

A box-model of metal flows through the Scheldt estuary (1981–1983 and 1992–1995)

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Abstract

The behaviour of Cu, Zn, Cd and Pb in the Scheldt estuary was investigated in the periods 1981 to 1983 and 1995. The Hg behaviour was studied between 1992 and 1994. A box model was used to establish the relationship between the trace metal inputs and the fate of these pollutants in the Scheldt estuary. Annual budgets were calculated for particulate and dissolved trace metals. For Hg, seasonal budgets of the various species (inorganic Hg, methylmercury, Hg⁰) could also be calculated. These budgets allow an evaluation of the consistency of each individual flux or process, such as the inputs of the various metals into the North Sea, the sedimentation flux of particulate metals in the area of high turbidity, the evasional fluxes and the formation rates of Hg⁰, etc. in relation to the other ones.

Introduction

The river Scheldt crosses France, Belgium and The Netherlands on its way to the North Sea (Figure 1). It has a length of 355 km and a drainage area of 22 000 km², mainly on Belgian territory. The average water flow is about 100 m³ s⁻¹ and varies from 20 m³ s⁻¹ during summer to 400 m³ s⁻¹ during winter. The Scheldt estuary is a macrotidal coastal plain estuary, with an average tidal range of 4 to 5 m and an average depth of 11 m. Under normal water flow conditions the estuary is well mixed. The residence time of the water in the estuary is of the order of one to three months, depending on the river flow rate.

From a morphological point of view the estuary can be divided into three zones. The lower estuary, called Western Scheldt, extends from the North Sea to the Belgian-Dutch border (km 0–60), the upper estuary is situated between the border and the river Rupel (km 60–100) and the fluvial river (fresh water zone) is situated between the Rupel mouth and Ghent (km 100–160), where a tidal range of two meter still exists. The upper estuary consists of one channel with a width between 0.4 and 2 km. The lower estuary is wider, up to 8 km, and consists of deep and shallow parts, with

different ebb and flow channels. The estuary, which is the zone under investigation, is situated between Rupelmonde and Vlissingen, and has a length of about 100 km.

From a physico-chemical point of view, the estuarine mixing zone can further be subdivided (e.g. Baeyens & Monteny, 1988). Zone I, situated from Antwerp to the confluence of the rivers Scheldt and Rupel, has salinities ranging from 0 to 2 psu, clay bottom sediments, low sedimentation rates and oxygen depletion throughout a large part of the year. Zone II is situated between the Belgian Dutch border and the city of Antwerp and is characterised by a turbidity maximum, high sedimentation rates, fine grain bottom sediments (Wartel, 1977), oxygen undersaturation particularly in the summer and salinities varying from 2 to 10 psu. Zones III and IV correspond to the Western Scheldt, which is characterised by coarse bottom sediments, aerobic conditions in the water column and salinities varying from 10 to 30 psu. For a better representation of the various metal-fluxes in the downstream estuary, especially the dissolved metal-flows, this zone has been further subdivided in zone III and zone IV. In zone III the oxygen concentration progressively increases due to re-aeration, and re-oxidation

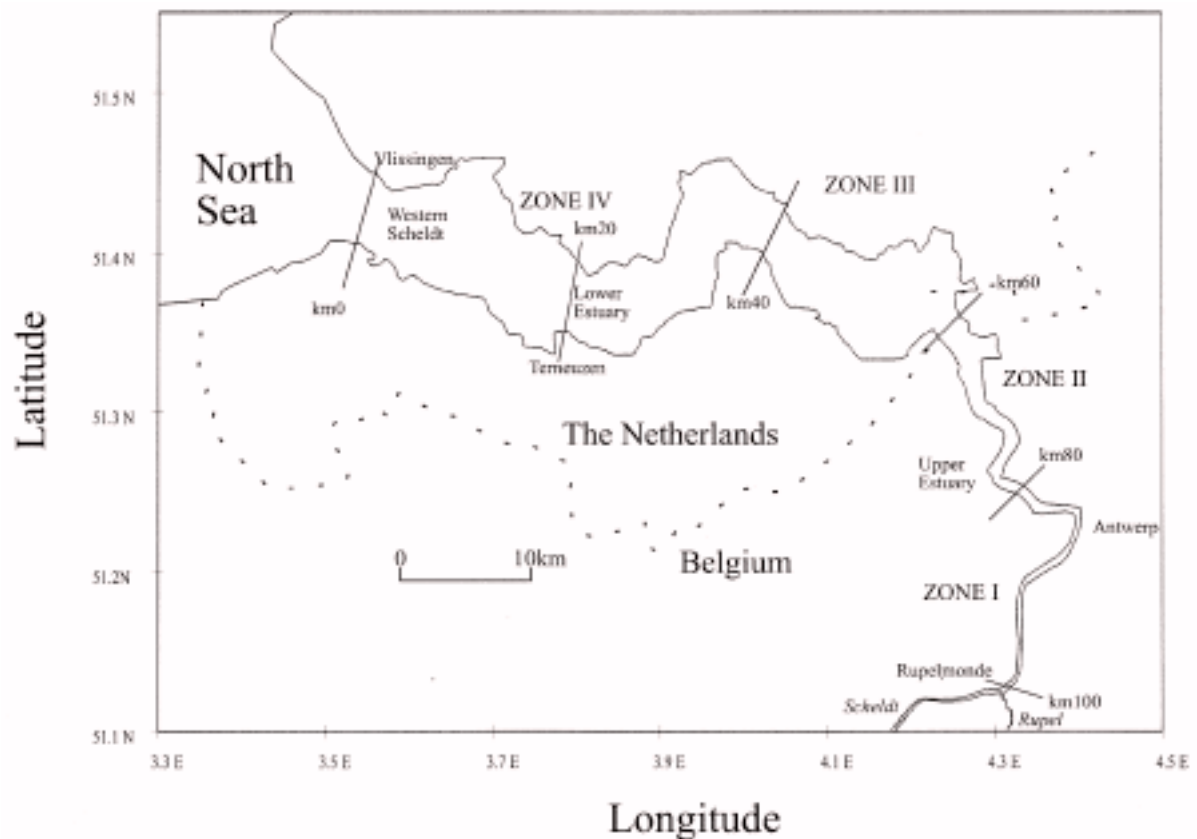


Figure 1. Map of the Scheldt estuary.

processes occur (salinity range from 10 to 20 psu). Zone IV, the mouth of the estuary, is always aerated and in the summer even oversaturated (salinity range from 20 to 27.5 psu).

Both the fluvial and the upstream river are heavily polluted as a result of large domestic, industrial and agricultural waste water discharges. A large fraction of the waste water is discharged without prior treatment, causing an intensive degradation of organic matter in the fluvial and upstream estuary. In the upper estuary a permanent oxygen undersaturation, and often a complete depletion is common in the water column (Figure 2). During summer, an anoxic region (km 60–100) from the mouth of the Rupel to the Belgian–Dutch border prevails. In winter, the entirely anoxic region is much smaller or missing, though a pronounced undersaturation of oxygen is still present.

The particulate matter flows (Figure 3) are based on average turbidity values, fresh water flow rates including side canals, discharge pipes, etc., sedimentation fluxes and bottom transport (the saline bottom cur-

rent transports marine derived material into the estuary). Previous sediment mass balance estimates for the Scheldt, based on measurements from the early eighties, were made by van Eck (1991) and Baeyens et al. (1998c), but they have been updated and refined for the downstream part of the estuary, taking into account the particulate metal-mass balances for that area. The assumption was made that the sediment mass balance estimates did not change substantially over a period of ten years (early eighties to early nineties).

In zones I and II, also called boxes, two separate sedimentation fluxes are presented. This is also the case for the particulate matter flows. One sedimentation flux is related to the sedimentation of continental derived particulate matter (downstream transport), arriving from the previous box. The second sedimentation flux is due to the sedimentation of particles, transported upstream by the more saline bottom current, after encountering and mixing with the downstream transported material.

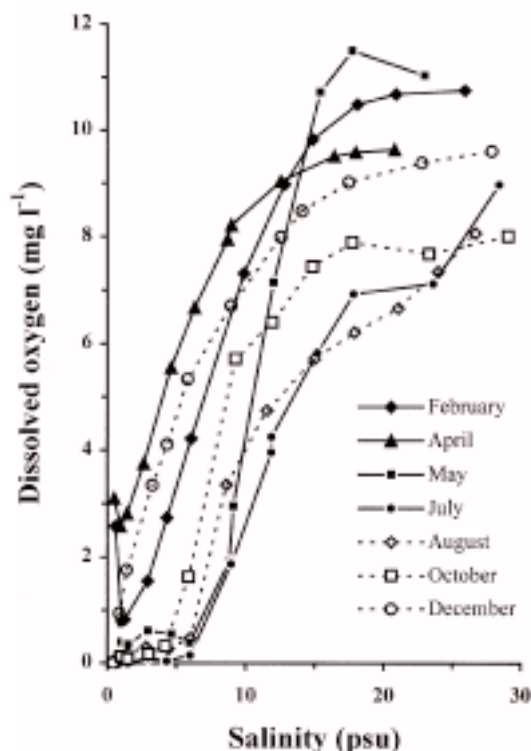


Figure 2. Dissolved oxygen concentrations in the Scheldt estuary.

Box I also receives an important lateral input resulting from anthropogenic activities in the area around the town of Antwerp. Box II is the area of high sedimentation. About two third of the particulate metals entering this box will accumulate at the bottom.

The inputs, discharges and/or losses of heavy metals from Belgium to the aquatic system reported in the Progress Report on the Protection of the North Sea, edited by Andersen and Niilonen (1995), are much higher than the Scheldt inputs into the North Sea. Furthermore, the Scheldt estuary contributes for about 90% of the total input of Belgium to the North Sea. Table 1 shows the aquatic and atmospheric emission of metals from the Belgian territory to the North Sea. This means that they were overestimated or that most of these aquatic inputs eventually accumulated in the sediments of the Scheldt and its tributaries.

Methods and results

The sampling and analytical methods used to determine the dissolved and particulate metal species are reported in related papers: for Cd, Cu, Pb and Zn in

Table 1. Aquatic and atmospheric emissions of metals by Belgium to the North Sea (Andersen & Niilonen, 1995)

		Water 10 ³ kg yr ⁻¹		Atmosphere 10 ³ kg yr ⁻¹	
		1985	1995	1985	1995
Hg	Point sources	0.3	0.1	13.3	7.2
	Diffuse	2.0	2.0	0.8	0.8
	Total	2.3	2.1	14.1	8.0
Cd	Point sources	14.7	2.5	11.2	3.6
	Diffuse	0.5	0.4	1.6	1.8
	Total	15.2	2.9	12.8	5.4
Cu	Point sources	42	21	132	55
	Diffuse	123	126	25	32
	Total	165	147	157	87
Pb	Point sources	58	29	320	294
	Diffuse	68	67	1387	311
	Total	126	96	1707	605
Zn	Point sources	284	127	483	414
	Diffuse	561	559	297	332
	Total	845	686	780	746

Baeyens et al. (1998a) for Hg in Baeyens (1992) and Baeyens et al. (1998b). In addition the assessment of the atmospheric Hg concentrations as well as the calculation of the evasion fluxes are described in Baeyens et al. (1991).

Mercury

The average concentrations of the various Hg species at the corresponding salinities are shown in Table 2. These values will be used to construct three Hg species budgets (total dissolved Hg, total dissolved methylmercury (MMHg), total particulate Hg) in the Scheldt estuary.

It appears clearly from these values and also from the particulate and dissolved Hg flows (see hereafter) that the particulate phase is the major carrier of Hg. The dissolved Hg fraction, relative to the particulate one, is highest at the mouth (about 6%), and decreases to about 2% in the upstream area. The dissolved Hg budget has thus only a small impact on the total Hg budget in the upstream estuary; its importance increases somewhat towards the mouth.

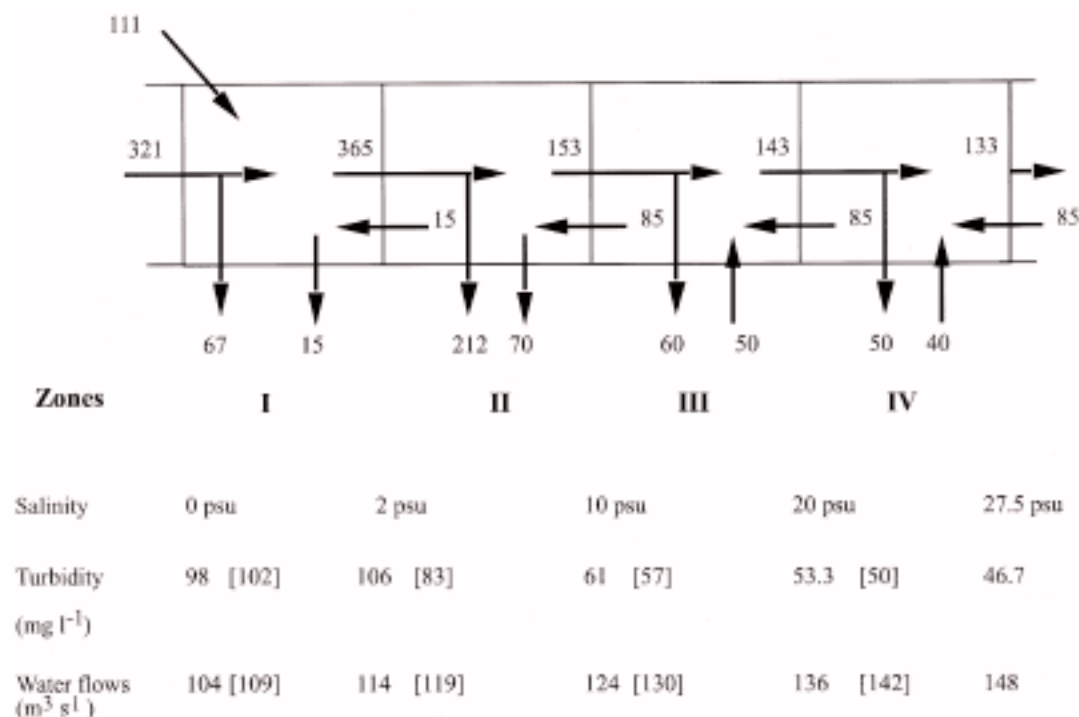


Figure 3. Particulate matter flows (10^6 kg yr^{-1}); 4 box model of the Scheldt estuary.

Cadmium, copper, lead and zinc

The average dissolved and particulate concentrations of the various metals at the corresponding salinities are shown in Table 3 for the 1981 to 1983 surveys and in Table 4 for the 1995 surveys. K_D values for the various metals and surveys are shown in Table 5.

Mercury species budgets

Mass fluxes were calculated in each of the four boxes of the Scheldt estuary for total particulate Hg, total dissolved Hg and total dissolved MMHg. The parameters used in these calculations are: (1) water flow rates for dissolved species; (2) particulate matter flows for particulate species; (3) average concentrations of the Hg species at the boundaries of the boxes and inside the boxes, which are assumed to be homogeneous; (4) an air-sea exchange model to estimate the evasion fluxes (Baeyens et al., 1991); (5) epibenthic fluxes based on Hg concentrations in the sediments (Leermakers et al., 1993) and on epibenthic fluxes of other metals in the Scheldt estuary (Baeyens et al., 1986).

Particulate mercury flows (Figure 4)

Box I: Two separate sedimentation fluxes are presented. One sedimentation flux is related to the sedimentation of continental derived particulate matter having a particulate Hg concentration of $1.46 \mu\text{g g}^{-1}$ (downstream transport) which sedimentates after entering the first box without further mixing with the material transported upstream by the more saline bottom current, having a particulate Hg concentration of $1.20 \mu\text{g g}^{-1}$. The second sedimentation flux is due to the sedimentation of the upstream transported particulates after mixing with the downstream transported material: the mixed material has a particulate Hg concentration of $1.44 \mu\text{g g}^{-1}$. This mixed material is also the material which is transported downstream to the next box.

The first box also receives an important lateral input, estimated at $160 \text{ kg Hg yr}^{-1}$ resulting from anthropogenic activities in the area around the town of Antwerp.

Box II: This is the area of high sedimentation. Due to this high sedimentation flux and the strong remobilisation of metals in the bottom sediments in this area (Baeyens et al., 1986; Leermakers et al., 1993), an

Table 2. Mercury concentrations in the 4 boxes of the Scheldt estuary

Species		Zone 1	Zone 2	Zone 3	Zone 4	Sea
Salinity	(psu)	0–2	2–10	10–20	20–27.5	32.5
Turbidity	(mg g ⁻¹)	102	83	57	50	
Sediment Hg	(μg g ⁻¹)		0.62	0.35	0.20	
Part. Hg	(μg g ⁻¹)	1.44	1.20	0.70	0.45	0.22
Part. Hg	(ng l ⁻¹)	147	100	40	22	22
Tot. diss. Hg						
summer	(ng l ⁻¹)	1.05	1.89	1.16	1.16	1.1
winter	(ng l ⁻¹)	2.65	1.72	1.57	1.45	1.2
Reactive Hg						
summer	(ng l ⁻¹)	0.45	0.78	0.55	0.55	
winter	(ng l ⁻¹)	0.55	0.49	1.06	1.33	
Diss. gas. Hg						
summer	(pg l ⁻¹)	83	85	80	108	
winter	(pg l ⁻¹)	41	49	48	48	
Diss. MMHg						
summer	(pg l ⁻¹)	183	335	181	382	
winter	(pg l ⁻¹)	105	83	23	39	

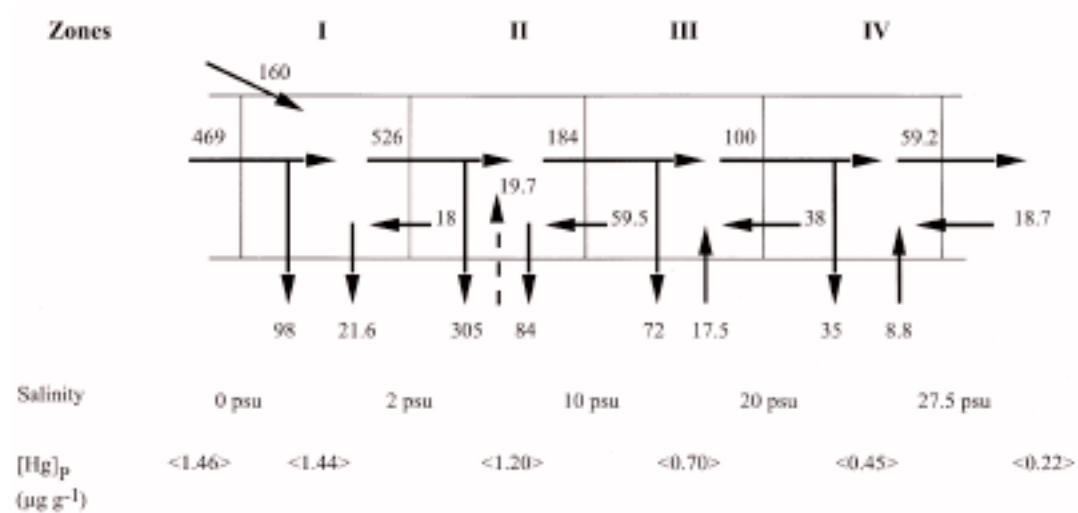
Figure 4. Particulate mercury flows (kg Hg yr⁻¹); 4 box model of the Scheldt estuary.

Table 3. Metal concentrations in the 4 boxes of the Scheldt estuary (1981–1983)

Species		Zone 1	Zone 2	Zone 3	Zone 4	Sea
Salinity	(psu)	0–2	2–10	10–20	20–27.5	32.5
Turbidity	(mg l ⁻¹)	102	83	57	50	
Part. Cd	(μg g ⁻¹)	27.9	22.8	8.2	2.8	0.70
Bottom Cd	(μg g ⁻¹)	5.0	5.3	0.54	0.26	
Diss. Cd	(μg l ⁻¹)	0.086	0.063	0.19	0.090	0.050
Part. Cu	(μg g ⁻¹)	278	207	95	35	26
Bottom Cu	(μg g ⁻¹)	29.4	33	3.5	4.6	
Diss. Cu	(μg l ⁻¹)	1.02	1.30	1.91	1.43	0.78
Part. Pb	(μg g ⁻¹)	288	254	153	101	64
Bottom Pb	(μg g ⁻¹)	45	55	13.2	11.9	
Diss. Pb	(μg l ⁻¹)	0.23	0.26	0.24	0.22	0.14
Part. Zn	(μg g ⁻¹)	800	397	272	157	95
Bottom Zn	(μg g ⁻¹)	192	216	39	39	
Diss. Zn	(μg l ⁻¹)	11.7	13.3	8.75	4.8	1.7

Table 4. Metal concentrations in the 4 boxes of the Scheldt estuary (1995)

Species		Zone 1	Zone 2	Zone 3	Zone 4	Sea
Salinity	(psu)	0–2	2–10	10–20	20–27.5	32.5
Turbidity	(mg l ⁻¹)	102	83	57	50	
Part. Cd	(μg g ⁻¹)	8.76	6.25	3.67	1.26	0.35
Diss. Cd	(μg l ⁻¹)	0.020	0.044	0.090	0.0625	0.0288
Part. Cu	(μg g ⁻¹)	112	80.7	47.2	21.8	15.5
Diss. Cu	(μg l ⁻¹)	0.68	1.17	1.37	1.04	0.37
Part. Pb	(μg g ⁻¹)	214	146	105	83.4	35.1
Diss. Pb	(μg g ⁻¹)	0.165	0.156	0.087	0.052	0.038
Part. Zn	(μg g ⁻¹)	610	423	275	144	82.0
Diss. Zn	(μg l ⁻¹)	6.24	6.04	4.48	2.16	1.06

epibenthic flux of 20 kg yr⁻¹ of dissolved Hg could be estimated (in all other boxes the epibenthic diffusive flux is negligible compared to the other Hg flows). The dissolved Hg diffusing into the water column will distribute between the dissolved and particulate phases according to the distribution coefficient or the ratio of

dissolved to particulate Hg flows, prevailing in box II. This yields a subsequent particulate epibenthic Hg flux of 19.7 kg Hg yr⁻¹. Regarding the other fluxes, we can hold the same reasoning as for box I.

Box III: In this box the magnitude of the flows is small-

Table 5. K_D -values in the 4 boxes of the Scheldt estuary; 1981–1983 and 1995

K_D		Zone 1	Zone 2	Zone 3	Zone 4	Sea
Salinity (psu)		0–2	2–10	10–20	20–27.5	32.5
Cd	'81–'83	324	362	43	31	14
(l g ⁻¹)	'95	438	142	41	20	12
Cu	'81–'83	273	159	50	24	33
(l g ⁻¹)	'95	165	69	34	21	42
Pb	'81–'83	1252	977	638	459	457
(l g ⁻¹)	'95	1300	936	1210	1600	924
Zn	'81–'83	68	30	31	33	56
(l g ⁻¹)	'95	98	70	61	67	77

er than in zone II; similarly, the interactions with the bottom are less. The bottom current is, however, strong enough in this box to bring a fraction of the local bottom sediments, which have a much lower Hg content than the suspended ones, into suspension where it will be mixed with inflowing material.

Box IV: In this box the processes are very similar to these occurring in box III.

Total dissolved mercury flows (Figure 5)

The behaviour of dissolved Hg in the Scheldt estuary is very sensitive to salinity and redox conditions, therefore speciation has been studied the year round as a function of these parameters (Leermakers et al., 1995; Baeyens et al., 1998b). During the summer, a large part of the upstream area becomes anoxic (Figure 2), resulting in the precipitation and co-precipitation of metal sulphides in addition to those resuspended from the reduced bottom sediments. In the downstream area, re-oxidation of these sulphides results in a temporary increase of dissolved mercury. During the winter, on the contrary, the undersaturation of oxygen does not lead to the presence of metal sulphides in the water column. Hence, total dissolved Hg budgets were calculated for summer and winter conditions.

Total dissolved Hg includes besides the inorganic mercury (II) fraction (Hg^{2+} , labile complexes with inorganic ligands, mainly chloro-complexes, and non-labile complexes with organic ligands, mainly humic acid-complexes), also gaseous and methylmercury

species. The behaviour and magnitude of the dissolved gaseous fraction is of major importance, since it is directly related to the loss of Hg^0 and the decrease of the dissolved Hg burden in the estuary. The evasion fluxes were calculated for each of the four boxes, in summer and in winter. The basic information necessary for these calculations is shown in Table 6. An average wind speed of 29 km h^{-1} was assumed resulting in an evasion velocity of 1.44 m d^{-1} .

Winter

Box I: The amount of dissolved Hg entering and leaving this box is almost constant. The evasion flux is only about 1% of the in- and out-flow.

Box II: Almost one third of the amount of dissolved Hg entering this box disappears onto the particulate phase. The high turbidity values and sedimentation rates are the main reasons for the important scavenging of the dissolved Hg compounds. As explained above, an epibenthic flux of 20 kg yr^{-1} could be estimated, but only 0.30 kg yr^{-1} remains after equilibration with the particulate phase into solution. This flux accounts for the evasion flux.

Boxes III and IV: The dissolved Hg flows in and out these boxes are nearly balanced. The evasion fluxes which are about one fourth to one fifth of the in and out-flows, must thus be supported by desorption or mobilisation fluxes, similar in magnitude, from the particulate phase.

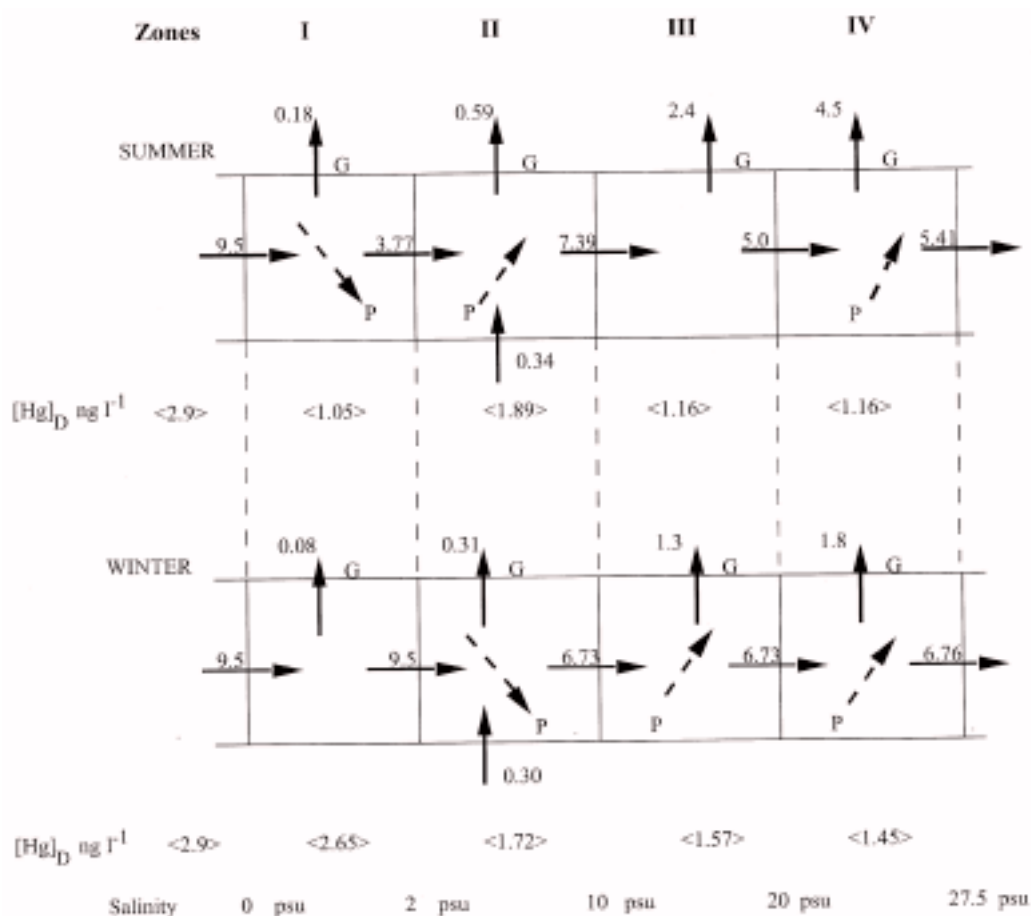


Figure 5. Dissolved Hg flows in the summer and in the winter (kg Hg yr^{-1}); 4 box model of the Scheldt estuary.

Summer

Box I: The out-flow of dissolved Hg is substantially lower than the in-flow. In this box, the water column is anoxic in summer so that insoluble, reduced Hg species such as Hg sulphides are formed. The shift from the dissolved to the particulate phase is pronounced for the dissolved species budget, but is hardly noticeable for the particulate one.

Box II: The out-flow of this box is much higher than the in-flow and again comparable to the levels observed during the winter. The dissolved Hg concentrations increase again once the oxygen levels reach 3 to 4 $\text{mg l}^{-1} \text{O}_2$ suggesting that oxidation and dissolution of reduced Hg compounds occurred. The process taking place here is thus the reverse of the one taking place in box I. The epibenthic flux during summer is about half the evasion flux.

Box III: The new production of dissolved Hg from box II must equilibrate with the particulate phase. That is probably the reason that in this box no dissolved Hg is transferred during the summer from the particulate phase (the K_D shows a slight increase) in contrast with the winter situation (the K_D decreases).

Box IV: In and out-flows are almost equal, so that the evasional flux should be balanced by a desorption flux from the particulate phase; that is similar to the winter situation. The high dissolved gaseous Hg concentration coincides with the presence of high plankton concentrations and a high biological activity, suggesting that Hg reduction is biologically mediated.

We also estimated the Hg^0 formation rates. Based on the dissolved Hg burden contained in the depth

Table 6. Hg exchange fluxes at the air-water interface

Water column concentrations of Hg ^o (pg l ⁻¹):				
Salinity (psu)	0–2	2–10	10–20	20–27.5
Summer	83	85	80	108
Winter	41	49	48	48

Atmospheric concentrations of Hg (ng m⁻³ and pg l⁻¹):

The gaseous Hg^o concentration equals 3 ng m⁻³; this corresponds to 10 pg l⁻¹ at the water surface

Fluxes in Summer

Box	Supersaturation	Transfer velocity	Flux	Surface	Total flux
Salinity (psu)	ng m ⁻³	m d ⁻¹	μg Hg m ⁻² yr ⁻¹	km ²	g Hg yr ⁻¹
0–2	73	1.44	38	4.8	180
2–10	75	1.44	39	15	590
10–20	70	1.44	37	66	2400
20–27.5	98	1.44	52	88	4500

Fluxes in winter

BOX	Supersaturation	Transfer velocity	Flux	Surface	Total flux
salinity (psu)	ng m ⁻³	m d ⁻¹	μg Hg m ⁻² yr ⁻¹	km ²	g Hg yr ⁻¹
0–2	31	1.44	16	4.8	80
2–10	39	1.44	20	15	310
10–20	38	1.44	20	66	1300
20–27.5	38	1.44	20	88	1800

integrated water column (between 15 and 20 μg m⁻³), conversion rates of 0.22 to 0.35% d⁻¹ during the winter (Table 7) are required to balance the estimated evasional fluxes of 16 to 20 μg m⁻² yr⁻¹. During the summer the integrated Hg burden in the water column varies from 8 to 17 μg m⁻³, hence conversion rates of 0.63 to 1.3% d⁻¹ are required to balance the evasional fluxes of 37 to 52 μg m⁻² yr⁻¹. These Hg^o formation rates are of the same order as those estimated by Mason et al. (1995b; 1995c) for open ocean waters (0.2 to 1% d⁻¹) but much lower than the values they found (2 to 4% d⁻¹) in the Upper Mystic Lake (Mason et al., 1995a).

Dissolved methylmercury flows (Figure 6)

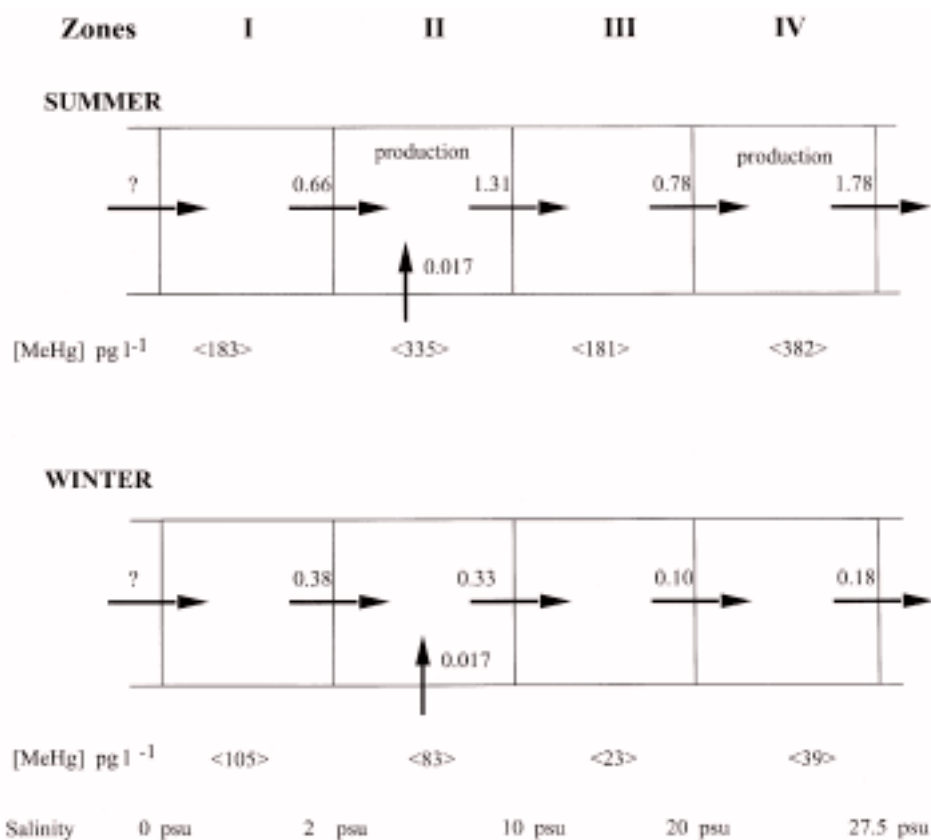
The dissolved methylmercury flows are generally small compared to the total dissolved Hg flows, except during summer and fall between boxes II and III (just downstream the anoxic area) and between box IV and the sea (at the mouth where high plankton population densities were observed). In those cases the methylmercury flows can represent between 20 and 30% of the total dissolved Hg flows, which are very high fractions.

Winter

Boxes I and II: The inflow of box I is unknown, but the in and out-flows of box II are fairly similar. An epibenthic flux of 48 10⁻³ kg yr⁻¹ has been estimated,

Table 7. Hg^0 formation rates in the 4 boxes of the Scheldt estuary

Species		Zone 1	Zone 2	Zone 3	Zone 4
Salinity	(psu)	0–2	2–10	10–20	20–27.5
Winter					
Tot. diss Hg	(ng l^{-1})	2.65	1.75	1.57	1.45
Depth	(m)	7.5	9	11	13
Integrated diss Hg	($\mu\text{g m}^{-2}$)	20	15.5	17.3	18.9
Evasion flux Hg^0	($\mu\text{g m}^{-2} \text{yr}^{-1}$)	16	20	20	20
Hg^0 formation rate	% yr^{-1}	80	129	116	106
	% d^{-1}	0.22	0.35	0.32	0.29
Summer					
Tot. diss Hg	(ng l^{-1})	1.05	1.89	1.16	1.16
depth	(m)	7.5	9	11	13
Integrated diss Hg	($\mu\text{g m}^{-2}$)	7.88	17	12.8	15
Evasion flux Hg^0	($\mu\text{g m}^{-2} \text{yr}^{-1}$)	38	39	37	52
Hg^0 formation rate	% yr^{-1}	482	229	289	347
	% d^{-1}	1.3	0.63	0.79	0.95

Figure 6. Dissolved methylmercury flows in summer and in winter (kg Hg yr^{-1}); 4 box model of the Scheldt estuary.

in an analogous way as for total dissolved Hg. Taking into account a particulate to dissolved methylmercury ratio (both expressed in the same units) of 1.9 (Baeyens et al., 1998a) a resulting epibenthic dissolved MMHg flux of $17 \cdot 10^{-3} \text{ kg yr}^{-1}$ was calculated.

The production of MMHg in the upper estuary is low during the winter due to the low temperature and the absence of anaerobic conditions in the water column restricting the activity of the sulphate reducing bacteria (Leermakers et al., 1993). The fraction of methylmercury in the total dissolved Hg flow is about 4 to 5%.

Boxes III and IV: In the downstream estuary the MMHg flows are still smaller than those in the upstream estuary (the fraction of MMHg in the total dissolved Hg flow is less than 2.5%).

Summer

Box II: The flows are significantly higher than during the winter (the in-flow 2 times, the out-flow 4 times). MMHg in this box is produced as a consequence of the redox gradient (the water column changes from anoxic over suboxic to oxic in the downstream direction). Sulphate reducing bacteria are very active in such conditions and have been shown to be very effective in methylating inorganic Hg (Leermakers et al., 1993). Their activity decreases, however, strongly once the system becomes more oxidised.

Box IV: A second production zone of dissolved methylmercury is observed close to and at the mouth of the estuary. The methylmercury out-flow of this box is 10 times higher in summer than in winter. The origin of this production is still under study, but the high amounts of planktonic species at the mouth during the summer, similar to the high dissolved gaseous Hg levels produced in this zone, may be involved.

Cadmium, copper, lead and zinc budgets

Mass fluxes were calculated in each of the four zones or boxes of the Scheldt estuary for total particulate and dissolved metals for the periods 1981–1983 and 1995. The parameters used in these calculations are: (1) water flow rates for dissolved species; (2) particulate matter flows for particulate species; (3) average concentrations of the metal species at the boundaries of the boxes and inside the boxes, which are assumed

to be homogeneous; and (4) epibenthic fluxes reported by Baeyens et al. (1986) for the period 1981–1983. The epibenthic fluxes for 1995 were adapted taking into account the sedimentation fluxes relative to that period.

The main particulate fluxes in each of the boxes are the same as those mentioned here above when discussing the particulate matter and particulate mercury flows. For the particulate phase, box II, or the area of high sedimentation, is the most important. Most of the particulate metals accumulate at the bottom, but a fraction is remobilised in the sediments and diffuses back into the water column. Because the behaviour of Cd, Cu, Pb and Zn in the dissolved phase is much simpler than that of Hg which includes at least three species (Hg^0 , Hg^{2+} and MMHg) each characterised by particular features, we combined the dissolved and particulate metal flows into one picture. Figures 7 to 14 show these particulate and dissolved metal flows through the Scheldt estuary.

From the dissolved and particulate metal flows in each of the boxes, the mass balances were calculated (Table 8). It appears that generally the in- and out-flows are fairly well-balanced, taking into account the uncertainties related to the magnitude of the particulate matter flows, especially sedimentation and resuspension, and to a lesser extent of the average particulate and dissolved metal concentrations.

The highest degrees of relative imbalance, expressed as the difference between total in- and out-flows divided by the total inflow, are observed in box IV. The average relative imbalance for box IV is 20%, while for the other boxes this value is below 10%. Box IV also contains the smallest flows, which results in much stronger relative imbalances for a similar deviation.

Looking at positive (a higher input than output) and negative imbalances, one observes that boxes I (only for the particulate mass balance) and III show a slight deficit, boxes II and IV a slight excess. The net sedimentation flux (the sum of sedimentation and resuspension) in boxes II and IV is probably slightly underestimated, the opposite being true in boxes I and III. However, since a simple mass balance model of water and particles coupled to a number of metals (dissolved and particulate phase) practically yields a closed budget for all these metals in the four zones of the estuary, evidence is provided that the various components of the model are reasonably well estimated.

The Scheldt inputs into the coastal area calculated in this paper are slightly different from the values pre-

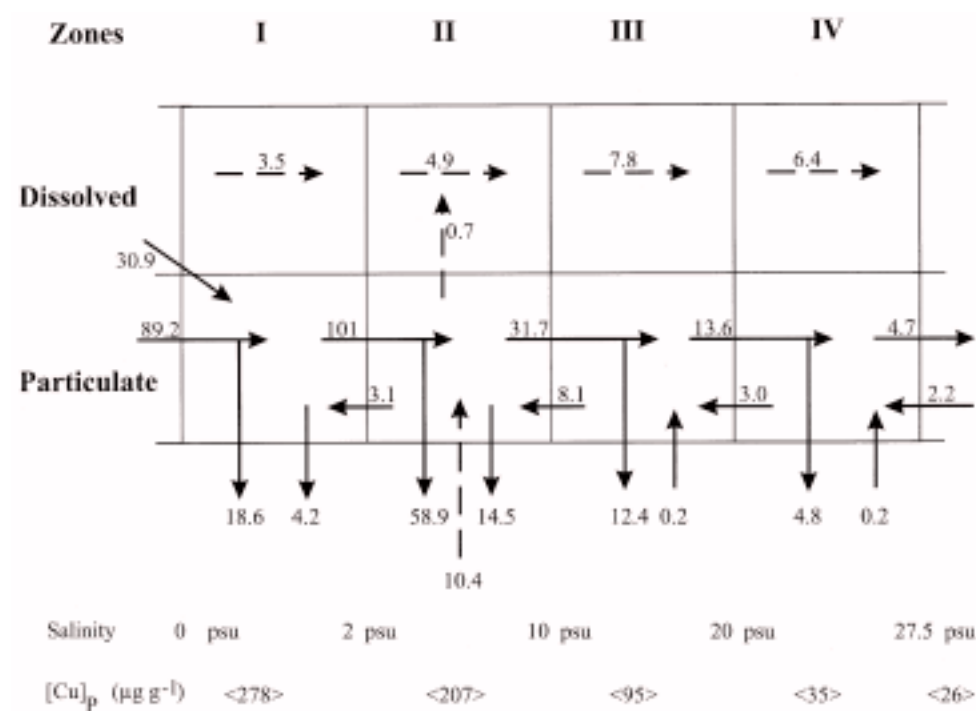


Figure 7. Dissolved and particulate Cu flows (10^3 kg yr^{-1}) in the period 1981–1983; 4 box model of the Scheldt estuary.

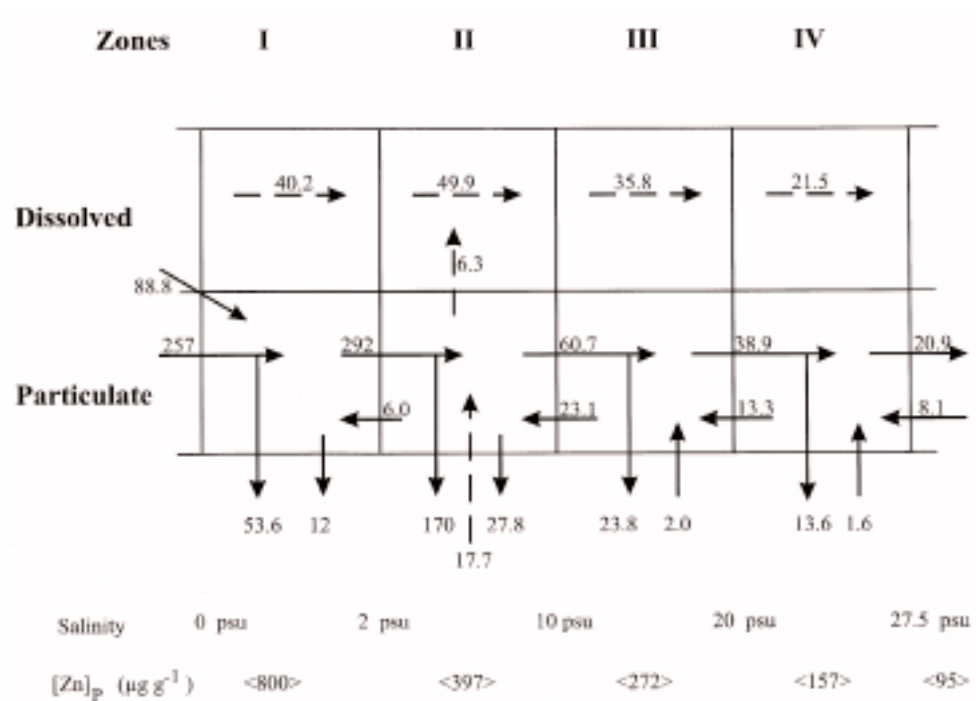


Figure 8. Dissolved and particulate Zn flows (10^3 kg yr^{-1}) in the period 1981–1983; 4 box model of the Scheldt estuary.

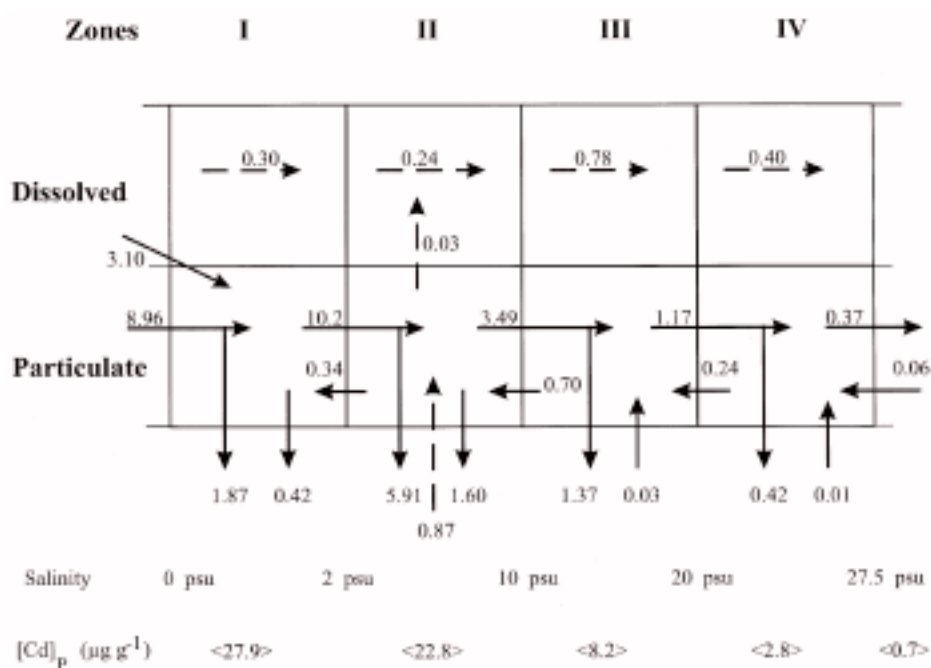


Figure 9. Dissolved and particulate Cd flows (10^3 kg yr^{-1}) in the period 1981–1983; 4 box model of the Scheldt estuary.

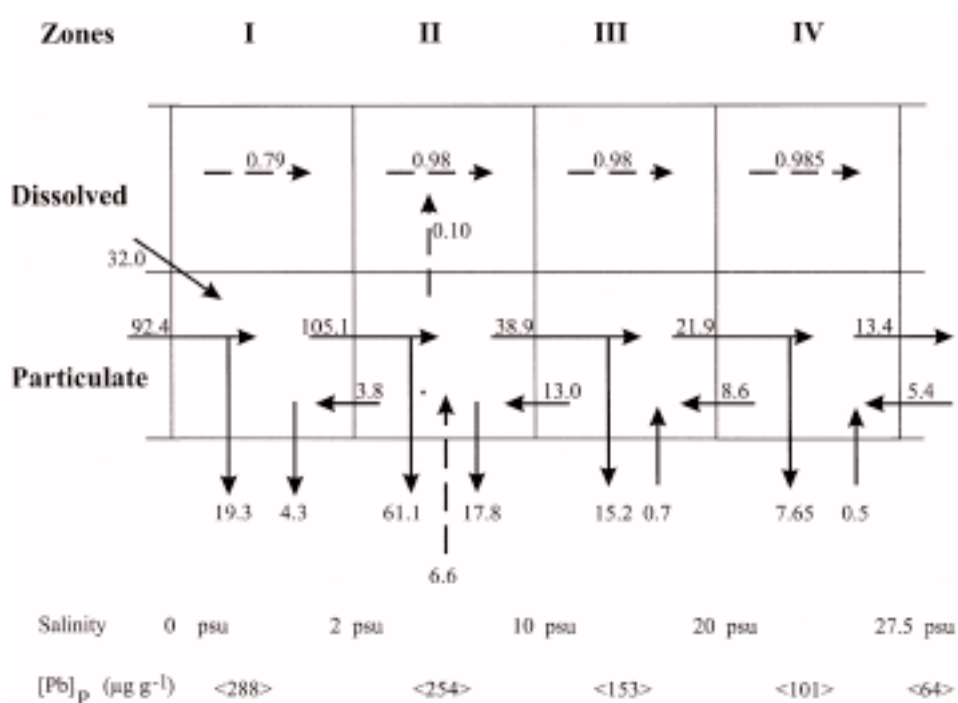


Figure 10. Dissolved and particulate Pb flows (10^3 kg yr^{-1}) in the period 1981–1983; 4 box model of the Scheldt estuary.

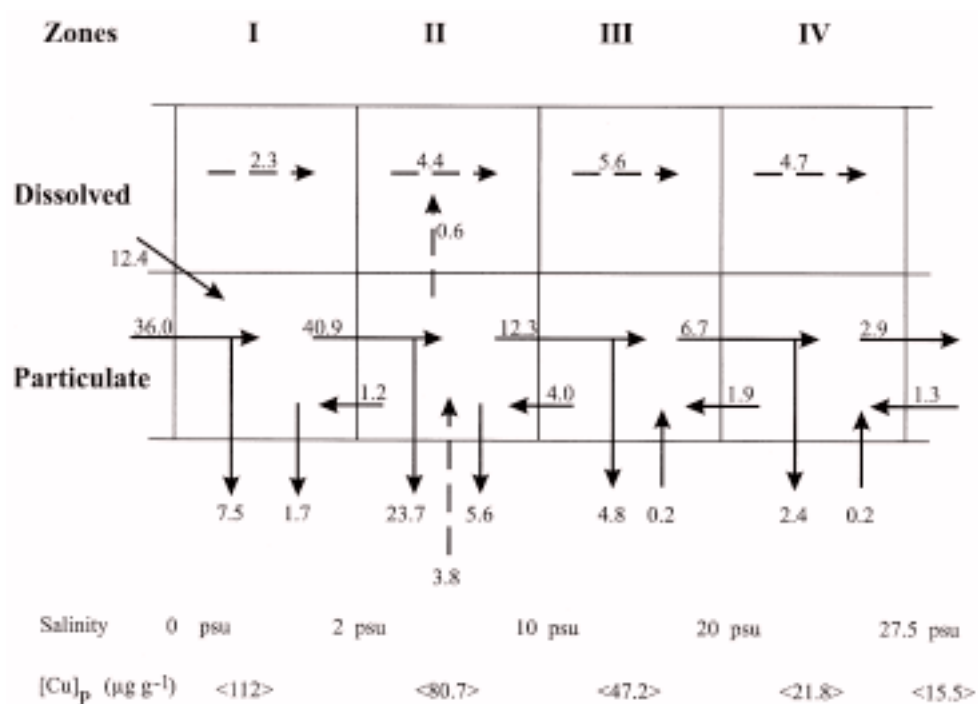


Figure 11. Dissolved and particulate Cu flows ($10^3\ kg\ yr^{-1}$) in 1995; 4 box model of the Scheldt estuary.

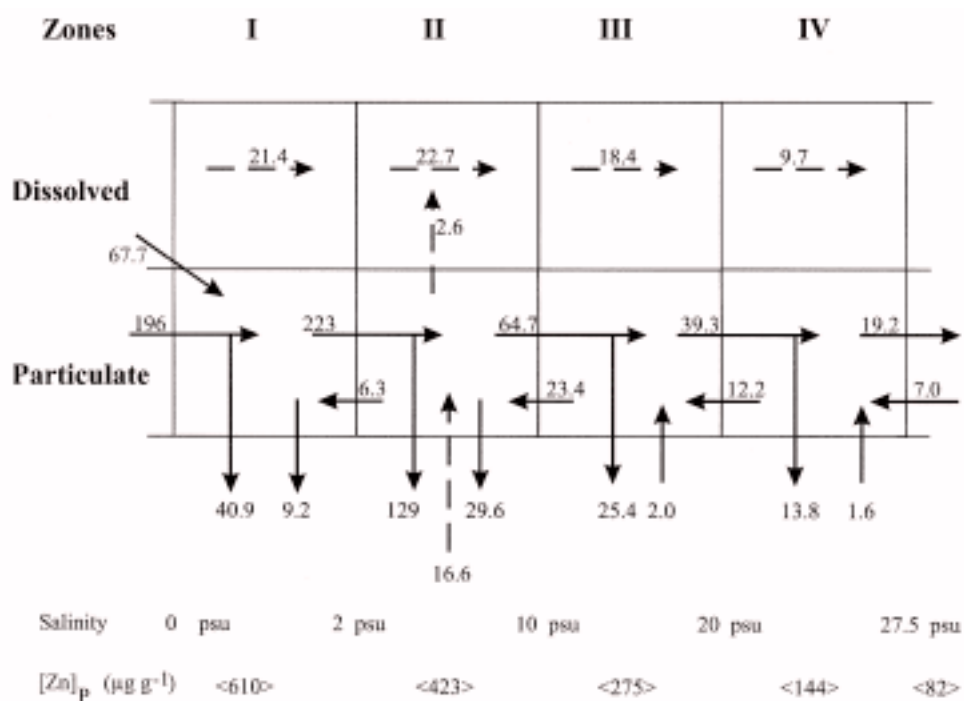


Figure 12. Dissolved and particulate Zn flows ($10^3\ kg\ yr^{-1}$) in 1995; 4 box model of the Scheldt estuary.

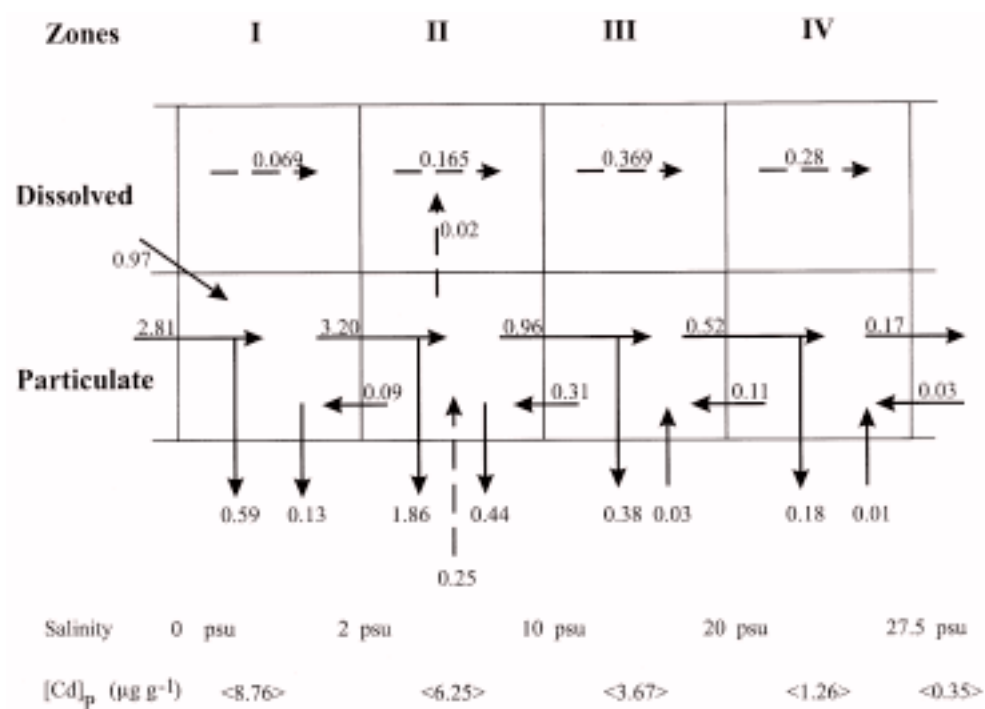


Figure 13. Dissolved and particulate Cd flows ($10^3\ kg\ yr^{-1}$) in 1995; 4 box model of the Scheldt estuary.

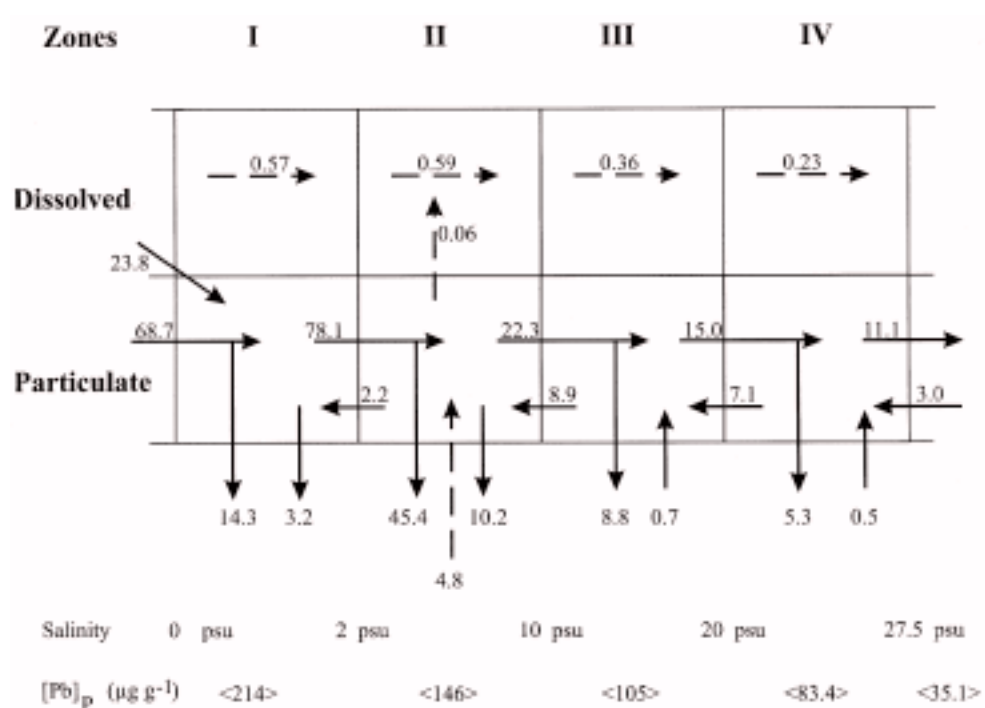


Figure 14. Dissolved and particulate Pb flows ($10^3\ kg\ yr^{-1}$) in 1995; 4 box model of the Scheldt estuary.

Table 8. Mass balances of dissolved and particulate metals (tons yr⁻¹, except for Hg in kg yr⁻¹), Δ = inputs–outputs

	Species	Zone I	Zone II	Zone III	Zone IV
'81–'83	Δ^P Cu	–0.6	+11.3	+0.8	+3.5
	Δ^D Cu		–1.4	–2.2	+1.4
	Δ^T Cu		+9.9	–1.4	+4.9
	% of Δ^T /total inflow		8%	3%	21%
'81–'83	Δ^P Zn	–5.8	+68.3	+9.8	+0.8
	Δ^D Zn		–16.0	+20.4	+14.3
	Δ^T Zn		+52.3	+10.6	+15.1
	% of Δ^T /total inflow		15%	9%	22%
'81–'83	Δ^P Cd	–0.09	+0.43	+0.52	+0.21
	Δ^D Cd		+0.06	–0.51	+0.38
	Δ^T Cd		+0.49	+0.01	+0.59
	% of Δ^T /total inflow		4%	0%	29%
'81–'83	Δ^P Pb	–0.5	+3.1	–1.9	–1.85
	Δ^D Pb		–0.29	+0.1	–0.005
	Δ^T Pb		+2.81	–1.8	–1.855
	% of Δ^T /total inflow		2%	4%	6%
'95	Δ^P Cu	–0.5	+5.9	–1.1	+1.0
	Δ^D Cu		–2.7	–0.6	+0.9
	Δ^T Cu		+3.2	–1.7	+1.9
	% of Δ^T /total inflow		6%	9%	14%
'95	Δ^P Zn	–3.1	+33.4	–9.2	+2.7
	Δ^D Zn		–3.9	+6.9	+8.7
	Δ^T Zn		+29.5	–2.3	+11.4
	% of Δ^T /total inflow		10%	2%	17%
'95	Δ^P Cd	–0.05	+0.41	–0.11	+0.10
	Δ^D Cd		–0.12	–0.18	+0.09
	Δ^T Cd		+0.29	–0.29	+0.19
	% of Δ^T /total inflow		7%	19%	23%
'95	Δ^P Pb	–0.9	+11.7	–2.6	–5.0
	Δ^D Pb		–0.10	+0.3	+0.1
	Δ^T Pb		+11.6	–2.3	–4.9
	% of Δ^T /total inflow		13%	7%	26%
Summer '92–'94	Δ^P Hg	+1.4	+14.2	+8.0	–4.7
	Δ^D Hg	+5.6	–3.9	0	–4.9
	Δ^T Hg	+7.0	+10.6	+8.9	–8.0
	% of Δ^T /total inflow	1.1	1.8%	3.5%	6.9%
Winter '92–'94	Δ^P Hg	+1.4	+14.2	+8.0	–4.7
	Δ^D Hg	–0.1	+2.8	–1.3	–1.8
	Δ^T Hg	+1.3	+16.9	+6.8	–6.2
	% of Δ^T /total inflow	0.2	2.8%	2.8%	5.0%

sented in a related paper on coastal inputs (Baeyens et al., 1998d). In this paper the average concentrations of the four metals in the dissolved and particulate phases in box IV (salinity range 20 to 27.5 psu) were used to calculate the input flows, while in the other paper (see Baeyens et al., 1998d) the metal concentrations, obtained by extrapolation to a salinity of 26.5 psu of the best fitting curve through the coastal data points (concentration versus salinity), were used. For the surveys between 1981 and 1983 the dissolved metal concentrations calculated in both ways are: for Pb (0.22 and $0.252 \mu\text{g l}^{-1}$), for Zn (4.8 and $4.1 \mu\text{g l}^{-1}$), for Cd (0.090 and $0.125 \mu\text{g l}^{-1}$) and for Cu (1.43 and $1.60 \mu\text{g l}^{-1}$), while in the particulate phase they are: for Pb (4.05 and $3.5 \mu\text{g l}^{-1}$), for Zn (7.85 and $5.5 \mu\text{g l}^{-1}$), for Cd (0.14 and $0.10 \mu\text{g l}^{-1}$) and for Cu (1.75 and $1.20 \mu\text{g l}^{-1}$).

Budget uncertainties

It is clear that the metal flows presented in Figures 4 to 14, which are based on averaged values of dissolved and particulate metal concentrations, and of water and suspended sediment flows, are not exact numbers but include a varying degree of uncertainty. In Table 9 the standard deviations on the mean dissolved and particulate metal concentrations in the period 81–83 are shown. The relative errors are always lower than 50%, except for Cd (zones I and IV) in the dissolved phase, and again for Cd (zones I, III and IV) and Zn (zone I) in the particulate phase. Cd concentrations in the Scheldt are much lower than those of the three other metals, which may be an explanation for the higher standard deviations observed for this metal.

The average water flow at the river/estuary interface (Schelle, 92 km from the mouth) amounts to $104 \text{ m}^3 \text{ s}^{-1}$, but the water flows obey a log-normal distribution. The average value minus (plus) the standard deviation equals $60 \text{ m}^3 \text{ s}^{-1}$ ($180 \text{ m}^3 \text{ s}^{-1}$), which as by hazard almost corresponds to the summer and winter averages. The average suspended sediment concentration at the river/estuary interface is calculated from 47 measurements at that location and yields a value of $101 \pm 54 \text{ mg l}^{-1}$. Hence, the suspended sediment flow entering the estuary shows a relative error of 80%. The determination of the suspended sediment flow at the estuary/sea interface is much more complicated, since in addition of the seaward surface current, a landward bottom current exists (Baeyens et al., 1998c). D'Hondt and Jacques (1982) estimated the suspended sediment

output to the sea at $300 \cdot 10^3 \text{ tons y}^{-1}$, while Van Eck (1991) suggested a value of $136 \cdot 10^3 \text{ tons y}^{-1}$. The latter author reported a landward flux of marine suspended matter of $79 \cdot 10^3 \text{ tons y}^{-1}$. As explained hereabove, we estimated a seaward suspended sediment flux of $133 \cdot 10^3 \text{ tons y}^{-1}$ and a landward flux of $85 \cdot 10^3 \text{ tons y}^{-1}$. The uncertainty on this flux is thus rather large and may be estimated at 100%.

Assuming a relative error of 50% on the average dissolved metal concentrations (period 1981–1983) and the same error on the water flow, leads to a relative error of 70% on the dissolved metal flows shown in Figures 7 to 10. The error on the particulate metal flows is larger, because the relative error on the suspended sediment flows vary from 80 to 100%. Assuming again a relative error of 50% on the average particulate metal concentrations (period 1981–1983), and an error of 90% on the suspended sediment flow results in a relative error of 100% on the particulate metal flows shown in Figures 7 to 10.

As a concrete example we calculated the minimum and maximum dissolved and particulate Cu flows (period 1981–1983) and for each box also the corresponding budget. For the calculation of the minimum (maximum) flows, the average values are decreased (increased) by the standard deviation. Results are shown in Table 10 and Figures 15 and 16.

Conclusions

From all metals under study here, the most striking decrease in aquatic metal input to the North Sea by Belgium is observed for Cd (see also Baeyens, 1997). This finding is also reported by Andersen and Niilonen (1995). Due to more stringent regulations regarding the waste water quality and the use of cadmium in particular industrial processes, the aquatic Cd input decreased in Belgium by more than a factor 5 between 1985 and 1995. These regulations had a clear effect on the dissolved and particulate Cd levels, especially in the upper and mid-estuary. Even at the mouth (zone IV and the coastal zone) a reduction of the Cd concentration by a factor 2 is still noticeable.

For Pb the aquatic input decreased by about 25% (the point sources by a factor 2), but a more drastic decrease of the atmospheric input (about a factor 3) resulted in much lower dissolved Pb values at sea and in the downstream estuary. Also the K_D values of Pb at the mouth and at sea showed the largest modifications of all metals between 1981–1983 and 1995.

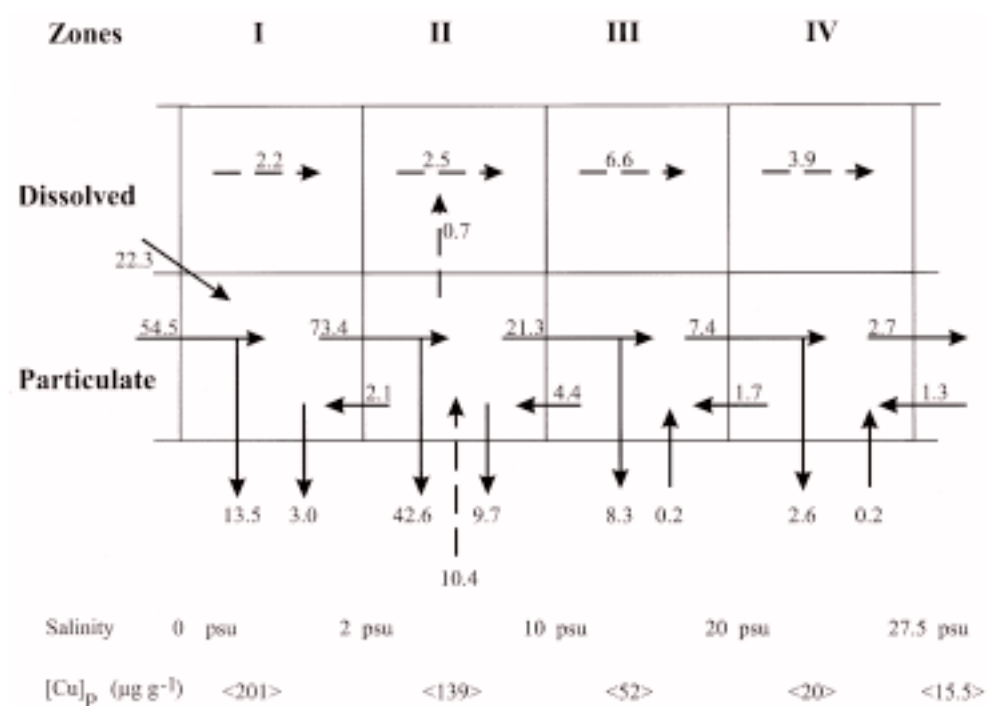


Figure 15. Minimum dissolved and particulate Cu flows (10^3 kg yr^{-1}) in the period 1981–1983; 4 box model of the Scheldt estuary.

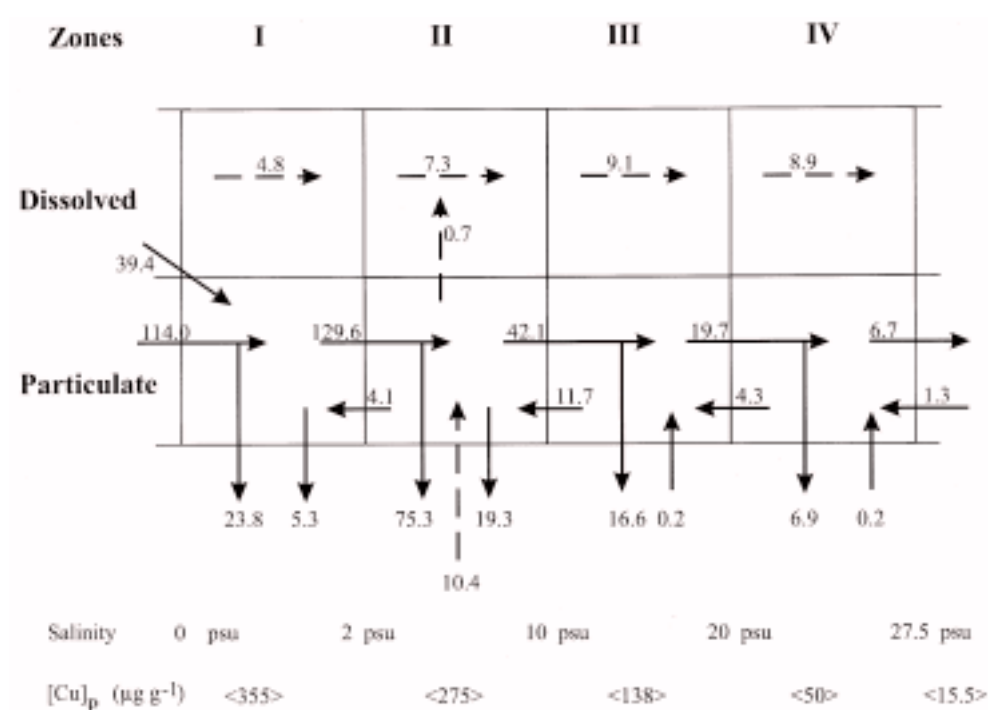


Figure 16. Maximum dissolved and particulate Cu flows (10^3 kg yr^{-1}) in the period 1981–1983; 4 box model of the Scheldt estuary.

Table 9. Average concentrations and standard deviations in the 4 zones of the Scheldt estuary (1981–1983)

	Dissolved metals ($\mu\text{g l}^{-1}$)							
	Cu	STD	Zn	STD	Cd	STD	Pb	STD
Zone I	1.02	0.38	11.7	1	0.086	0.067	0.23	0.05
Zone II	1.3	0.64	13.3	5.3	0.063	0.027	0.26	0.07
Zone III	1.91	0.3	8.75	1.6	0.19	0.045	0.24	0.12
Zone IV	1.43	0.55	4.8	2.1	0.09	0.056	0.22	0.07

	Particulate metals ($\mu\text{g g}^{-1}$)							
	Cu	STD	Zn	STD	Cd	STD	Pb	STD
Zone I	278	77	800	410	27.9	14.6	288	104
Zone II	207	68	397	120	22.8	9.5	254	58
Zone III	95	43	272	62	8.2	5.8	153	9
Zone IV	35	15	157	60	2.8	2.1	101	26

Table 10. Mass balances of average, minimum and maximum dissolved and particulate copper (tons yr^{-1}) in the period 1981–1983, Δ = inputs–outputs

Species		Zone I	Zone II	Zone III	Zone IV
Average values	$\Delta^P \text{ Cu}$	–1.1	11.8	0.8	3.5
	$\Delta^D \text{ Cu}$		–2.1	–2.2	1.4
	$\Delta^T \text{ Cu}$		9.7	–1.4	4.9
	% of Δ^T /total inflow		8%	4%	21%
Minimum values	$\Delta^P \text{ Cu}$	–11.0	12.5	3.1	1.9
	$\Delta^D \text{ Cu}$		–1.0	–3.4	2.7
	$\Delta^T \text{ Cu}$		11.5	–0.3	4.6
	% of Δ^T /total inflow		13%	1%	30%
Maximum values	$\Delta^P \text{ Cu}$	–1.2	10.9	–1.4	3.3
	$\Delta^D \text{ Cu}$		–3.2	–1.1	0.2
	$\Delta^T \text{ Cu}$		7.7	–2.5	3.5
	% of Δ^T /total inflow		5%	5%	12%

The dissolved Zn concentrations decreased by almost a factor 2 similar to the decrease of the point sources, while the particular Zn concentrations did not change substantially. This is in contrast with Cu for which the particulate concentrations decreased stronger over the last decade than the dissolved ones. The aquatic point sources of Cu decreased by a factor of 2, but the atmospheric point sources even more.

Mercury concentrations could not be compared because the analytical methodologies changed too much over the last ten years, but it has been thoroughly studied during the past few years. The behaviour of the dissolved Hg fraction is quite different in summer than in winter. Anoxic redox conditions in the upstream estuary in summer provoke on the one hand a trans-

fer from the dissolved to the particulate phase and on the other hand methylation of inorganic Hg. Once re-aeration occurs and the estuary becomes again oxic, the dissolved Hg level increases probably due to the oxidation of reduced, insoluble species with which it is associated or of reduced Hg species itself. At the mouth of the estuary in summer, methylation was also observed. At the same time high plankton population densities prevailed.

The production of Hg^0 is a very important process because it purifies the estuary via increased transfer to the atmosphere. The Hg^0 formation rates we calculated from our field data range from 0.22 to 0.35% d^{-1} in winter and from 0.63 to 1.3% d^{-1} in summer. These

rates are in the same range as the values reported by Mason et al. (1995b; 1995c) for open ocean waters.

For all metals, the particulate flows are the major ones in the estuary except for Cu and Cd at the mouth.

High accumulation occurred in zone II, the area of maximum turbidity and high sedimentation. If we assume a linear decrease of the metal sedimentation flux between values measured in the period 1981–1983 and in 1995, following sedimentated amounts have been calculated: 49 tons of Cd, 510 tons of Cu, 670 tons of Pb and 1800 tons of Zn. Even if part of this load has been dredged or transported elsewhere in the estuary by the tidal action, it will still take many years for the estuary to recover.

The Scheldt inputs into the North Sea (particulate + dissolved), estimated from measurements in the mouth of the estuary of trace metal concentrations, residual waterflows and suspended sediments, amount to: 46.6 kg yr⁻¹ for Hg, 8.9 tons yr⁻¹ for Cu (81–83), 34.3 tons yr⁻¹ for Zn (81–83), 0.71 tons yr⁻¹ for Cd (81–83), 8.99 tons yr⁻¹ for Pb (81–83), 6.3 tons yr⁻¹ for Cu (95), 21.9 tons yr⁻¹ for Zn (95), 0.42 tons yr⁻¹ for Cd (95) and 8.33 tons yr⁻¹ for Pb (95).

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