant source of MeI to the ocean. The volatilisation flux of MeI, in the Scheldt estuary in May, was found to be in the same range than the net estuarine flux predicted by the mixing model

Table 3. Seasonal river and estuarine fluxes of volatile iodine and selenium compounds. 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 MeI and Me_2Se concentrations *vs.* salinity relationship at the seawater end-member. Thus the difference between $F_{Estuary}$ and F_{River} corresponds to the net flux balance (F_{Net}, removal or input) within the estuary. These calculations were performed assuming that the estuarine system is in a steady state during the sampling period, and that lifetimes of dissolved gaseous compounds are in the order of their estuarine residence time

Estuary	MeI				Me_2Se			
	F_{River}	$F_{Estuary}$	F_{Net}	$F_{Volatilisation}$	F_{River}	$F_{Estuary}$	F_{Net}	$F_{Volatilisation}$
Scheldt								
Dec. 96	9	66	57	1238	43	28	–15	3293
May 98	24	4165	4141	10754	79	52	–27	5976
July 96	5	5	0	1313	4	42	38	2898
Oct. 98	15	619	603	4114	286	156	–130	16900
Gironde								
Feb. 98	130	130	0	2342	165	404	239	2130
June 97	177	177	0	5771	6	51	45	625
Sept. 97	97	97	0	3045	394	512	117	4291
Oct. 96	30	30	0	1181	24	69	45	517
Rhine								
Nov. 97	111	1048	937	1439	700	3692	2993	5585
March 98	428	428	0	1099	428	1895	1467	1875
July 97*	—	—	—	—	238	269	31	219
Oct. 96	297	297	0	755	304	800	495	904

*No data available for MeI in July 9.

(Table 3). MeI produced at high salinity easily evades without being exposed to degradation pathways taking place within the estuarine system. In this case, MeI volatilisation seems to occur faster than its degradation and thus removal of MeI within the estuary is mainly driven by its evasion to the atmosphere.

For Me_2Se, in the three estuaries, the concentration profiles exhibit non conservative behaviour in the upper estuary. Me_2Se is produced at low salinity and/or originates from fresh water inputs and is then removed from the estuary, via degradation and/or volatilisation pathways. Me_2Se, in the Scheldt in both spring and fall season, is strongly removed so that $F_{Estuary}$ is lower than F_{River}(c.a. 52 mmol d^{-1} and 156 mmol d^{-1} for $F_{Estuary}$ compared to 79 mmol d^{-1} and 286 mmol d^{-1} for F_{River} in May and October, respectively). In contrast, for the Gironde and Rhine estuaries, estuarine fluxes were found to be higher than the riverine inputs (see Table 3). Thus these estuarine systems represent source of Me_2Se to the ocean. In the Scheldt and the Gironde, where the water residence time is long (few weeks to months), removal of Me_2Se is potentially important, via degradation or absorption pathways. The volatilisation fluxes are 10 to 200 times higher than the net fluxes, calculated from the model. In such estuaries with a long water residence time, the evasion of Me_2Se to the atmosphere appears then to be the preferential elimination pathway of volatile selenium species. In contrast, for the Rhine estuary, the volatilisation fluxes are in the same order of magnitude than the export fluxes of Me_2Se to the ocean, obtained from the mixing model. The Rhine presents also a short water residence time (few days) due to its high river discharge. Me_2Se produced upstream is rapidly removed from the estuary, without important degradation. The production occurring within the Rhine estuary seems then to be the result of the balance between volatilisation processes and estuarine export to the coastal environment.

Both estimations on estuarine mass balance of MeI and Me_2Se indicate that volatilisation fluxes of such species are major, or at least significant, removal pathways from surface waters. Assuming that the estuarine behaviour of all alkyl-iodides and selenides are similar, water to air exchange of such species may contribute to a significant atmospheric transfer of total I and Se during estuarine mixing. Flux calculations were estimated from TVI and TVSe average flux rates obtained in this work and roughly extrapolated to the whole European estuaries surface area. The results suggest that I and Se emissions from European estuaries to the atmosphere would represent about 20% of European emissions from fossil fuel combustion (Pacyna 1984). This indicates that estuarine and adjacent coastal environments submitted to significant anthropogenic pressure may contribute to a large extent to the remobilization of I and Se in the atmosphere as alkylated derivatives.

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