

Mercury in the Southern North Sea and Scheldt estuary

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Received 10 October 2000; received in revised form 30 April 2001; accepted 4 May 2001

Abstract

Dissolved and particulate mercury and methylmercury concentrations were determined in the Southern Bight of the North Sea and the Scheldt estuary in the period 1991–1999. Mercury and methylmercury concentrations are higher before 1995 than after 1995, especially in the fluvial part.

The North Sea: In the offshore stations, dissolved Hg concentrations are generally higher in winter than in summer while the reverse is true for particulate Hg K_D values (K_D = the concentration of particulate Hg (Hg_p in pmol kg^{-1}) divided by the concentration of dissolved Hg (Hg_D in pmol l^{-1})) range from 100,000 to 1000,000 l kg^{-1} . Dissolved methylmercury concentrations vary from 0.05 to 0.25 pmol l^{-1} in summer and from d.l. to 0.23 pmol l^{-1} in winter and particulate methylmercury concentrations from 1.8 to 36 pmol g^{-1} in summer and from 0.9 to 21 pmol g^{-1} in winter. The K_D ranges from 9,000 to 219,000 l kg^{-1} .

The Scheldt estuary: In winter, dissolved Hg concentrations are elevated in the upper estuary, decrease exponentially in the low salinity range followed by a very slow decrease towards the mouth. In summer, they are low in the fluvial part, increase in the low salinity range or in the mid-estuary and sometimes show an increase in the lower estuary. Particulate Hg concentrations do not show any seasonal trend.

Dissolved MMHg concentrations are much lower in winter, when maximum concentrations are found in the upper estuary, than in summer. In summer, the MMHg concentrations are low at low salinity, they show a first increase in the salinity range from 3 to 12, a decrease in the mid-estuary and a second increase in the lower estuary.

The highest particulate MMHg concentrations are found in the upper estuary, while in the lower estuary generally lower and more constant values are observed. The ratio of dissolved MMHg to dissolved Hg (cruise averages between 1.3% and 20%), is higher than the ratio of particulate MMHg to particulate Hg (cruise averages of 0.27–0.90%). The K_D values for MMHg are lower in the summer (30,000–65,000) than in autumn and winter (77,000–114,000).

The Scheldt river: In the fluvial part of the Scheldt, dissolved increases in the most upstream stations, while particulate Hg shows no particular pattern. Dissolved MMHg ranges from 0.1 to 0.39 pmol l^{-1} and particulate MMHg from 3.1 to 43.5 pmol g^{-1} . The MMHg concentrations are comparable to those found in the estuary and no seasonal variations could be observed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Coastal seas; Estuaries; Mercury; Methylmercury; Speciation

1. Introduction

As estuaries and coastal zones form the link between the terrestrial and marine environment, an

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understanding of the behavior and fate of mercury in these zones is essential in evaluating the input of fluvial Hg to the ocean and the impact of anthropogenic influences. Coastal zones are very dynamic and are subject to varying influences of riverine and atmospheric input, coastal and seafloor erosion and biological activities. Hg exists in a large number of physical and chemical forms, which determine its complex distribution, its biological enrichment and toxicity. The most important chemical forms are elemental Hg (Hg^0), inorganic Hg (Hg^{2+}), monomethylmercury (MMHg, CH_3Hg^+) and dimethylmercury (DMHg, CH_3HgCH_3). Recent investigations have focussed on the transformation processes of Hg in estuaries, coastal waters and open ocean (Benoit et al., 1998; Mason et al., 1993; 1999; Coquery et al., 1997; Leermakers et al., 1995; Pongratz and Heumann, 1998; Baeyens and Leermakers, 1998). The main transformation pathways between the various Hg species in the different environmental compartments have been identified, although the reaction mechanisms and/or biological species involved in the interconversion of Hg species in the ocean remain uncertain. The in situ (bacterial) conversion of inorganic Hg species to MMHg is an important feature of the Hg cycle in aquatic systems as it is the first step in the bioaccumulation process. Methylation occurs both in the water column as in the sediments (its origin in the atmosphere is still unknown) and has been shown to be predominantly due to sulfate reducing bacteria in freshwater and estuarine systems.

In this study, we examine the behavior of Hg species along an estuarine gradient and in the adjacent coastal waters, focussing on the evolution of the Hg concentrations in the last decade and on processes controlling the formation of methylmercury. A detailed description of the study site can be found in Baeyens et al. (1998a).

2. Methods and materials

2.1. Sampling procedures

Sixteen surveys were carried out on the Scheldt estuary between November 1991 and April 1998 on

board of the research vessels *R.V. Belgica* and *R.V. Argus*. Samples were collected from the mouth of the estuary (salinity 25–30) up to the confluence of the Scheldt and the Rupel (salinity 0.3–1). From 1995 onwards samples were also taken in the Southern Bight of the North Sea. The sampling stations in the Scheldt estuary and coastal zone (Fig. 1) belong to the Belgian national sampling network. In 1991, 1993 and 1998, offshore water samples in the Channel and adjacent zones (Atlantic Ocean and Southern North Sea) were also taken (Fig. 2) and in 1996 the Scheldt river and part of the upper estuary between Antwerp and Ghent was also sampled using the vessels *Veremans* and *Scaldis II* (Fig. 1). Sediment samples were collected in the Scheldt estuary and coastal waters in 1995 and 1999.

Samples of surface water were collected by hand from a rubber boat by submerging Teflon (FEP) and borosilicate glass bottles approximately 20 cm beneath the water surface. Arm-length gloves were used during sampling. The rubber boat moved gently against the current during sampling and was positioned approximately 100 m up current of the research vessel. FEP and borosilicate glass bottles had been rigorously cleaned by consecutive washes with Decon-90, concentrated HNO_3 and HCl 1% at 60 °C overnight. After the final rinse with Milli-Q water, the bottles were filled with a 1% HCl solution (Merck, *suprapur*) and stored double bagged until use. The sampling bottles were rinsed twice with the sample water before being filled. When sampling from a rubber boat was not possible due to weather conditions, subsurface samples (10-m depth) are collected from the research vessel *R.V. Belgica* using NOEX (Technicap, France) (Go-Flo type) sampling bottles and plastic coated messengers. A Kevlar cable is mounted on the oceanographic winch. NOEX bottles are cleaned with a laboratory detergent, 2% Decon-90, rinsed thoroughly with deionized and Milli-Q water, filled with 1% HCl (Merck pro analysis) in which they are kept for 2 weeks, rinsed thoroughly with deionized and Milli-Q water, again filled with 1% HCl, but this time Merck *suprapur*, in which they are kept for at least 2 weeks and finally rinsed thoroughly with Milli-Q water before the expedition. Table 1 shows a comparison between samples taken by surface grab (the water column is assumed to be very homogeneous at the samples

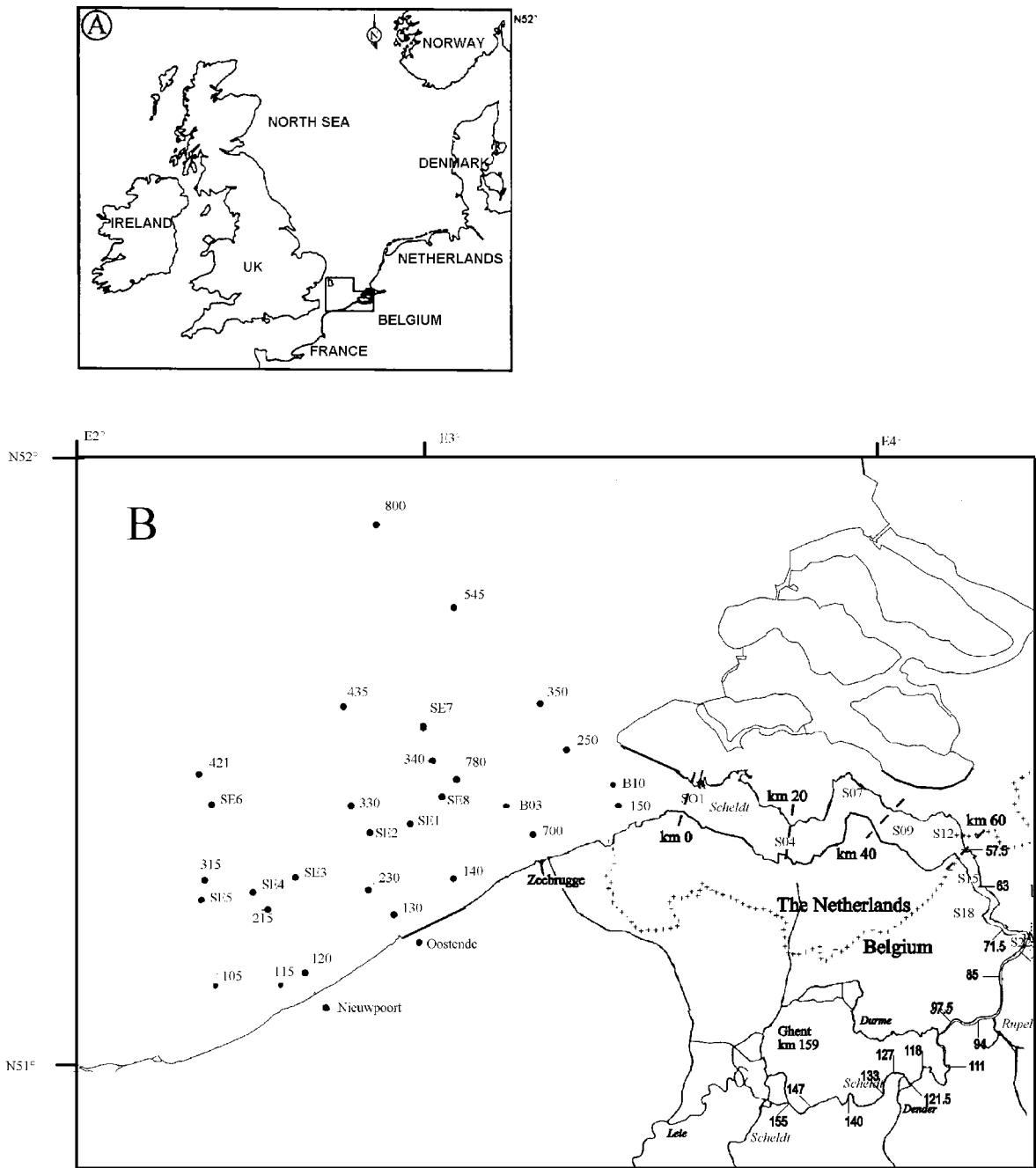


Fig. 1. Map of sampling stations in the Belgian coastal zone, the Scheldt estuary and Scheldt river.

stations) and by NOEX bottles (at a depth of -10 m) for the analysis of total Hg in an unfiltered sample (Hg_T) and in an filtered sample (Hg_{TD}). A

good agreement was found between both methods. A significant difference was only found for the unfiltered sample at station 780, which can probably be

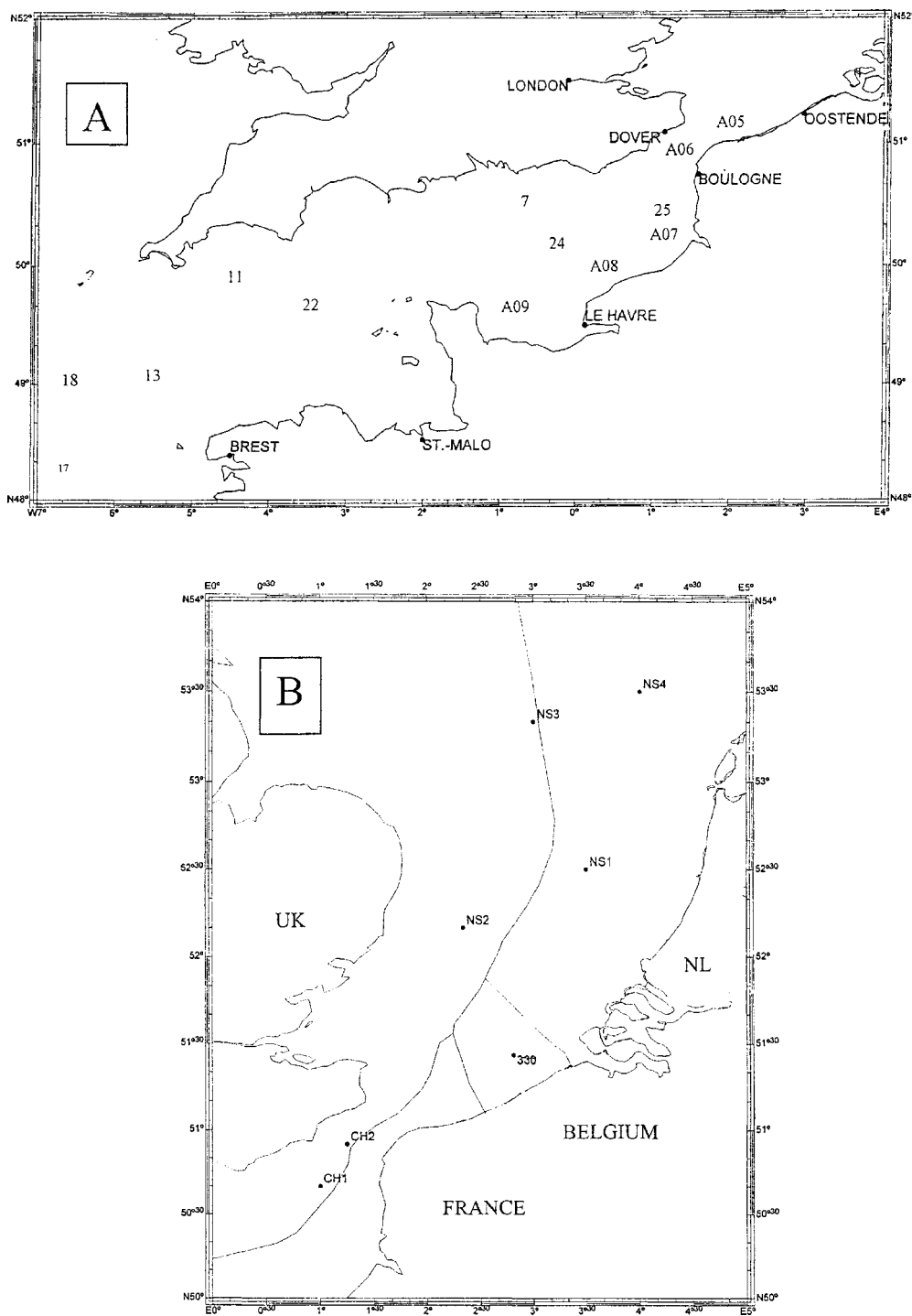


Fig. 2. Map of sampling stations in the English Channel and adjacent areas in the Atlantic Ocean sampled in September 1991 and November 1993 (A); sampling stations in the English Channel and Central North Sea sampled in April and September 1998 (B).

Table 1

Comparison between surface grab and NOEX bottles as sampling techniques of seawater for Hg analysis (Hg_T , total Hg unfiltered and Hg_{TD} , total dissolved Hg)

Station		Surface grab Hg ($ng\ l^{-1}$) $x \pm s (n)$	NOEX Hg ($ng\ l^{-1}$) $x \pm s (n)$	$ t P=0.1$	t
435	Hg_T	$0.30 \pm 0.01 (2)$	$0.34 \pm 0.02 (2)$	2.920	-2.343
	Hg_{TD}	$0.24 \pm 0.03 (2)$	$0.28 \pm 0.07 (2)$	2.920	-0.743
780	Hg_T	$4.70 \pm 0.13 (2)$	$5.55 \pm 0.07 (2)$	2.920	-8.256
	Hg_{TD}	$0.53 \pm 0.01 (2)$	$0.55 \pm 0.08 (2)$	2.920	-0.320

ascribed to differences in turbidity between the surface water sample and the sample taken at -10 m. Larger differences were found for other dissolved trace metals especially Cu and Pb, with lower values obtained by surface grab (Ducastel, 1995).

2.2. Sample handling

Filtration is performed in a clean air bench on board of the research vessel directly after collection of the sample. From 1995 onwards, filtrations were performed in a clean lab container installed on the research vessel. The filtration apparatus consists of a FEP separating funnel onto which a Teflon filter holder is connected. Filtration is performed by pressure filtration using N_2 gas. Hg is removed from the gas stream by a gold column.

Each batch of filters was analyzed before use to check the blank. Both types of filters (Millipore cellulose acetate or Nuclepore polycarbonate) had similar and low blanks. In the beginning of our work, we mainly used Millipore filters due to their convenience in use and the fact that they readily dissolve in acid. However, it was not possible to analyze particulate MMHg by KOH extraction and ethylation on these filters due to strong interferences during the ethylation step. This interference did not occur with Nuclepore filters.

The samples are collected in acid cleaned borosilicate or FEP bottles. The acid in the bottle is discarded and the bottle placed under the filter holder. The first 20 ml collected is discarded. After filtration, samples for reactive Hg (Hg_R) and total dissolved Hg (Hg_{TD}) are acidified with 0.5% HCl (Merck, suprapur) whereas samples for dissolved methylmercury ($MMHg_D$) are stored deep frozen and unacidified. The sampling bottles are tightly

capped and double bagged in zip-loc bags. The filters are stored in Millipore filter holders, sealed in PE bags and stored deeply frozen. Analysis is performed on the wet filters. Parallel filters are taken for turbidity measurements.

2.3. Analytical methods for Hg speciation

Total dissolved Hg (Hg_{TD}), was determined by cold vapour atomic fluorescence spectrometry (CVAFS) using a BrCl oxidation step and reduction with $NH_2OH \cdot HCl$ prior to reduction with $SnCl_2$ and Au-amalgamation preconcentration step (Gill and Fitzgerald, 1987; Bloom and Creclius, 1983). The detection limit was $0.25\ pmol\ l^{-1}$ for Hg_{TD} .

Total dissolved MMHg ($MMHg_D$) was analyzed by aqueous phase ethylation-gas chromatography (GC)-AFS detection (Bloom, 1989; Liang et al., 1994). MMHg was separated from the interfering chloride matrix by an extraction with methylene chloride (Bloom, 1989). For estuarine samples 50 ml of water is extracted into 40 ml of methylene chloride after addition of 5 ml of the 10% HCl/KCl saturated solution. Through solvent evaporation methylmercury is then back extracted into 30 ml of Milli-Q and 30 μl NaAc buffer is added to the bottles. The same procedure is used for seawater but to improve detection limits extractions were performed with larger volumes of seawater. In 500-ml separatory funnels, a total of 200 ml seawater is acidified to pH 1.9 with HCl and extracted three times with 10 ml methylene chloride; further treatment is identical to the procedure described above. Hg species are transformed to their volatile ethyl derivatives using sodium tetraethylborate (STEB), purged out of solution and collected on Carbotrap or Tenax columns. GC separation is either performed

cryogenically (Bloom, 1989) or isothermally (Liang et al., 1994). For the cryogenic separation, the ethylated compounds are subsequently removed from the traps at 270 °C and transferred to a cryogenic gas-chromatographic trap, held in liquid nitrogen. The species are separated by controlled heating of the GC column from –196 °C to 180 °C and the final measurement is made by CVAFS. In the isothermal procedure, the GC column was held at a constant temperature of 75 °C and the Tenax column is heated for 20 s at 350 °C. In the isothermal procedure the resolution between Hg^0 and MeHg is 2 and between MeHg and DeHg is 1.8. Extraction blanks are typically 5 ± 1 pg. This results in a detection limit of 0.3 pmol l^{-1} (60 pg l^{-1}) for a 50-ml sample and $0.075 \text{ pmol l}^{-1}$ (15 pg l^{-1}) for a 200-ml sample. Internal spikes are added to each set of samples, in order to control extraction recoveries. The spike recoveries vary from 70% to 95% and are taken into account. The successive steps to determine total particulate Hg were: (1) digesting the filters in 5 ml HNO_3/HCl (4:1) at 60 °C for 12 h in Teflon digestion vessels; (2) diluting the sample to 50 ml; (3) analysis of a fraction of the sample by CVAFS as described above.

Particulate MMHg (MMHg_p) was extracted either by distillation (Horvat et al., 1993) or using a room temperature KOH extraction (Bloom, 1989). After extraction the Hg compounds are analyzed in the same way as MMHg_D .

Prior to 1999, total Hg and MMHg in sediments were determined in the same way as the suspended matter on filters. Methylation artefacts during analysis using the distillation method cannot be totally excluded. For the 1999 samples, MMHg was extracted using 4 M HNO_3 and analyzed by ethylation-GC-AFS using a headspace injection method (Baeyens et al., 1999; Galletti, 2000). No methylation artefact was observed using this method.

2.4. QC procedures and participation in intercomparison exercises

Blanks, spiked samples and certified reference materials (CRMs) were analyzed daily. As no CRMs exist for MMHg in water, CRMs of biological material are used (NRC DORM-2, NRC DOLT-2, NRC TORT-2) and sediments (IAEA 405, BCR 580).

From 1993 to 1996, we participated in Aquacheck intercomparison exercises for total mercury in water and from 1996 onwards we participated in the Quasimeme intercomparison exercises for total Hg in water. We also participated in an intercomparison exercise for the analysis of total Hg and MMHg in fresh water in November 1993 (Bloom et al., 1995) as well as in the certification of the BCR 580 sediment sample for MMHg.

2.5. Other analysis

Dissolved organic nitrogen (DON) measurements are based on the combination of a total dissolved nitrogen (TDN) and an independent dissolved inorganic nitrogen (DIN) measurement with a Technicon Autoanalyzer. To determine the TDN amount, the sample is oxidized with peroxodisulfate in a microwave oven as described in Dafner et al. (1999).

Particulate organic carbon (POC) and particulate nitrogen (PN) were analyzed by a Carlo Erba NA 1500 element analyzer (Nieuwenhuize et al., 1994). Glass fiber filters were exposed to HCl fumes for 2 h to remove inorganic carbonates prior to elemental analysis.

Data of temperature, salinity, pH, oxygen and Chlorophyll a (Chla) were obtained from the Management Unit for Mathematical Modelling of the North Sea (MUMM) and the Rijksinstituut voor Kust en Zee (RIKZ), the Netherlands.

3. Results

3.1. Evolution of total Hg and MMHg concentrations in the Scheldt estuary

In Fig. 3a–c, the mean total dissolved (Hg_{TD}) and particulate Hg (Hg_p) concentrations and K_D values for 14 cruises between 1991 and 1998 are presented. Because the standard deviations on the cruise averages are relatively large, any conclusion drawn from a regression analysis must be considered very carefully. In this context, the best linear fit through the data points shows a decreasing trend for both dissolved and particulate Hg but no trend for the K_D s.

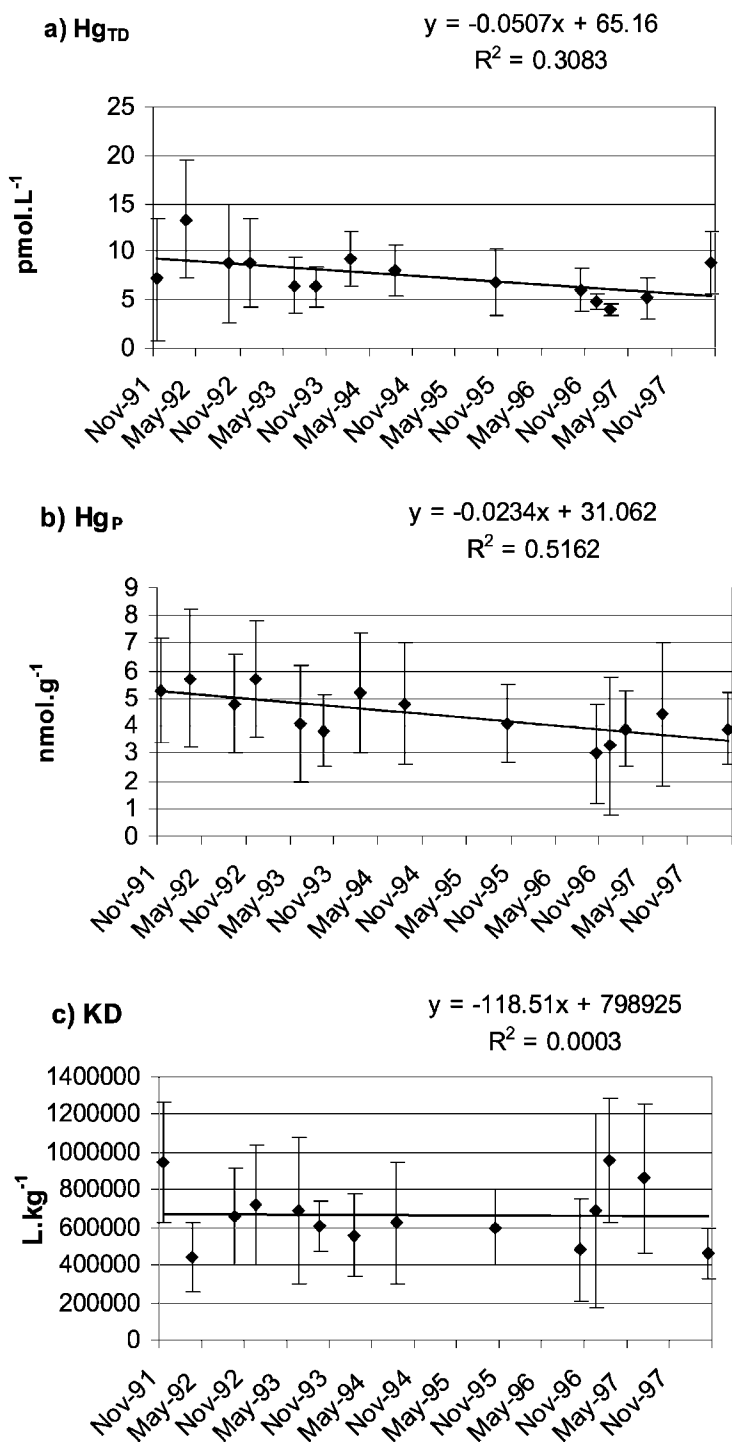


Fig. 3. Average concentrations and standard deviations of (a) total dissolved Hg (Hg_{TD}); (b) particulate Hg (Hg_P); and (c) the distribution coefficient of Hg (K_D) in the Scheldt estuary measured in the different surveys between 1991 and 1998.

Average particulate Hg concentrations measured at the fluvial end member are significantly higher before 1995 ($7.3 \pm 0.4 \text{ nmol g}^{-1}$) than after 1995 ($3.6 \pm 1.0 \text{ nmol g}^{-1}$). At the marine end member, the difference is less pronounced with $2.1 \pm 0.4 \text{ nmol g}^{-1}$ before 1995 and $1.5 \pm 0.65 \text{ nmol g}^{-1}$ afterwards. From 1995 onwards, maximum concentrations of particulate Hg are also no longer found in the riverine end member, but rather at salinities 6–12. This may be due to an increased importance of lateral inputs from the industrial area around Antwerp relative to the fluvial contribution, or the inputs from resuspended bottom sediments.

The dissolved and particulate MMHg concentrations in the Scheldt (Table 2) reveal much higher values in summer than in winter, but more remarkable are the higher concentration levels observed prior to 1995 compared to the more recent ones, similar to the above mentioned decrease of the total Hg levels. As for the total Hg concentrations, the K_{Ds} ($= \text{MMHg}_{\text{p}} (\text{pmol kg}^{-1}) / \text{MMHg}_{\text{D}} (\text{pmol l}^{-1})$) have not changed significantly when the same seasons are compared.

3.2. Distribution of Hg species in the Scheldt estuary

Fig. 4 shows the data of oxygen, suspended matter and Chla for the surveys were both total Hg and methylmercury measurements were made. The summer surveys are characterised by higher temperatures, anoxic conditions in the low salinity range and an increase in oxygen as salinity rises due to mixing

with aerated seawater as well as phytoplankton activity. The low oxygen concentrations are due to the high organic loading of the riverine input and heterotrophic bacterial degradation consuming oxygen. Anoxic conditions are most pronounced in the summer months, when high temperatures and low flow rates prevail. In autumn low oxygen concentrations are still observed in the upper estuary, whereas during the winter the oxygen concentrations do not decrease below 4 mg l^{-1} . Oxygen is also influenced by primary production in the estuary. In the upper estuary, elevated Chla concentrations can be found and are the result of the absence of herbivores and the consequent building up of a large biomass of primary producers. These species decrease rapidly as salinity rises. In the lower estuary, suspended matter concentrations decrease from winter to summer—resuspension of bottom sediments is in shallow coastal areas including the estuarine mouth partly controlled by the wind-stress field which is much weaker in summer—resulting in an increase in light penetration and the development of phytoplankton blooms.

Suspended matter concentrations are higher in the upper estuary (turbidity maximum) and decrease sharply with increasing salinity. In the lower estuary, an increase can also be observed at salinity 20, probably resulting from an input of the canal Ghent–Terneuzen.

In Fig. 5, the concentrations of the different Hg species are plotted. In winter, Hg_{TD} concentrations are elevated in the upper estuary, decrease exponentially in the low salinity range followed by a very

Table 2

Average concentrations of dissolved and particulate methylmercury and the distribution constant of methylmercury in the Scheldt estuary

Cruise	River discharge ($\text{m}^3 \text{ s}^{-1}$)	Spm (mg l^{-1})	MMHg _D (pmol l^{-1})	MMHg _P (pmol g^{-1})	MMHg _P (pmol l^{-1})	K_{D} MMHg (l kg^{-1})
Jun 1993	35	49	1.15			
Nov 1993	50	46	1.37			
Feb 1994	150	86	0.32	13.7	1.03	77,000
Aug 1994	30	28	1.33	35.2	1.01	30,000
Average before 1995			1.0 ± 0.5	24 ± 15	1.02 ± 0.01	$54,000 \pm 33,000$
Oct 1995	40	15	0.40			
Oct 1996	50	38	0.13	7.74	0.29	86,000
Dec 1996	110	22	0.06	7.11	0.15	114,000
Jul 1997	65	21	0.26	12.7	0.26	65,000
Average after 1995			0.21 ± 0.15	9.2 ± 3	0.26 ± 0.07	$88,000 \pm 25,000$

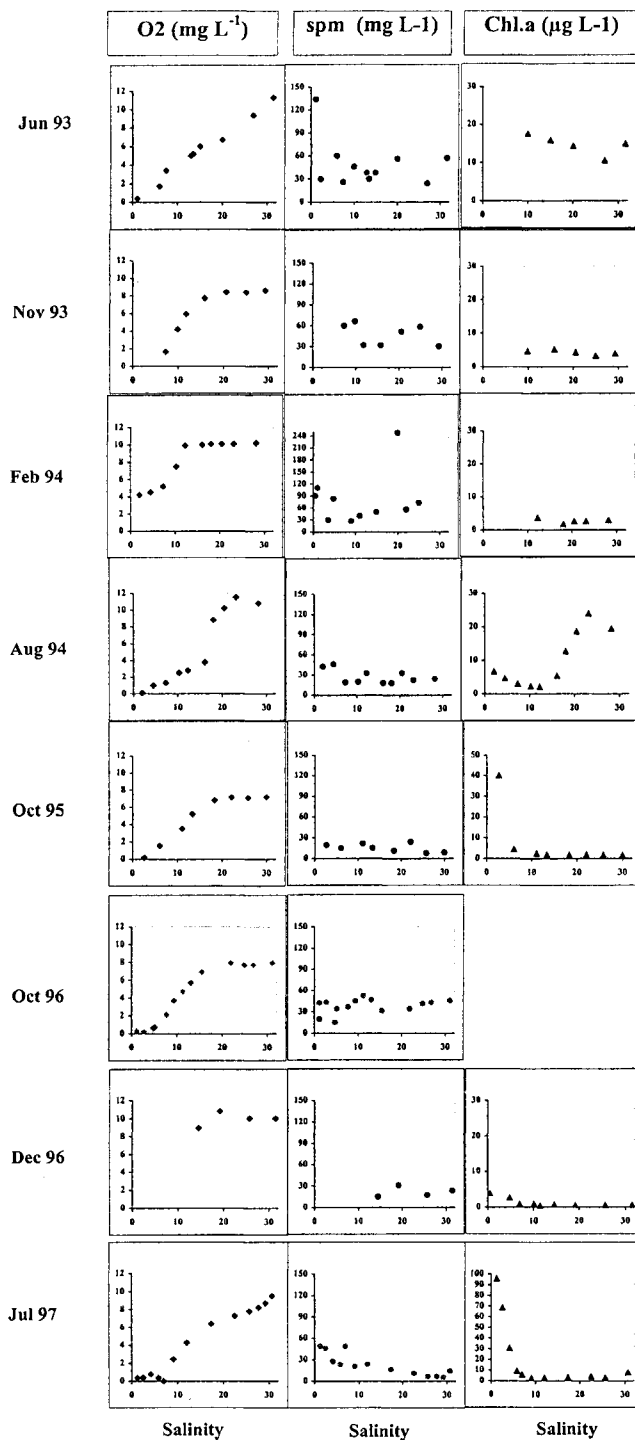


Fig. 4. Longitudinal profiles of dissolved oxygen (O₂, mg l⁻¹), suspended matter (spm, mg l⁻¹) and Chlorophyll a (Chl.a, µg l⁻¹) in the Scheldt estuary.

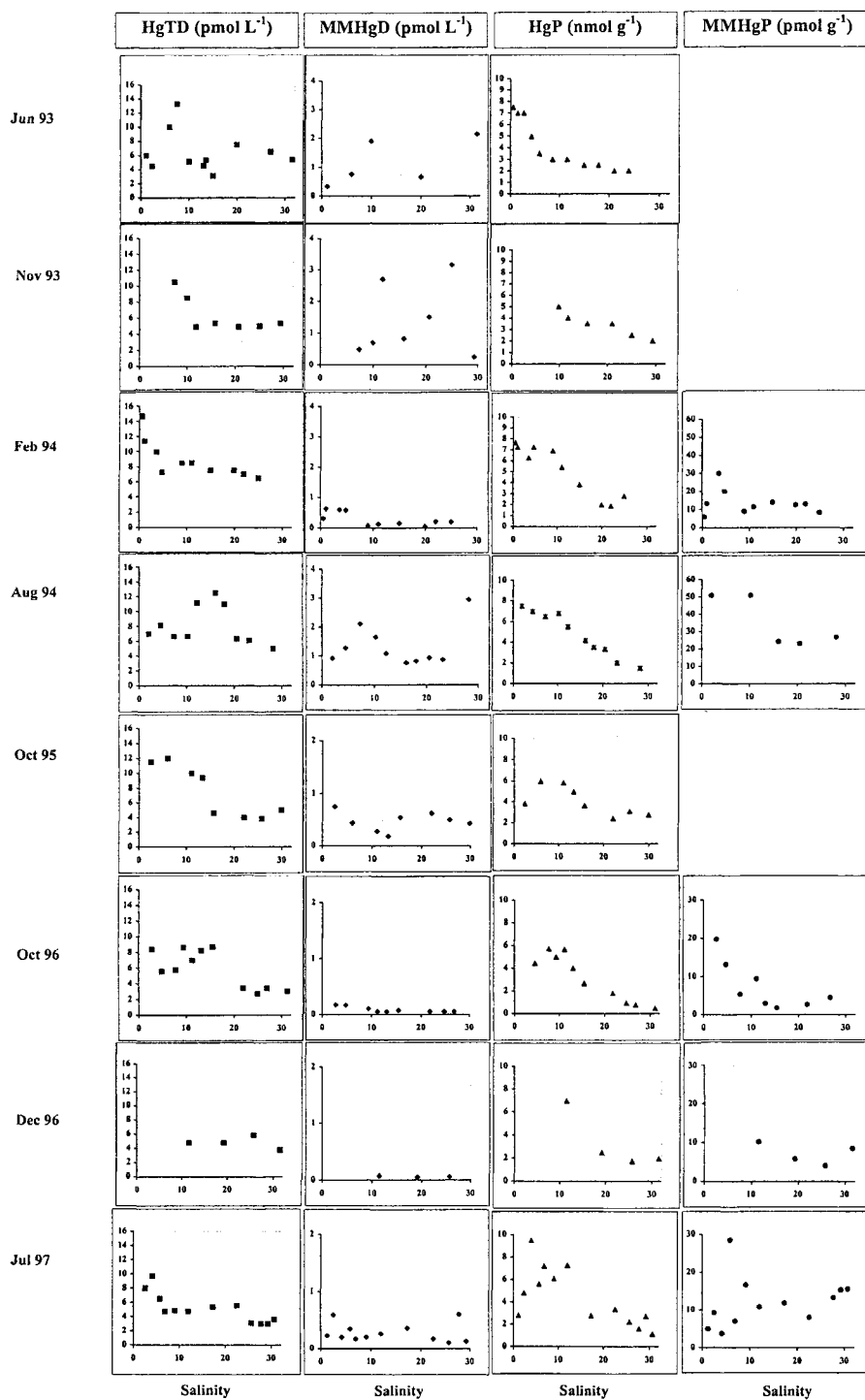


Fig. 5. Longitudinal profiles of total dissolved Hg (Hg_{TD} , pmol l^{-1}), dissolved methylmercury (MMHg_{D} , pmol l^{-1}), particulate mercury (Hg_{P} , nmol g^{-1}) and particulate methylmercury (MMHg_{P} , pmol g^{-1}) concentrations in the Scheldt estuary.

slow decrease towards the mouth. In summer, Hg_{TD} concentrations are low in the fluvial part, increase in the low salinity range or in the mid-estuary and sometimes show an increase in the lower estuary. Hg_P concentrations do not show any seasonal trend but an evolution can be observed with maximum Hg_P values in the fluvial end member prior to 1995 and maximum values in the salinity range 6–12 from 1995 onwards. The decrease in Hg_P towards the mouth is generally not linear, showing first a rapid removal followed by a slower decrease at higher salinities.

In winter, $MMHg_D$ concentrations are much lower (about four times considering mean values over the estuary) than in summer and autumn. The concentration ranges are the following: 0.055–0.65 $pmol\ l^{-1}$ in winter and 0.35–2 $pmol\ l^{-1}$ in summer prior to

1995 and 0.050–0.075 $pmol\ l^{-1}$ in winter and 0.075–0.6 $pmol\ l^{-1}$ in summer in the recent period. In winter, maximum concentrations are found in the upper estuary (salinities 1–5) while they remain relatively constant in the lower estuary. The percentage of $MMHg_D$ to Hg_{TD} ranges from 0.7% to 8% during the February 1994 cruise.

In summer, the profiles of $MMHg_D$ concentration vs. salinity observed in June 1993, August 1994 and July 1997 are very similar. $MMHg_D$ concentrations are low at low salinity, they show a first increase in the salinity range of 3–12, a decrease in the mid-estuary and a second increase in the lower estuary, at $S = 25–30$. During the July 1997 cruise, the high $MMHg_D$ values in the upper estuary correspond with high $MMHg_P$, POC and Chla and low oxygen levels. The higher $MMHg_D$ values at the mouth extend

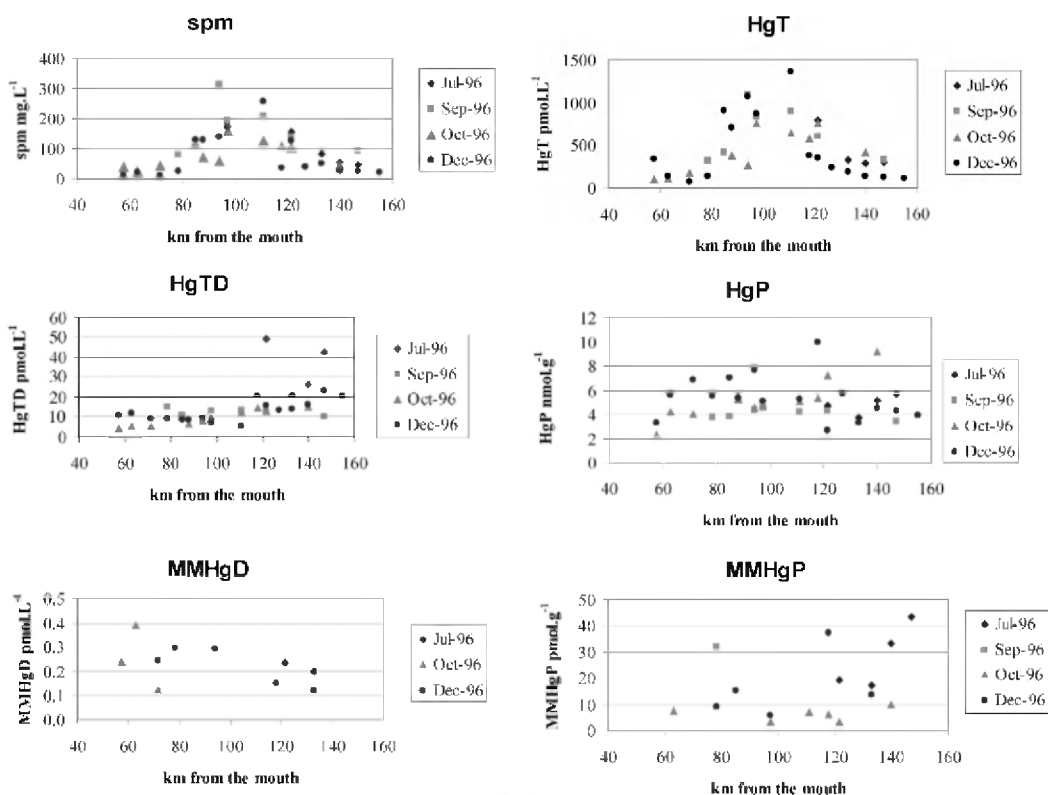


Fig. 6. Longitudinal profiles of suspended matter (spm), total Hg (Hg_T), total dissolved Hg (Hg_{TD}), particulate mercury (Hg_P), dissolved methylmercury ($MMHg_D$) and particulate $MMHg$ ($MMHg_P$) concentrations in the Scheldt river between Antwerp and Ghent. Sampling stations are plotted as distance from the mouth of the river as there is no salinity gradient in the riverine section.

further in the coastal-estuarine zone (see further). Much higher percentages of MMHg_D to Hg_{TD} were observed in summer than in winter: during the July 1997 cruise they ranged from 2.1% to 20%. A good inverse correlation between Hg_R (dissolved reactive mercury) and MMHg_D was observed ($r = 0.73$ and 0.82 for summer and winter, respectively) (Baeyens et al., 1998b).

Highest MMHg_P concentrations are found in the upper estuary, while in the lower estuary generally lower and more constant values are observed. The

summer values are generally higher than the winter ones, but this is not the case for the winter 1996 and summer 1997 surveys that are comparable. Compared to the fraction of MMHg_D to Hg_{TD} (cruise averages between 1.3% and 20%), the fraction of MMHg_P is much lower. MMHg_P accounts for 0.27–0.90% (cruise averages) of the Hg_P . The MMHg fraction in the dissolved phase relative to the total MMHg concentrations increases from winter (1.3–3.2%) to summer (5.6–20%) with an intermediate value in fall. The K_D values for MMHg are lower in

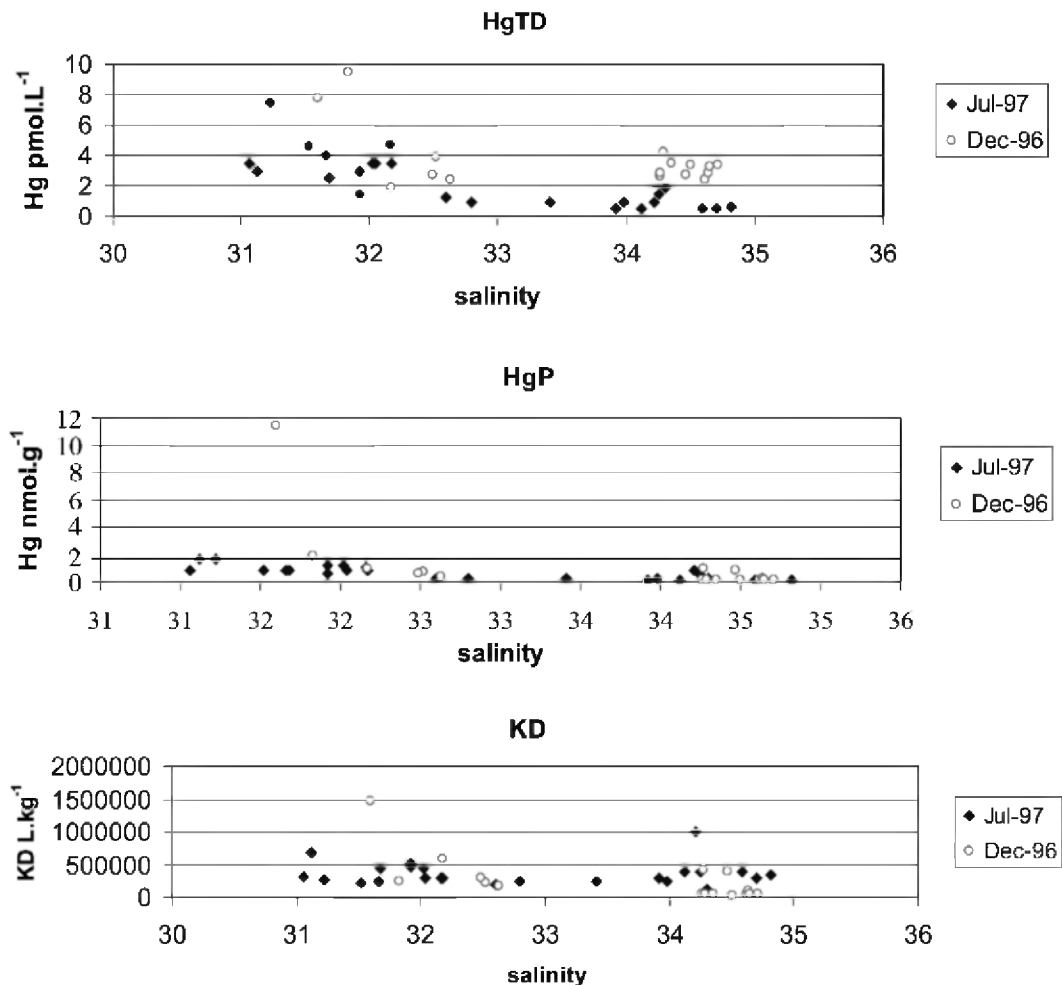


Fig. 7. Total dissolved (Hg_{TD}) and particulate mercury (Hg_P) concentrations and their distribution coefficient (K_D) vs. salinity in the Belgian coastal zone.

the summer (30,000–65,000) than in autumn and winter (77,000–114,000).

3.3. Hg speciation in the sediments of the Scheldt river

The vertical sediment profiles of mercury and methylmercury, obtained by sampling the muddy central part of the intertidal flat Groot Buitenschoor in the Scheldt estuary (located at the border of Belgium and the Netherlands) in August 1990 show

an increasing trend in both mercury and methylmercury with depth (Leermakers et al., 1993). This is in agreement with the observed decrease in mercury concentrations in the water column in the last decade. Total mercury concentrations varied from 3.5 to 7 nmol g⁻¹ with MMHg concentrations varying from 25 to 110 pmol g⁻¹. The ratio of methylmercury to total mercury varied between 1% and 1.5%. In the top layer relatively higher MMHg/total Hg ratios were found.

From 1992 to 1993, seasonal sampling was performed over the entire Groot Buitenschoor mud flat

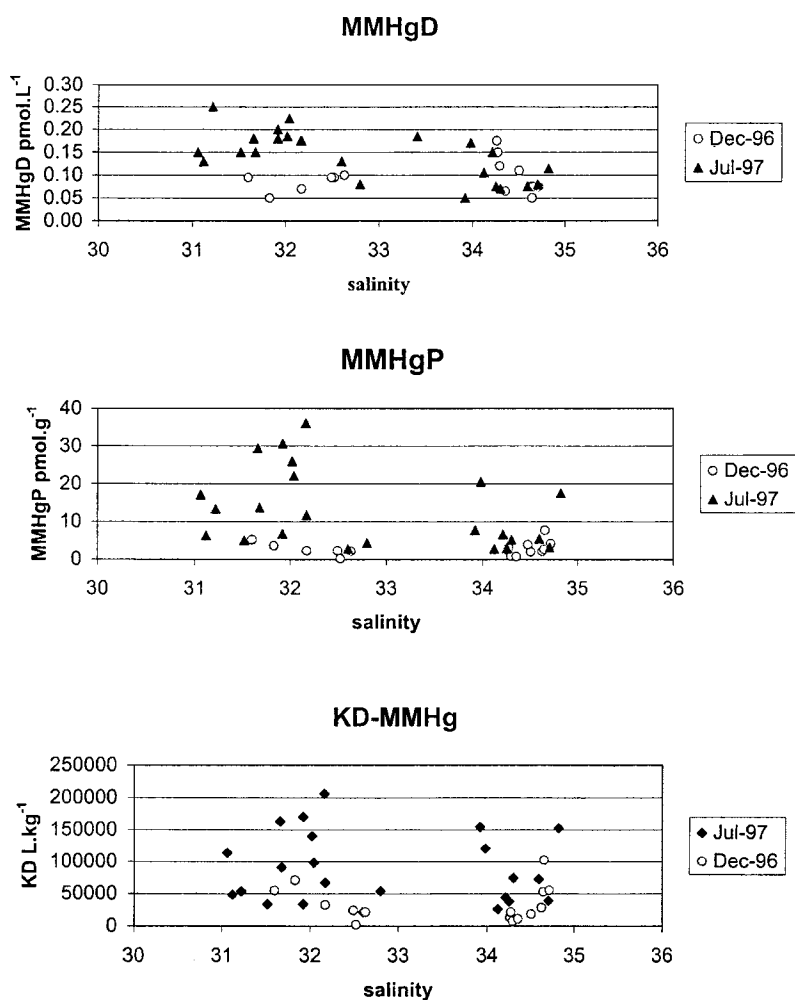


Fig. 8. Dissolved methylmercury (MMHg_D) and particulate methylmercury (MMHg_P) concentrations and their distribution coefficient (K_D MMHg) vs. salinity in the Belgian coastal zone.

(Muhaya et al., 1997). Total mercury concentrations in surface sediments (0–5 cm) ranged from 0.7 to 9.5 nmol g⁻¹ with 4–30 pmol g⁻¹ in the MMHg form, accounting for 0.4–0.8% of the total mercury present. Both total mercury and MMHg concentrations increase with increased organic matter content and increased fine grain size fraction. MMHg concentrations are significantly lower in winter compared to the other seasons.

In 1995, sediments from the navigation channel were taken along the salinity gradient. Total Hg concentrations ranged from 0.02 to 3.7 nmol g⁻¹ and MMHg concentrations from 0.035 to 2.4 pmol g⁻¹. Higher levels were observed in the upper estuary and also at the mouth of the estuary.

3.4. Hg speciation in the fluvial part of the Scheldt river

Water samples of the Scheldt river were collected in July, September, October and December 1996. Concentrations of dissolved and particulate total mercury and methylmercury are shown in Fig. 6. Total Hg concentrations ranged from 72 to 1360 pmol l⁻¹ and followed the spm concentrations. Hg_{TD} ranged from 5 to 49 pmol l⁻¹ and increased in the most upstream stations. Hg_P ranged from 2.3 to 9.1 nmol g⁻¹ and showed no particular pattern. MMHg_D

ranged from 0.1 to 0.39 pmol l⁻¹ and MMHg_P from 3.1 to 43.5 pmol g⁻¹. The MMHg concentrations are comparable to those found in the estuary and no seasonal variations could be observed.

3.5. Hg speciation in the Belgian coastal waters

Distribution of Hg_{TD} and Hg_P in the Belgian coastal waters in December 1996 and July 1997 is shown in Fig. 7 as a function of salinity. Hg_{TD} concentrations range from 0.5 to 9.5 pmol l⁻¹ and Hg_P from 0.1 to 2.2 nmol g⁻¹, with 1 exceptionally high value of 11.3 nmol g⁻¹ at a sludge disposal site (station 700). In the offshore stations Hg_{TD} concentrations are generally higher in winter than in summer while for Hg_P the reverse is observed, resulting in higher *K_D* rates in the summer. Hg_{TD} and Hg_P concentrations in the low salinity zone are similar in summer and in winter.

Distribution of MMHg_D and MMHg_P in the Belgian coastal waters in December 1996 and July 1997 is shown in Fig. 8. POC, PON, DON and Chl a distributions are shown in Fig. 9. MMHg_D vary from 0.05 to 0.25 pmol l⁻¹ in summer and from d.l. to 0.23 pmol l⁻¹ in winter and those of MMHg_P from 1.8 to 36 pmol g⁻¹ in summer and from 0.9 to 21 pmol g⁻¹ in winter. The *K_D*s range from 9000 to 219,000 l kg⁻¹. The percentages of MMHg to total

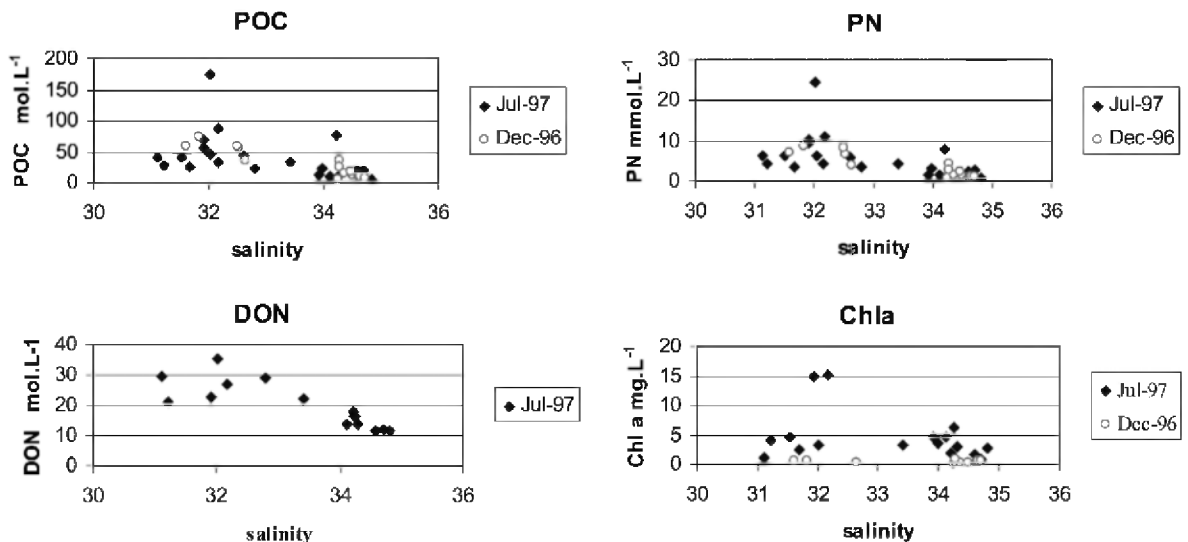


Fig. 9. Particulate organic carbon (POC), particulate nitrogen (PN), dissolved organic nitrogen (DON) and Chlorophyll a (Chl a) concentrations vs. salinity in the Belgian coastal zone.

Hg in the dissolved phase vary from 3.2% to 21% in summer and from 0.3% to 6.6% in winter and in the particulate phase from 0.3% to 8.8% in summer and from 0.1% to 5.4% in winter.

Sampling stations can be divided in a low salinity and a high salinity group. At high salinities (> 32), seasonal differences in MMHg concentrations, in the dissolved as well as the particulate phases, are insignificant. However, in the low-salinity zone (salinity < 32), concentrations are significantly higher in summer than in winter. The low salinity zone is strongly influenced by the Scheldt outflow, coastal inputs and resuspended bottom sediments.

In summer 1997, a dilution profile between the coastal and the marine water mass is observed for MMHg_D , MMHg_P , DON and somewhat less for POC. In winter 1996, only MMHg_P shows such a behavior. As a consequence, positive correlations between MMHg_D , MMHg_P , DON and POC can be found in summer (e.g., MMHg_D vs. DON and MMHg_D vs. POC, Fig 10).

Sediment samples in the coastal zone were collected in October 1995 and on four occasions in 1999. The 1995 samples consisted of a single grab sample per station (all taken at coastal stations and in the mouth of the estuary), whereas the 1999 samples

Table 3

Hg concentrations in sediments of the Scheldt estuary and Belgian coastal zone

Date	Station	Hg (nmol g^{-1})	MMHg (nmol g^{-1})
<i>Scheldt estuary</i>			
Oct 1995	S01	1.32	0.790
Oct 1995	S04	0.275	0.215
Oct 1995	S07	0.160	0.110
Oct 1995	S09	0.020	0.035
Oct 1995	S12	0.145	0.114
Oct 1995	S15	3.67	2.35
Oct 1995	S18	2.12	0.724
Oct 1995	S22	2.15	0.872
<i>Belgian coastal zone</i>			
Nov 1999	SE1	0.0177	0.08
Nov 1999	SE2	0.0435	0.07
Nov 1999	SE3	0.0177	0.074
Nov 1999	SE4	0.0423	0.13
Nov 1999	SE7	0.0161	0.05
Nov 1999	SE8	0.134	0.66
Oct 1995	115	1.25	1.200
Oct 1995	120	0.21	0.225
Oct 1995	130	1.415	2.360
Oct 1995	700	3.505	1.335
Oct 1995	150	1.1	0.560
Oct 1995	B03	0.275	0.025
Oct 1995	B10	0.585	2.900

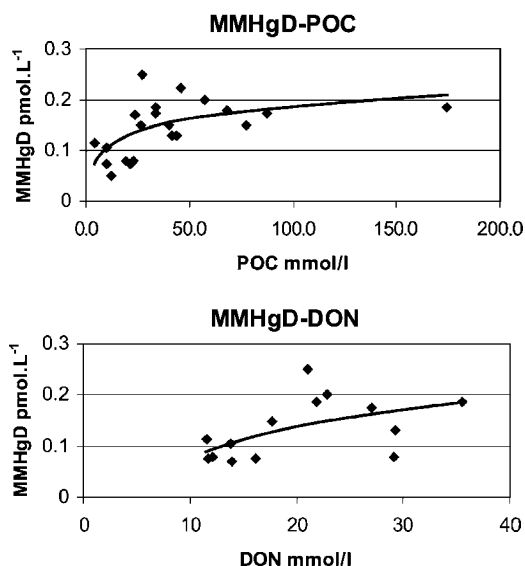


Fig. 10. Dissolved methylmercury concentrations vs. particulate organic carbon and dissolved organic nitrogen in the Belgian coastal zone.

consisted of 10 grab samples at each station (taken on sand banks and at a dredged sludge disposal site, St8). The results of the 1995 samples and October 1999 samples (St1 to St8) are shown in Table 3. Total Hg concentrations in the sandy sediments (St1 to St7) range from 0.01 to 0.14 nmol g^{-1} and MMHg concentrations from 0.02 to 0.16 pmol g^{-1} . In the stations, with muddy sediments Hg concentrations range from 0.035 to 3.5 nmol g^{-1} and MMHg from 0.03 to 2.9 pmol g^{-1} . Although the 1995 data are less representative than the 1999 ones as only one grab sample per station was taken, they demonstrate the high levels that can be found in coastal sediments. The spatial variability of the MMHg concentrations found at St8 can be expected at the other coastal stations.

3.6. Hg speciation in the Southern Bight of the North Sea and English Channel

The English Channel and Central North Sea were sampled in 1991, 1993 and 1998. Hg concentrations

Table 4

Concentrations of total Hg (Hg_T), total dissolved Hg (Hg_{TD}), particulate mercury (Hg_P) and total methylmercury ($MMHg_T$) in surface waters of the North Sea and English Channel

Date	Station	Salinity	Spm ($mg\ l^{-1}$)	Hg_T ($pmol\ l^{-1}$)	Hg_{TD} ($pmol\ l^{-1}$)	Hg_P ($nmol\ g^{-1}$)	Hg_P ($pmol\ l^{-1}$)	$MMHg_T$ ($pmol\ l^{-1}$)
Jun 1991	7	35.08		3.00				
Jun 1991	11	35.32		2.00				
Jun 1991	13	35.39		0.95				
Jun 1991	17	35.54		1.25				
Jun 1991	18	35.58		1.45				
Jun 1991	22	35.45		1.75				
Jun 1991	24	35.45		2.25				
Jun 1991	25	35.44		2.50				
Nov 1993	A09	34.75	5.2	4.35				0.17
Nov 1993	A08	34.85	9.3	1.60				0.18
Nov 1993	A07	34.83	5.6	0.75				0.08
Nov 1993	A06	34.68	4.8	1.90				0.32
Nov 1993	A05	34.3	16.8	3.15				0.10
Apr 1998	CH1	35.26	2.2	1.56	1.43	0.059	0.13	
Apr 1998	CH2	35.12	5.7	2.40	1.75	0.114	0.65	
Apr 1998	330	34.42	6.8	2.14	1.41	0.108	0.74	
Apr 1998	NS1	35.17	2.7	1.74	1.54	0.076	0.21	
Apr 1998	NS2	35.06	4.9	2.59	1.74	0.172	0.85	
Apr 1998	NS3	34.31	7.7	2.43	1.80	0.082	0.64	
Apr 1998	NS4	33.96	3.1	3.06	1.44	0.524	1.63	
Sep 1998	CH1	35.13	0.47	1.00	0.92	0.170	0.08	
Sep 1998	CH2	35.18	1.1	1.32	1.03	0.264	0.29	
Sep 1998	330	33.69	6.8	2.42	1.64	0.115	0.78	
Sep 1998	NS1	35.11	2.1	1.49	1.14	0.167	0.35	
Sep 1998	NS2	35.07	2.7	3.44	1.70	0.646	1.75	
Sep 1998	NS3	34.33	1.7	1.90	1.37	0.312	0.53	
Sep 1998	NS4	34.3	2.3	1.89	1.27	0.267	0.62	

are reported in Table 4. Total Hg ranges from 0.75 to 4.35 $pmol\ l^{-1}$ with a Hg_{TD} fraction between 50% and up to 90%. The highest concentrations were found in the Seine Bay. Hg_P ranges from 0.059 to 0.646 $nmol\ g^{-1}$ and $MMHg_T$ from 0.077 to 0.324 $pmol\ l^{-1}$. The Hg concentrations do not show any significant changes between 1991 and 1998 and the data are in good agreement with previous measurements made by Cossa and Fileman (1991).

4. Discussion

4.1. Evolution of total Hg and $MMHg$ concentrations in the Scheldt estuary

The decreasing best linear fit through the cruise averaged dissolved and particulate Hg concentrations in the Scheldt estuary is in accordance to the de-

crease in riverine inputs of Hg measured in the freshwater end member at Schelle (OSPARCOM, 1998) (Table 2). A 65% reduction of the Hg inputs to water was calculated for the period 1985 and 1995 due to measures taken in the chlor-alkali and phosphate industry and the installation of amalgam separators in dentistry (Andersen and Niilonen, 1995). Long term measurements of particulate Hg concentrations at the Belgian Dutch border reveal the history of Hg pollution in the Scheldt estuary (Fig. 11).

In addition to the decrease in the Hg concentrations, the overall water quality of the Scheldt estuary also significantly improved in the last decade (Van Maldegem et al., 1993; Baeyens, 1998; Zwolsman, 1999; Nolting et al., 1999). The most pronounced changes are: (1) a decrease in the suspended matter concentrations in the upper estuary; (2) an increase in the redox potential in the upper estuary, all over the year with a faster restoration of dissolved oxygen

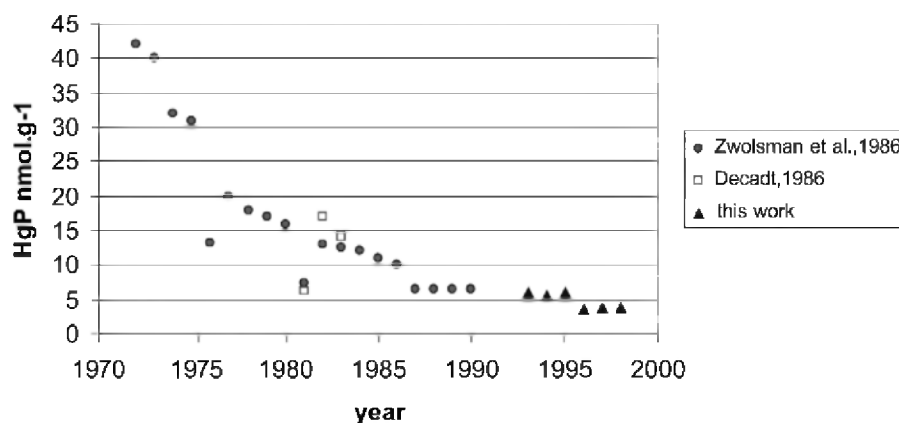


Fig. 11. Long-term evolution of the particulate mercury concentration in the Scheldt estuary at the Dutch–Belgian border (55 km from the mouth).

in the upper estuary; (3) a reduction of the organic loading: the organic matter content of fluvial spm has decreased from 40–60% to 10–15%; (4) an increase in the phytoplankton concentration in the upper estuary; (5) higher pH values all over the estuary in the winter and a less pronounced pH minimum in spring and summer; (6) lower Cd, Cu, Pb and Zn concentrations in the estuary. These changes may have an effect on the speciation and methylation of mercury. In addition, large amounts of polluted sediment have been removed from the upper estuary. Between 1992 and 1996, 2.5 Mton of silty sediment has been dredged from the entrance channels to the harbor of Antwerp, twice as high as the external supply of mud to this area from the Scheldt river and North Sea (Salden, 1998 in Zwolsman, 1999).

4.2. Methylation of Hg in the Scheldt estuary and the coastal North Sea

There are a number of processes in an estuary that induce spatial and temporal variability of metal concentrations. In the Scheldt estuary, a polluted partially anoxic estuary, four major causes can be distinguished (Baeyens, 1998):

1. the Scheldt is a tide-governed estuary, which means greater residence times;
2. the upper estuary receives large inputs of biodegradable organic matter which leads to oxy-

gen depletion in winter and to anoxic conditions in summer;

3. inputs of toxic pollutants from the industrial zone of Antwerp occur in the upper estuary;
4. the anoxic zone, the zone of pollutant input and the zone of the turbidity maximum coincide geographically.

In summer, the upper estuary can be subdivided into two parts: the most upstream part with low dissolved MMHg concentrations and the downstream part with higher dissolved MMHg concentrations. The increase of the MMHg concentration in the salinity range 3–12, corresponds to the reappearance of dissolved oxygen in the water column. The presence of dissolved sulphide (0.2–0.9 μM of total dissolved sulphide) in the anoxic, most upstream part of the estuary (Zwolsman and van Eck, 1993) results in a scavenging of dissolved Hg^{2+} species from the water column. These sulfide concentrations are insufficient for the formation of polysulfides (Davies-Colley et al., 1985) but sufficient for the removal of all Hg^{2+} from solution by sulfide precipitation. Indeed, in the upstream Scheldt estuary at a pH of 7.5, a total dissolved sulphide concentration of 0.5 μM ($[\text{S}^{2-}] = 1.8 \times 10^{-14} \text{ M}$) and a total dissolved Hg concentration of 10^{-11} M (winter concentration), the solubility product equals about 10^{-25} which is by far higher than the solubility of cinnabar which is about 10^{-54} (Morel et al., 1998). Possible reasons for the

fact that we find in summer still about one third of the winter concentration are: (1) the strong complexation of Hg with organic ligands such as humic acids (Mantoura et al., 1978), and (2) colloidal precipitates that pass the 0.45- μm Millipore filter (Guentzel et al., 1996). The amount of substrate available for methylation in the water column as well as in the sediments is, however, significantly reduced. In addition, MMHg produced in the summer period will also interact with the high concentration of sulfides and suspended matter and enrich the particulate rather than the dissolved phase. For those reasons, no high dissolved MMHg concentrations will be found in the anoxic most upstream estuarine area. However, once the oxygen level slowly restores in the water column the conditions for a high sulfate reduction rate (SRR) are still good, especially in the sediments, while the sulfide concentrations in the water column drop; this is the zone where the MMHg_D concentrations reach their maximum.

Outside the upper estuary ($S > 10$) the dissolved MMHg levels in winter are low and comparable to the values in the Southern Bight (average of 0.20 pmol l^{-1} in February 1994 and 0.06 pmol l^{-1} in December 1996). This shows that the production of MMHg in winter is limited to the upper estuary. While in summer the decrease of total dissolved Hg is very quick, MMHg concentrations drop much more slowly. The faster removal of Hg^{2+} compared to MMHg can be attributed to (1) a differential association with Fe and Mn oxides, precipitating in the middle estuary (Paucot and Wollast, 1997) and (2) the difference between Hg^{2+} and MMHg species in complexation with organic ligands. From a theoretical calculation (Leermakers et al., 1993), it appears that at $S = 12.5$, 63% of the total dissolved inorganic Hg species are chloride compounds and only 37% is complexed to humic acids, while still 96% of the MMHg species at that salinity are present as humic acid complexes.

The sediments are an important production site of MMHg and a potential source for this compound in the water column after resuspension of the upper sediment layer and mobilization from interstitial waters. MMHg concentrations in suspended matter in the upper estuary are comparable to the concentrations of MMHg in the organic-rich sediments of the mud flats (Muhaya et al., 1997). Incubation experi-

ments performed on sediments of mud flat Groot Buitenschoor confirmed the importance of sulfate reducing bacteria in the methylation of mercury (Leermakers et al., 1993). In the sediments of the Groot Buitenschoor the SRR increases in spring as temperature rises, is maximal in summer, decreases in autumn and is minimal in winter (Panutrakul, 1993). MMHg concentrations in these sediments follow the same trend as the SRR.

Seasonal variations are observed in the distribution coefficient (K_D) of MMHg with lower values in summer (30,000–65,000) than in winter (77,000–114,000). The MMHg fraction in the dissolved phase relative to the total MMHg concentrations, increases from winter (1.3–3.2%) to summer (5.6–20%). This supports the observation that reducing conditions in the sediments promote the liberation of MMHg from sediments (Bloom et al., 1999). In Lavaca Bay sediments similar variations in the K_D values in sediments were found (Bloom et al., 1999).

In summer, dissolved and particulate MMHg concentrations observed at the mouth and in the coastal-estuarine zone ($S < 32$) are increased. The higher MMHg concentrations found in those oxygenated waters may be related to at least two factors.

1. *Mobilisation of MMHg from sediments.* Reducing conditions in the muddy sediments of the estuarine coastal area may favor, especially in summer, the production and mobilisation of MMHg. After the spring phytoplankton bloom, large amounts of fresh organic matter produced in the euphotic zone are deposited resulting in reducing conditions in the sediments. In combination with the higher temperature in summer the activity of the sulphate reducing bacteria and hence the production of MMHg, is stimulated. Like in the upper Scheldt estuary, the resuspension of fine sediment grains enriched in MMHg and the subsequent adjustment to the water column K_D is an input route for the coastal-estuarine zone. Under less reducing (suboxic) conditions, bacterial degradation of organic matter in the sediments is accompanied by the reduction and dissolution of Fe and Mn. Important seasonal mobilisation of Fe and Mn from sediments has been observed in the North Sea (Dehairs et al., 1989; Schoemann et al., 1998). Fe and Mn remobilisation from sediments may be accompanied by the mobilisation of MMHg from sediments (Bloom et al., 1999).

2. *Direct influence of phytoplankton blooms and associated pelagic heterotrophs.* Pongratz and Heumann (1998) found maximal methylated species (DMHg and MMHg) in the remote ocean regions (Southern Atlantic, Arctic, Southern Pacific) in areas with highest biological activity and showed the production of MMHg and DMHg by polar macroalgae in model experiments.

Cleckner et al. (1999) showed that Hg could be methylated by periphyton communities of the Everglades and that SRB were methylating Hg. Methylation was found to be coupled to photosynthesis. Photosynthetic microbial sulfide oxidation may stimulate methylation through the removal of sulfide and/or providing substrate for SRB.

The coastal estuarine waters are characterised by increased Chla, POC, PN, DOC concentrations in summer due to the development of *phaeocystis* sp. phytoplankton blooms and also of increased MMHg concentrations. Colonial *phaeocystis* sp. forms can be considered as reducing microenvironments playing an important role in the speciation of elements such as Fe and Mn (Davidson and Marchant, 1987; Hutchins and Bruland, 1994). During summer, significantly higher amounts of dissolved gaseous Hg, and lower amounts of reactive Hg were also found in that zone (Baeyens and Leermakers, 1998).

The relative importance of both sources (sediments and phytoplankton) has still to be determined.

Knowing the average MMHg concentrations in the Scheldt estuary before and after 1995 (Table 2) and knowing the average fresh water rate ($100 \text{ m}^3 \text{ s}^{-1}$), $6.4 \text{ mol MMHg year}^{-1}$ (period before 1995) and $1.4 \text{ mol MMHg year}^{-1}$ (after 1995) must be produced in the Scheldt. Mason et al. (1999) estimated that in the much larger Chesapeake Bay ecosystem $63.2 \text{ mol MMHg year}^{-1}$ must be produced.

Acknowledgements

The authors gratefully acknowledge the technical assistance of the captain and crew members aboard R.V. Belgica, R.V. Argus, vessels Veremans and Scaldis II. They thank the MUMM for providing ship time. We are particularly indebted to the Ministry of Science Policy for their continuous and

lasting interest regarding oceanographic research, and more specifically for the financial support they offered to us in the previous years.

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