

## Overview of trace metal contamination in the Scheldt estuary and effect of regulatory measures

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### Abstract

Seasonally, dissolved and particulate metal concentrations in the Scheldt estuary were assessed over a period of 4 years (1995–1998). High quality data were obtained following stringent analytical protocols for each step: sampling, sample treatment, sample storage and analysis. Of the 5 trace metals, Ni showed the most conservative behaviour, while Cd and Cu were clearly transferred from the particulate to the dissolved phase in the middle estuary. A substantial part of the particulate metals entering the estuarine system are lost through sedimentation. General seasonal patterns are the following: lower concentrations in spring and higher ones in winter (sometimes late fall/early winter) for dissolved metals, while in summer a pronounced rise of the longitudinal concentration profile is observed for the particulate metals. A comparison of the trace metal concentrations (dissolved and particulate) at the mouth of the estuary in 1995–1998 with those from 1981 to 1983, reveal reductions between 30 and 58%. Reductions based on direct emission measurements for almost the same period suggest reductions (dissolved + particulate) between 42 and 64%. Biomagnification (BMF) is the accumulation of a compound through the food-chain. It is in our case expressed as the ratio of the metal concentration in the organism ( $\mu\text{g g}^{-1}$ , d.w.)/the metal concentration in total suspended matter ( $\mu\text{g g}^{-1}$ , d.w.). Almost all BMF-values of Periwinkle, *Nereis diversicolor* and *Macoma balthica* (3 bottom organisms in the Scheldt estuary) are negative meaning that these organisms contain less heavy metals than the particulate suspended matter. For all organisms log BMFs for Pb, respectively Ni, are around  $-1.8$ , respectively  $-0.7$ . For Cd, Periwinkle shows slight enrichment (0.05) and for Cu even more (0.45), while negative values were observed for *Nereis diversicolor* and *Macoma balthica*. The latter organisms are more enriched in Zn ( $-0.09$ ) than Periwinkle ( $-0.43$ ).

### Introduction

Action plans for a better protection of the North Sea were presented at the successive North Sea Conferences (Bremen, 1984; London, 1987; The Hague, 1990; Esbjerg, 1995; Bergen, 2002). These plans included far-reaching undertakings to reduce aqueous discharges and atmospheric emissions of substances such as trace metals that are toxic, persistent and liable to bioaccumulate. For cadmium, lead and mercury the reduction targets were achieved, but an additional effort is still necessary for copper and zinc. It is interesting to compare,

for the various trace metals, the above mentioned emission reduction percentages with immission reduction levels observed in the Scheldt estuary over the same period.

The Scheldt estuary is not only a receiving water body: evacuation of pollutants to the sea, storage in the bottom sediments and depuration via efflux to the atmosphere (especially for mercury) all contribute to a reduction of the metal burden in the water column. All in- and outgoing flows have been put together in a box-model, and a mass balance for each box has been calculated. Only in 5 boxes on 30, the imbalance was larger

than 20%, with a highest value of 29% (Baeyens et al., 1998a). For all particulate metals, sedimentation appears to be a very important process, reducing strongly the output into the sea. Dissolved metals show a different behaviour: in case of Ni dilution is dominating, but the other ones (Cd, Cu, Pb and Zn) show a non-conservative behaviour vs. salinity. As a consequence, the ratio output into the sea/riverine input into the estuary for the dissolved phase varies significantly amongst the five trace metals (Fig. 1).

For mercury, food-chain transfer in the Scheldt, including bioconcentration and bioaccumulation factors, has been reported (Baeyens et al., 2003), but no data for the other trace metals was available. In this paper the levels of Cd, Cu, Ni, Pb and Zn in three organisms (*Periwinkle*, *Nereis diversicolour* and *Macoma balthica*) have been related to the corresponding metal levels in the watercolumn and bioconcentration and biomagnification factors in the Scheldt estuary have been calculated. Mercury is not included here because its behaviour in the Scheldt estuary has

been reported in several other papers (e.g. Leermakers et al., 2001; Baeyens et al., 2003).

### Methods and materials

During 14 surveys in the Scheldt estuary (1995–1998), the longitudinal metal concentration profiles in the dissolved and the particulate phases were assessed. In Table 1 the period of sampling, the fresh water flow rate measured at Schelle (90 km from the mouth) and the dissolved oxygen levels occurring at the station showing the lowest salinity are presented. Low oxygen levels in the upstream area of the Scheldt estuary are generally observed from May to December.

A summary of the overall analytical procedure is reported below. The complete description of the various steps including Quality Assurance and Control can be found in Parmentier (2003).

Sampling is a crucial step in order to obtain reliable results, so a maximum of precautions was

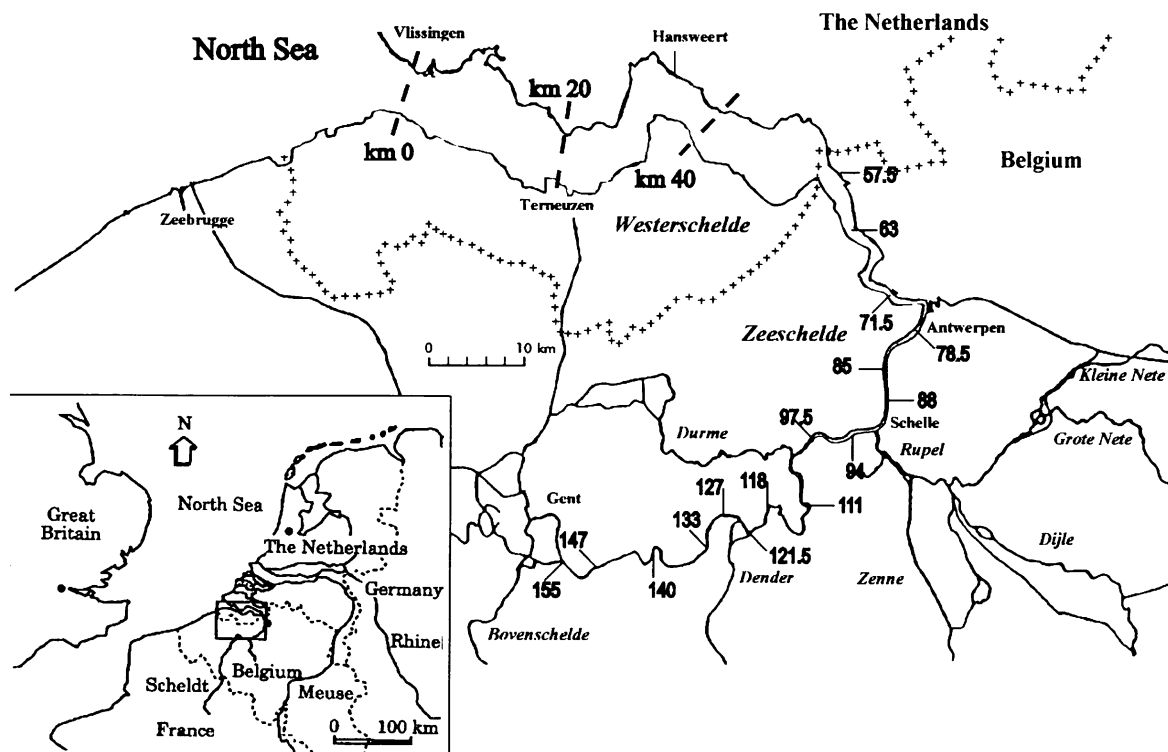


Figure 1. Map of the Scheldt estuary.

Table 1. Scheldt surveys in the period 1995–1998. Fresh water flow rates at Schelle (90 Km) and dissolved oxygen levels at the station of lowest salinity

Survey	Flow rate (m <sup>3</sup> s <sup>-1</sup> )	Salinity (psu)	Dissolved oxygen level (mg l <sup>-1</sup> )
March 95	226	0.48	5.9
May 95	100	0.67	0.7
October 95	51	2.6	0.2
December 95	87	1.2	1.0
February 96	105	1.0	2.6
May 96	65	1.4	0.7
October 96	60	2.7	0.2
December 96	135	11.5	9.0
February 97	173	0.51	4.6
April 97	63	1.5	1.5
July 97	78	1.3	0.2
November 97	79	2.1	0.4
April 98	148	0.52	0.2
September 98	158	0.29	0.4

taken to avoid contamination. In the first place, all materials in contact with the samples during the sampling process were cleaned and stored following a strict standard procedure. Contamination free sampling and handling of water samples are key elements in obtaining reliable results, so water samples were collected according to clean trace metal protocols. Afterwards, all samples were immediately filtered in the Clean Laboratory Container (class 100) aboard the research vessel. The filtered samples were collected in bottles, and immediately acidified to a pH < 1. The acidified solutions were stored at room temperature and preconcentrated and/or analysed within a few weeks after collection. Filters are dried in a laminar flow and weighed.

Due to the low concentrations of heavy metals dissolved in seawater and estuarine water and the interference of high salt concentrations, a preconcentration is required in order to reach the amounts and purity required for a quantitative determination. In this study, a slightly modified Danielsson solvent extraction method is applied (Danielsson et al., 1978, 1982). Ni, Cu, Zn, Cd and Pb in the concentrated solutions were analysed using graphite furnace-atomic absorption spectrometry (ET-AAS) for the 1995 samples, or Inductively Coupled Plasma-Mass Spectrometry

(ICP-MS) for 1996–1998 samples. In each batch of six preconcentrated solutions, one preconcentrated standard reference material and one blank were included for quality assurance purposes. In addition, participating at the AQUACHECK and QUASIMEME intercalibration exercises (1995–1998) allowed us to verify the quality of the obtained data.

In order to determine Ni, Cu, Zn, Cd and Pb in the particulate phase, an acid mineralization procedure was carried out. The filters were placed in PTFE bombs, and 4 ml HNO<sub>3</sub> (sub-boiled) and 1 ml HCl (Merck, Suprapur) were added. The bombs were tightly closed and oven-heated for 12 h at 60 °C to obtain complete digestion. After digestion, samples were diluted up to 50 ml with ultrapure water and transferred in pre-cleaned PE bottles. Analysis was performed with Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) for 1995 samples and ICP-MS for samples from 1996 and later. Quality assurance was performed by including a blank and a reference material in every 10 PTFE bombs.

## Results and discussion

For all metals, a typical summer and winter profile of the dissolved and the particulate phase is presented to illustrate spatial-temporal variations (Figs. 2 and 3). General trends are, however, discussed using all seasonal profiles of trace metals (a complete dataset is available in the IDOD database of [www.mumm.ac.be/datacentre](http://www.mumm.ac.be/datacentre) and in Parmentier, 2003). As an illustration all longitudinal profiles of dissolved and particulate Cu and Ni are shown in Figs. 4–7.

### *Spatial distribution of dissolved metals*

Dissolved Ni concentrations linearly decrease from the upper estuary towards the mouth. The fresh water end-member ranges from 50 nM to 110 nM, the marine one from 5 nM to 28 nM. The lowest dissolved Ni concentrations are observed in 1998, during the April cruise. Elimination of this campaign makes the freshwater end-member vary between 75 and 110 nM.

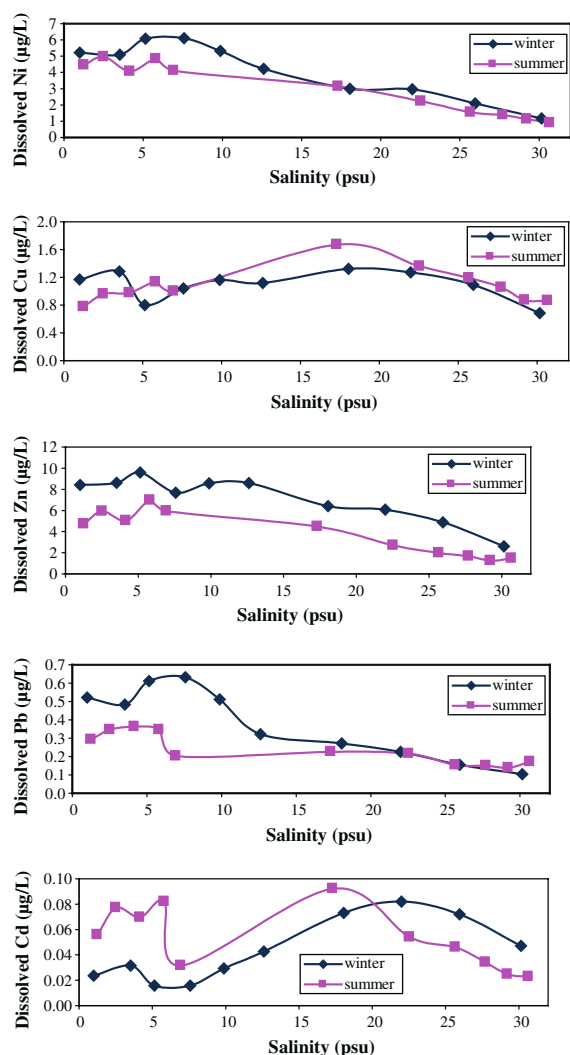


Figure 2. Dissolved metal concentrations in the Scheldt estuary. A typical longitudinal winter and summer profile.

All longitudinal dissolved Cu-profiles have a convex shape. The fresh water end-member ranges from 8 nM to 25 nM, the marine one from 8 nM to 18 nM and the curve's maximum from 16 nM to 42 nM. Aberrations from convexity are most often encountered in the upper estuary, in the early mixing zone. The present values are comparable to those found for the period 1981–1983 (Baeyens et al., 1998b), both in terms of shape and end-member values. The height of the maximum for the period 1981–1983 (30 nM) was comparable to those observed in the period 1995–1998.

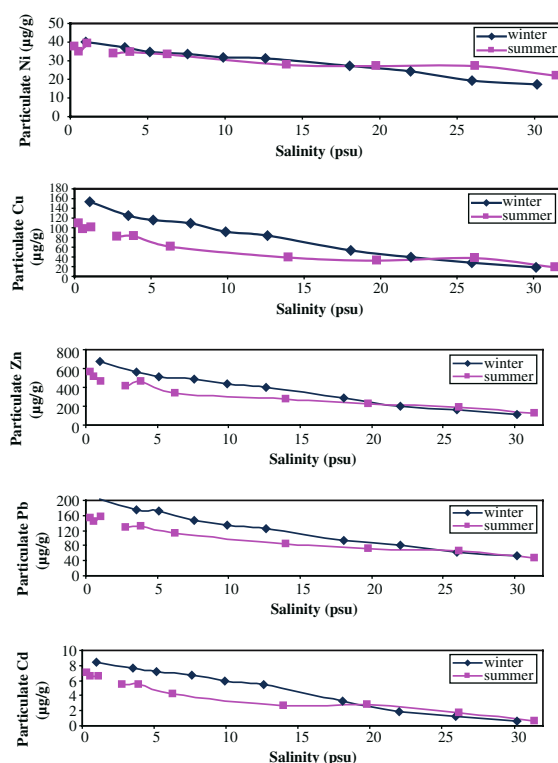


Figure 3. Particulate metal concentrations in the Scheldt estuary. A typical longitudinal winter and summer profile.

The shape of the dissolved Cd profiles is similar to that of dissolved Cu, although the latter show a broader convexity. In a number of cases, substantial increase of dissolved Cd starts only at a salinity of 8 psu. The curve maximum fits in a salinity window of 12–22 psu, and the highest curve maximum observed amounts to 1.35 nM. In some cases, high values in the upper and middle estuary may disturb the common profile. The freshwater end-member ranges from 0.03 nM to 0.26 nM, the marine/marine end-member is difficult to determine. It varies relatively strong, since the end of the curve is often not yet reached in the estuary. Dissolved Cu and Cd profiles seems to be governed by oxidation processes at the oxic/anoxic interface (upper/middle estuary) in summer periods and desorption reactions, sometimes disturbed by phytoplankton activity, in the lower estuary. Strong complexing organic ligands, respectively, chlorinity have a major impact on the dissolved and especially the free metal concentrations of Cu, respectively, Cd (Baeyens et al., 1998c). The observed shape of the curve is comparable to the

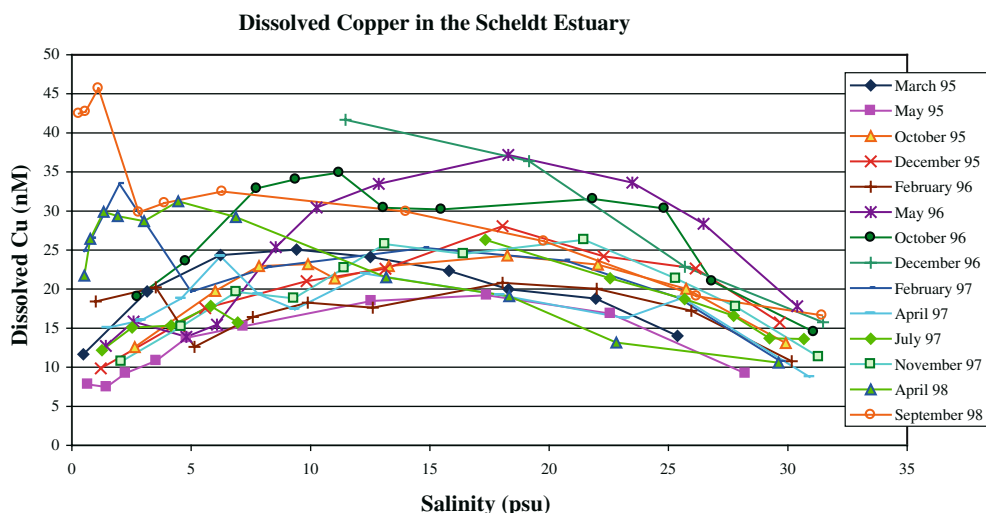


Figure 4. All longitudinal dissolved copper concentration profiles in the Scheldt estuary for the period 1995–1998.

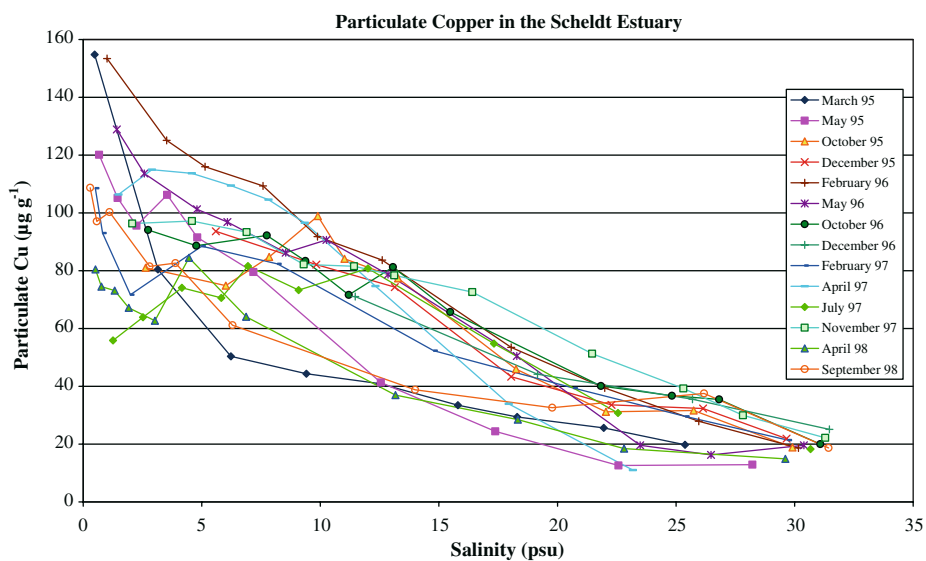


Figure 5. All longitudinal particulate copper concentration profiles in the Scheldt estuary for the period 1995–1998.

one described for the period 1981–1983 (Baeyens et al., 1998b). The values for the latter period are, however, much more elevated (almost double).

The dissolved Zn and Pb profiles are completely different from those of Ni, Cu and Cd. First, it should be stated that Zn is the element determined with the lowest accuracy (the lowest Z-scores were obtained for Zn in the intercalibration exercises), and this is certainly hampering

interpretation of the results. The dissolved Zn curve shows a dilution profile throughout the estuary, except in the low salinity area. Particularly in (late) spring some mobilisation trend is noticeable, whereas in winter only small aberrations from linearity occur. Sometimes the riverine end-member first slightly decreases, then progressively increases before finally obeying a dilution pattern. The riverine end-member varies from

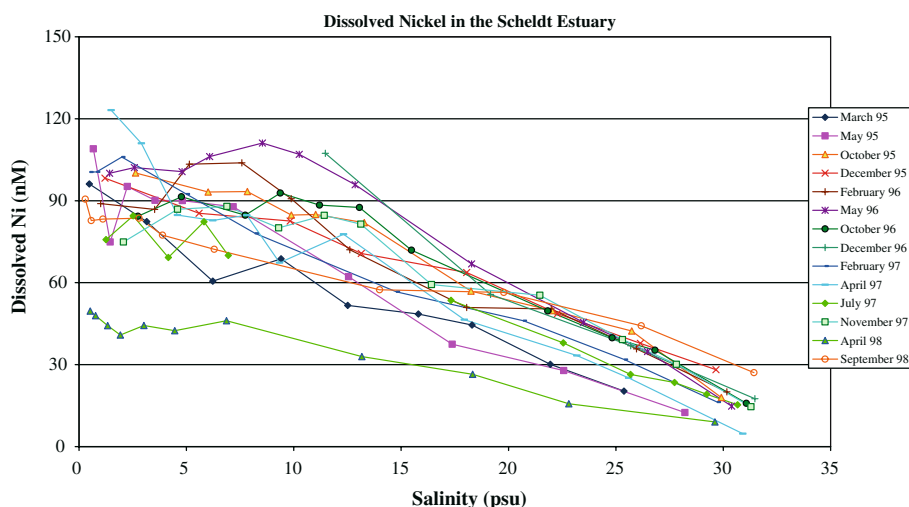


Figure 6. All longitudinal dissolved nickel concentration profiles in the Scheldt estuary for the period 1995–1998.

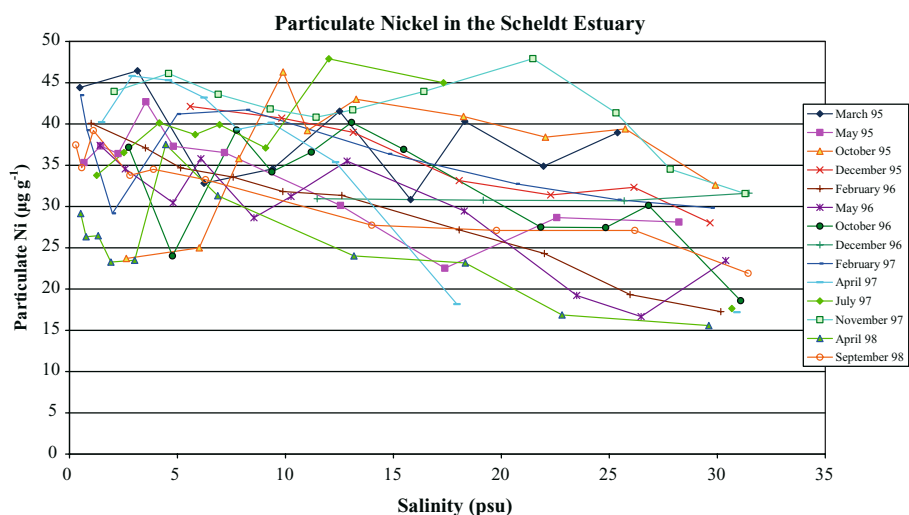


Figure 7. All longitudinal particulate nickel concentration profiles in the Scheldt estuary for the period 1995–1998.

42 nM to 144 nM, the mid-estuarine values from 41 nM to 157 nM, and the marine end-member from 2 nM to 40 nM.

The dissolved Pb concentrations decrease almost linearly from river to mouth, but sometimes high concentrations occur, usually in the middle estuary (2–10 psu). The riverine end-member concentrations vary from 0.6 nM to 2.6 nM, values in the middle estuary from 0.4 nM to 3.0 nM, and the marine end-member from 0.2 nM to 1.0 nM.

Dissolved Zn and Pb values in the upper and middle estuary are roughly only half of the values observed for the period 1981–1983

(Baeyens et al., 1998b), the marine end-member values and the shape of the curves are very comparable.

#### *Spatial distribution of particulate metals*

The longitudinal profiles of particulate Ni hardly show any variation along the estuary. The freshwater end-member ranges from  $23.7 \mu\text{g g}^{-1}$  to  $44.4 \mu\text{g g}^{-1}$ , the marine end member from  $15.6 \mu\text{g g}^{-1}$  to  $38.9 \mu\text{g g}^{-1}$ . In 8 out of 12 cruises, the maximum value does not coincide with the riverine end-member, but it can be as well near the

freshwater end-member as near the marine end-member, or in the middle of the estuary. This maximum ranges  $37.4 \mu\text{g g}^{-1}$  to  $47.9 \mu\text{g g}^{-1}$ . A clear trend is hard to determine, since concentrations do not follow a consistent pattern along the salinity gradient. Nevertheless, a slight tendency of decreasing concentration while increasing salinity can be noticed. Differences in particulate Ni load between the freshwater and marine environment are not very pronounced.

The longitudinal profiles of particulate Cu and Cd are dilution dominated ( $R^2$ -values  $> 0.9$  for 11 out of 14 for Cu, 9 out of 14 for Cd), and usually show no significant differences. Deviations from the ideal dilution line, observed during several campaigns in all seasons, suggest transfer from the solid to the dissolved phase. Indeed, depletions in the particulate phase concentration are often matching an increase in dissolved metal concentration. Particulate metal values are much lower than observed for the period 1981–1983 (Baeyens et al., 1998b), 2–3 times for Cu and 3–4 times for Cd.

The longitudinal profiles of particulate Zn and Pb are both dominated by dilution. For Zn correlations between the particulate metal concentration and salinity are very high with  $R^2$ -values  $> 0.9$  for 9 out of 14 campaigns. The riverine end-member ranges from  $340 \mu\text{g g}^{-1}$  to  $860 \mu\text{g g}^{-1}$ , the marine one from  $70 \mu\text{g g}^{-1}$  to  $180 \mu\text{g g}^{-1}$ . Particulate Pb shows even higher linear correlation between the particulate metal concentration and salinity with  $R^2$ -values  $> 0.9$  for 10 out of 14 campaigns. The riverine end-member ranges from  $90 \mu\text{g g}^{-1}$  to  $300 \mu\text{g g}^{-1}$ , the marine one from  $20 \mu\text{g g}^{-1}$  to  $70 \mu\text{g g}^{-1}$ . Particulate Zn and Pb values in the upper and middle estuary are considerably lower than the values observed for the period 1981–1983 (Baeyens et al., 1998b), the marine end-member values and the shape of the curves are again comparable.

### *Seasonal patterns*

**Dissolved Ni:** Dissolved Ni profiles show weak seasonal trends, but the slope of concentration vs. salinity curves is generally somewhat steeper during bloom periods. The highest concentrations near the mouth are found in September 1998, the lowest in all spring campaigns from 95 to 98.

**Dissolved Cu:** In seven out of 13 campaigns, the freshwater end-member was lower than the marine one, especially during fall and summer. In most cases, the curve maximum is situated near 18 psu. The highest value in this salinity range lays around 40 nM. The lowest dissolved Cu concentrations are observed during spring and winter. During one cruise (summer 1998) exceptional concentrations between 40 and 45 nM were observed in the upper-estuary.

**Dissolved Cd:** The maximum value in the estuary fluctuates seasonally with much lower concentrations in spring (maximum 0.25 nM in May; 0.46 nM in April) and in winter (maximum values between 0.49 and 0.73 nM). Higher values are observed in summer and fall (maximum values between 0.71 and 1.35 nM). These findings are comparable to those of Zwolsman & Van Eck (1993). The freshwater end-member varies between 0.03 and 0.26 nM (omitting some exceptionally high values of one cruise). In spring, this variation is only 0.03–0.08 nM, in summer 0.04–0.15 nM, in fall 0.11–0.20 nM, and in winter 0.15–0.26 nM. In 10 out of 13 campaigns, the freshwater end-member is lower than the marine one.

**Dissolved Zn:** In general, during winter, higher concentrations of dissolved Zn are noted in the upper estuary, whereas very low values occur during spring. In the middle estuary, concentrations are highest during late summer and fall. In the lower estuary, very low values occur during spring, and to a lesser extent during summer. Highest concentrations occur during winter.

**Dissolved Pb:** Seasonal variations are weak, although values during late fall and early winter tend to be higher.

**Particulate Cu and Cd:** In summer, and to a limited extent in spring, a positive deviation from the dilution curve occurs in the upper and middle estuary, both for particulate Cu and Cd. These perturbations are more pronounced for particulate Cd, a phenomenon that can be linked to the higher seasonal variations for dissolved Cd. The particulate copper values in fall and winter tend to be higher than in spring and summer. Riverine end-member values for copper can be as low as  $56 \mu\text{g g}^{-1}$  in summer, and as high as  $155 \mu\text{g g}^{-1}$  in winter. Marine end-member values are between  $11 \mu\text{g g}^{-1}$  in spring and  $25 \mu\text{g g}^{-1}$  in fall. This trend is not followed by particulate cadmium,

where values tend to be higher during spring, and lowest during fall. Riverine end-member values for cadmium can be as low as  $2.8 \mu\text{g g}^{-1}$  in summer, and as high as  $10.3 \mu\text{g g}^{-1}$  in winter. Marine end-member values can vary from  $1.3 \mu\text{g g}^{-1}$  in spring to  $0.55 \mu\text{g g}^{-1}$  in winter.

Particulate Zn and Pb: During summer, correlations between particulate Zn respectively Pb and salinity can be low, due to a rise of particulate Zn in the middle estuary, respectively particulate Pb in the upper and middle estuary.

### Input–Output – Loss

Table 2 shows the metal fluxes (dissolved and particulate) at the riverine–estuarine and the estuarine–marine interfaces. They are calculated as the average annual fresh water flow multiplied by the average metal concentration (over the period 1995–1998) at both interfaces. The input respectively output average annual water flow amounts to  $104 \text{ m}^3 \text{ s}^{-1}$  respectively  $148 \text{ m}^3 \text{ s}^{-1}$  with a relative standard deviation of about 30%. Similar calculations are presented in Baeyens et al. (1998a). In the dissolved phase, the riverine (input) flux of Ni, Pb and Zn is about 2–3 times higher than the output flux to the marine system. However, due to mobilization processes in the

estuary the reverse is true for Cd and Cu. The output flux of dissolved Cd is more than 2 times the input flux, while for Cu the difference is much smaller. For the particulate phase, all marine output fluxes are significantly lower than the riverine input fluxes. About 60% of the riverine particulate metal flux sedimentates in the zone of maximum turbidity. This zone is located in the upstream estuary corresponding to a salinity range of 5–10 psu. The marine output flux is in some cases only around 5% of the input flux.

### Reduction of the output fluxes over a 15-year period

The marine output fluxes of dissolved and particulate Cd, Cu, Pb and Zn were also estimated in the period 1981–1983 (Baeyens et al., 1998a). This allows us to calculate reduction percentages for those metals in the dissolved and particulate phases which range from 30% (particulate lead and zinc) up to 58% for particulate cadmium. These reductions can be compared to estimates made in the framework of the International Conferences on the Protection of the North Sea (Progress Reports and Quality Status Reports). Emission fluxes of metals into the atmosphere and surface

Table 2. Dissolved and particulate trace metals in the Scheldt estuary. Inputs – Sinks–Outputs

	Dissolved phase (tons year <sup>-1</sup> )		
	Riverine inputs	Marine outputs	
Ni	18.3 ± 7.3	5.0 ± 2.4	
Cd	0.055 ± 0.055	0.136 ± 0.088	
Cu	3.2 ± 1.8	4.0 ± 1.5	
Pb	0.99 ± 0.67	0.59 ± 0.32	
Zn	20.1 ± 9.4	6.6 ± 2.9	
	Particulate phase (tons year <sup>-1</sup> )		
	Riverine inputs	Marine outputs	Sedimentation flux Zone 2–10 psu
Ni	14.7 ± 5.1	3.2 ± 1.3	8.7 ± 2.9
Cd	3.8 ± 1.4	0.135 ± 0.063	2.3 ± 0.9
Cu	48 ± 19	2.66 ± 0.97	29 ± 10
Pb	93 ± 36	6.4 ± 2.7	56 ± 19
Zn	263 ± 98	18.7 ± 7.4	159 ± 57

Table 3. Reduction of trace metal concentrations at the mouth of the Scheldt estuary

Reduction of discharges into the Scheldt between 1985–2000 based on emission measurements (%)	Reduction of concentrations measured at the mouth of the Scheldt estuary between 1981–1983 and 1995–1998
Cd: 64	Cd: 55% (D), 58% (P)
Cu: 47	Cu: 35% (D), 53% (P)
Pb: 42	Pb: 50% (D), 30% (P)
Zn: 55	Zn: 50% (D), 30% (P)

waters, resulting from anthropogenic activities, are measured by the Regional authorities. In addition, emission estimates are also made knowing the consumption of these metals by specific industrial and agricultural activities. Both approaches (Baeyens et al., 2001) led to the following observations (see Table 3).

**Cadmium:** compared to the reference values of 1985, the reduction in cadmium emissions to the surface waters in 2000 amount to 64% (from 16.9 to 6.1 tons year<sup>-1</sup>). Reductions of emissions are mainly achieved in the fertilizer industry, the non-ferrous metal industry and iron and steel industry.

**Copper:** compared to the reference values of 1985, the reduction in copper emissions to the surface waters in 2000 amount to 47% (from 148 to 78 tons year<sup>-1</sup>). Means to achieve these reductions are mainly based on the strengthening of emission discharge limits and the introduction of environmental taxes on the copper load in the waste water discharges.

**Lead:** compared to the reference values of 1985, the reduction in lead emissions to the surface waters in 2000 amount to 42% (from 126 to 73 tons year<sup>-1</sup>). Means to achieve these reductions are equal to those for copper.

**Zinc:** compared to the reference values of 1985, the reduction in zinc emissions to the surface waters in 2000 amount to 55% (from 284 to 127 tons year<sup>-1</sup>). Means to achieve these reductions are equal to those for copper.

The reduction percentages for Cu and Pb (Baeyens et al., 2001) lay between those obtained from measurements in the dissolved and particulate phases at the mouth of the Scheldt estuary (Table 3). For Cd the former estimates are slightly higher than the latter ones, while for zinc the reductions measured at the mouth are too low compared to the emission based reductions

(Baeyens et al., 2001). The fact that zinc is analysed with the lowest accuracy (e.g. Parmentier, 2003) is perhaps a possible explanation.

### Bioconcentration and biomagnification

Bioconcentration factors (BCF) represent the distribution between solid and dissolved phases. In open ocean waters this solid fraction is mostly biogenic but in estuaries and coastal areas the non-biogenic fraction may become very important. The BCF values for Cd, Cu, Ni, Pb and Zn in the Scheldt estuary, with  $BCF = \frac{\text{particulate metal concentration } (\mu\text{g g}^{-1}\text{-suspended particulate matter, d.w.})}{\text{dissolved metal concentration } (\mu\text{g mg}^{-1}\text{-water})}$ , corresponding in this case to the  $K_D$ -values, are presented in Table 4. The  $K_D$ s of Zn are quite stable, those of Pb decrease most of all in downstream direction while those of Ni are the only ones that increase in downstream direction.

#### $K_D$ Ni

The distribution coefficient,  $K_D$ , of Ni remains almost constant throughout the lower and middle estuary and varies little (4000–13 000). Near the mouth of the estuary, the  $K_D$  values as well as their range (7000–40 000) increase. For most sampling cruises, a net increase in  $K_D$  throughout the estuary takes place. This increase is very explicit near the mouth, in the salinity range 20–32 psu, corroborating the patterns observed for the dissolved metal fraction.

#### Cu and Cd $K_D$ values

The distribution coefficient  $K_D$  of Cu decreases exponentially with increasing salinity. In the upper

Table 4. Median metal concentrations in solution (D), suspended particulate matter (P) and  $K_D$ -values (Based on the median value at the given salinity of 14 longitudinal profiles)

Salinity (psu)		Ni	Cu	Zn	Cd	Pb
28	D ( $\mu\text{g ml}^{-1}$ )	0.0017	0.0010	0.0016	0.00004	0.00010
	P ( $\mu\text{g g}^{-1}$ )	28.1	25	150	1	40
	$10^{-3} * K_D$	16	24	91	25	380
25	D ( $\mu\text{g ml}^{-1}$ )	0.0021	0.0012	0.0022	0.00006	0.00010
	P ( $\mu\text{g g}^{-1}$ )	29.3	30	170	1.42	63
	$10^{-3} * K_D$	13	24	78	25	610
20	D ( $\mu\text{g ml}^{-1}$ )	0.0029	0.0015	0.0033	0.00008	0.00011
	P ( $\mu\text{g g}^{-1}$ )	31.1	40	240	2.25	75
	$10^{-3} * K_D$	10	26	73	30	670
15	D ( $\mu\text{g ml}^{-1}$ )	0.0037	0.0016	0.0042	0.00006	0.00013
	P ( $\mu\text{g g}^{-1}$ )	33	60	310	3.9	100
	$10^{-3} * K_D$	8.5	38	72	64	750
12	D ( $\mu\text{g ml}^{-1}$ )	0.0042	0.0015	0.0048	0.00005	0.00015
	P ( $\mu\text{g g}^{-1}$ )	34.1	73	380	4.97	120
	$10^{-3} * K_D$	7.8	48	78	102	810
10	D ( $\mu\text{g ml}^{-1}$ )	0.0045	0.0015	0.0052	0.00004	0.00016
	P ( $\mu\text{g g}^{-1}$ )	34.8	80	420	5.55	132
	$10^{-3} * K_D$	7.4	54	80	135	850

estuary, the  $K_D$  ranges from  $4 \times 10^4$  to  $24 \times 10^4$ , while downstream this parameter stabilizes around  $2 \times 10^4$ – $3.5 \times 10^4$ . The highest  $K_D$  values of Cu are observed in May and March 1995. The  $K_D$  profile of Cd shows an exponential decrease with increasing salinity. A maximum Cd- $K_D$  of  $9 \times 10^5$ – $23 \times 10^5$  is found in spring while in other seasons this value is much lower ( $0.5 \times 10^5$ – $6 \times 10^5$ ). The upstream  $K_D$  of Cd in the period 1981–1983 reached a value of about  $4 \times 10^5$  (Baeyens et al., 1998b). In general,  $K_D$  values for Cu and Cd compare well with those observed in the former period.

#### Zn and Pb $K_D$ values

The distribution coefficient  $K_D$  of Zn is higher in the upper estuary ( $7 \times 10^4$ – $15 \times 10^4$ ) and near the mouth ( $5 \times 10^4$ – $15 \times 10^4$ ), and lower in the middle estuary ( $3 \times 10^4$ – $8 \times 10^4$ ). Values tend to be higher during bloom periods, especially in the upper estuary, and in summer also near the mouth. The  $K_D$  profiles of Pb are almost constant throughout the estuary and vary from  $3 \times 10^5$ – $16 \times 10^5$ . Both  $K_D$  values are comparable to the highest  $K_D$  values

(upstream) in the period 1981–1983 (Baeyens et al., 1998b).

#### BCF and BMF of trace metals in Scheldt organisms

In the Scheldt estuary trace metal concentrations were reported in Periwinkle (*Littorina littorena*) for the period 1998 by De Wolf et al. (2000) and in *Nereis diversicolor* and *Macoma balthica* for the period 1993–1994 by Srinetr (1997). These values (Table 5) allowed us to calculate log-BCF values, with  $\text{BCF} = \text{metal concentration in the organism } (\mu\text{g g}^{-1}\text{-organism, d.w.}) / \text{dissolved metal concentration } (\mu\text{g mg}^{-1}\text{-water})$ , for these three organisms at various salinities (between 10 and 28 psu) in the Scheldt estuary (Table 6). No strong variations with salinity were observed. The highest log-BCF values (above 4.6) were observed for Cu and Cd in Periwinkle, and Zn in *Nereis diversicolor* and *Macoma balthica*. Zn and Cu are essential oligo-elements for those organisms and are thus evidently more liable for uptake by these organisms. Lowest log-BCFs (below 3.3) were found for Ni in all three organisms.

Table 5. Metal concentration ranges in solution (D), suspended particulate matter (P) and KD-values in the salinity ranges 9–11, 18–20 and 27–29.5 psu

Salinity range		Ni	Cu	Zn	Cd	Pb
psu						
27–29.5	D ( $\mu\text{g ml}^{-1}$ )	0.00053–0.0021	0.00059–0.0013	0.00052–0.0023	0.000009–0.000073	0.000043–0.00020
N = 8	P ( $\mu\text{g g}^{-1}$ )	6–35	13–36	97–230	0.55–1.6	35–70
	$10^{-3} \times \text{KD}$	14–38	22–32	57–190	9.0–95	210–920
18–20	D ( $\mu\text{g ml}^{-1}$ )	0.0016–0.0039	0.0012–0.0024	0.0026–0.0064	0.000036–0.00013	0.000052–0.00027
N = 8	P ( $\mu\text{g g}^{-1}$ )	18–41	29–54	170–290	1.4–4.3	46–140
	$10^{-3} \times \text{KD}$	7.5–15	19–41	30–78	17–130	340–2700
9–11	D ( $\mu\text{g ml}^{-1}$ )	0.0039–0.0065	0.0011–0.0022	0.0027–0.0098	0.000018–0.000097	0.00010–0.00052
N = 8	P ( $\mu\text{g g}^{-1}$ )	31–46	44–99	230–550	2.8–8.2	90–170
	$10^{-3} \times \text{KD}$	5.0–10	28–87	35–200	65–460	260–1600

Table 6. Bioconcentration factors (log-BCF) of trace metals in three organisms in the Scheldt estuary

Salinity (psu)	Ni	Cu	Zn	Cd	Pb
BCF Periwinkle ( <i>Littorina littorea</i> )					
28	3.31	4.83	4.69	4.36	3.92
25	3.46	4.96	4.51	4.39	4.05
20	3.40	4.92	4.42	4.78	4.17
15	3.15	5.05	4.34	4.79	3.88
12	3.04	4.97	4.34	5.02	4.04
Mean	3.28	4.95	4.46	4.67	4.01
BCF <i>Nereis diversicolour</i>					
25	3.35	4.30	4.91	3.65	4.16
15	3.21		4.75	4.08	4.16
12	3.23	4.19	4.80	4.54	3.96
10	3.04	4.28	4.76	4.57	4.23
Mean	3.21	4.26	4.80	4.21	4.13
BCF <i>Macoma balthica</i>					
15	3.18	4.11	4.88	4.02	4.21
12	3.33	4.13	4.87	4.31	4.16
Mean	3.26	4.12	4.88	4.17	4.19

Biomagnification (BMF) is the accumulation of a compound through the food-chain. It is in our case expressed as the ratio of the metal concentration in the organism ( $\mu\text{g g}^{-1}$ , d.w.) / the metal concentration in total suspended matter ( $\mu\text{g g}^{-1}$ , d.w.). Table 7 shows the log-BMF values for Periwinkle, *Nereis diversicolour* and *Macoma balthica* at various salinities in the Scheldt estuary. Almost all values are negative indicating that the organisms contain less heavy metals than the

particulate suspended matter. For all organisms log BMFs for Pb are around  $-1.8$ , those for Ni around  $-0.7$  to  $-0.8$ . For Cd, Cu and Zn differences in BMF between Periwinkle and the 2 other organisms were found. Periwinkle shows slight enrichment in Cd (0.06) and even more in Cu (0.45), while negative values were observed for *Nereis diversicolour* and *Macoma balthica*. The latter organisms are more enriched in Zn ( $-0.09$ ) than Periwinkle ( $-0.43$ ). So for some metals (Ni

Table 7. Biomagnification factors (log-BMF) of trace metals in 3 organisms in the Scheldt estuary

Salinity (psu)	Ni	Cu	Zn	Cd	Pb
<b>BMF Periwinkle (<i>Littorina littorea</i>)</b>					
28	-0.91	0.44	-0.27	-0.04	-1.7
25	-0.68	0.56	-0.38	0.003	-1.7
20	-0.62	0.50	-0.44	0.30	-1.7
15	-0.80	0.47	-0.52	-0.01	-2.0
12	-0.87	0.28	-0.55	0.02	-1.9
Mean	-0.78	0.45	-0.44	0.06	-1.79
<b>BMF <i>Nereis diversicolor</i></b>					
25	-0.79	-0.09	0.01	-0.74	-1.62
15	-0.74		-0.11	-0.72	-1.72
12	-0.68	-0.50	-0.10	-0.46	-1.95
10	-0.85	-0.46	-0.14	-0.56	-1.70
Mean	-0.77	-0.35	-0.09	-0.62	-1.75
<b>BMF <i>Macoma balthica</i></b>					
15	-0.77	-0.48	0.02	-0.78	-1.66
12	-0.58	-0.56	-0.02	-0.69	-1.75
Mean	-0.68	-0.52	0.00	-0.74	-1.71

Table 8.  $K_D$ -values ( $10^{-3}$ ) in the Scheldt and other estuaries in the salinity range 10–20 psu

Estuary	Cd	Cu	Pb	Zn	Ni	
<b>Scheldt estuary</b>						
1978	53.6	–	–	42.9	10	Duinker et al. (1982)
1980	26.3	76.5	1140	–		Valenta et al. (1986)
1981–1983	43.2	50	638	30.9		Baeyens (1998)
1987	41.6	37.3	–	40.0		Zwolsman & van Eck (1993)
1991–1994	47.2	35.5	–	30.0	6.8	Paucot & Wollast (1996)
1995	41.1	34.3	1210	61.1		Baeyens (1998)
1995–1998	64	38	750	72	8.5	Parmentier (2003)
<b>Other estuaries</b>						
Seine (France)	5.2	100	21	23	–	Ouddane et al. (1992)
Lena (Russia)	–	69	2300	340	79	Martin et al. (1993)
Galveston (USA)	–	19	140	52	–	Benoit et al. (1994)
Humber (U.K.)	2.6	4.9	–	15	4.3	Comber et al. (1995)
Mersey (U.K.)	66	55	125	29	5.1	Comber et al. (1995)
Gironde (France)	4.9	45	1300	200	120	Kraepiel et al. (1997)

and Pb), a comparable behaviour of the three organisms is found while for others (Cd, Cu and Zn) differences in biomagnification are noticeable.

#### *K<sub>D</sub> values in the Scheldt estuary and other estuaries.*

Table 8 summarizes  $K_D$ -values observed in the Scheldt estuary in the salinity range 10–20 psu,

for the 5 trace metals over a period of 20 years (1978–1998). Especially the  $K_D$ -values of Zn and to a lesser extent also those of Cd show a tendency to increase (the relative importance of the particulate versus the dissolved phase becomes stronger) in more recent years.  $K_D$ -values of Cu, Pb and Zn in the Scheldt estuary are in the middle of the range observed in estuaries like

Humber (U.K.), Mersey (U.K.), Galveston (USA), Seine (Fr), Gironde (Fr) and Lena (Russia) (Table 8). The  $K_D$ -values of Cd and Ni are at the extreme end of the observed range: for Cd at the high side together with that in the Mersey, for Ni at the low side together with those in Humber and Mersey.

### Conclusion

The longitudinal profiles of dissolved and particulate Ni confirm the strong influence of dilution, and of varying freshwater influx in the early mixing zone. Particulate Ni follows a vague dilution trend throughout the estuary, the difference between Ni concentration on marine and fluvial suspended matter being too small to establish clear trends. Compared to other estuaries, the Ni contamination level seems to be in the range of other polluted rivers of Western Europe.

Dissolved Cu and Cd profiles are governed by oxidation processes at the oxic/anoxic interface (upper/middle estuary) in summer periods and by desorption reactions, but sometimes the profiles are disturbed by phytoplankton activity in the lower estuary. Strong complexing organic ligands respectively chlorinity have a major impact on the dissolved and especially the free metal concentrations of Cu respectively Cd (Baeyens et al., 1998c). Particulate Cu and Cd are controlled by dilution, but the changes occurring in the dissolved phase are also reflected in the particulate phase: mobilization due to oxidation processes and phytoplankton activity (in the upper estuary during summer, in the lower estuary during spring). Moreover, during periods of high flow, the increased oxidation capacity in the upper estuary can cause local perturbation of the normal patterns.

Zn shows only non-conservative behaviour in the low salinity area. Dissolved Zn maxima occur at low salinity, and are low or even absent in winter. The dissolved Pb concentrations decrease almost linearly from river to mouth, but sometimes high values in the middle estuary are to be noted. Pb appears for over 90% present in the particulate phase. Correlations between particulate Pb or Zn and salinity are very good and high chlorophyll-a levels during spring and summer

correspond with the negative deviation from the ideal dilution line.

Marine output fluxes of all particulate metals are significantly lower than their riverine input fluxes. About 60% of the riverine particulate metal flux sedimentates in the zone of maximum turbidity. This zone is located in the upstream estuary corresponding to a salinity range of 5–10 psu (Baeyens et al., 1998a). The marine output flux is in some cases only around 5% of the input flux. For the dissolved phase, the riverine (input) flux of Ni, Pb and Zn is about 2–3 times higher than the output flux to the marine system. However, due to mobilization processes in the estuary itself, the reverse is true for Cd and Cu. The output flux of dissolved Cd is more than 2 times the input flux, while for Cu the difference is much smaller.

The reduction percentages for Cu (47%) and Pb (42%) reported by Baeyens et al. (2001) are of the same order of magnitude as those resulting from measurements in the dissolved (Cu is 35% and Pb is 50%) and particulate phases (Cu is 53% and Pb is 30%) at the mouth of the Scheldt estuary in the periods 1981–1983 and 1995–1998. For Cd the former estimate (64%) is slightly higher than the latter ones (dissolved is 55% and particulate is 58%), while for zinc the reductions measured at the mouth (dissolved is 50% and particulate is 30%), are too low compared to the 55% reduction reported by Baeyens et al. (2001). The fact that zinc is analysed with the lowest accuracy (Parmentier, 2003) is perhaps a possible explanation.

Log-BCF values for Periwinkle (*Littorina littorea*), *Nereis diversicolor* and *Macoma balthica* at various salinities (between 10 and 28 psu) in the Scheldt estuary were calculated. No strong variations with salinity were observed. The highest log-BCF values (above 4.6) were observed for Cu and Cd in Periwinkle, and Zn in *Nereis diversicolor* and *Macoma balthica*. Zn and Cu are essential oligo-elements for those organisms. Lowest log-BCFs (below 3.3) were found for Ni in all 3 organisms. All organisms showed similar log-BMFs for Pb and for Ni. For Cd, Cu and Zn differences in biomagnification between Periwinkle and the two other organisms were found.

Future research should provide more information on diagenetic processes in the sediments especially in the area of high sedimentation, on

processes occurring at the riverine/estuarine interface because little is known about trace metals in the riverine part and on the transfer of trace metals through the whole food-web.

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### References

- Baeyens, W., 1998. Evolution of trace metal concentrations in the Scheldt estuary (1978–1995). A comparison with estuarine and ocean levels. *Hydrobiologia* 366: 157–167.
- Baeyens, W., F. Monteny, R. Van Ryssen & M. Leermakers, 1998a. A box-model of metal flows through the Scheldt estuary (1981–1983 and 1992–1995). *Hydrobiologia* 366: 109–128.
- Baeyens, W., M. Elskens, G. Gillain & L. Goeyens, 1998b. Biogeochemical behaviour of Cd, Cu, Pb and Zn in the Scheldt estuary during the period 1981–1983. *Hydrobiologia* 366: 15–43.
- Baeyens, W., L. Goeyens, F. Monteny & M. Elskens, 1998c. Effect of organic complexation on the behaviour of dissolved Cd, Cu and Zn in the Scheldt estuary. *Hydrobiologia* 366: 81–90.
- Baeyens, W., R. Van Grieken & R. Wollast, 2001. Evaluation of the chemical contamination of the North Sea and estimation of the terrestrial pollution (in Dutch). Final Report, Federal Office for Scientific, Technical and Cultural Affairs (DWTC-SSTC), Belgium, 374 pp.
- Baeyens, W., M. Leermakers, T. Papina, A. Saprykin, N. Brion, J. Noyen, M. De Gieter & L. Goeyens, 2003. Mercury speciation in North Sea and Scheldt estuary fish. *Archives of Environmental Contaminant and Toxicology* 45: 498–508.
- Benoit, G., S. D. Oktay-Marshall, A. Cantu., E. M. Hood, C. H. Coleman, M. O. Corapcioglu & P. H. Santschi, 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Marine Chemistry* 45: 307–336.
- Comber, S. D. W., A. M. Gunn & C. Whalley, 1995. Comparison of the Partitioning of Trace Metals in the Humber and Mersey Estuaries. *Marine Pollution Bulletin* 30: 851–860.
- Danielsson L.-G., B. Magnusson, & S. Westerlund, 1978. An improved metal extraction procedure for the determination of trace metals in sea water by atomic absorption spectroscopy with electrothermal atomisation. *Analytica Chimica Acta* 98: 47–57.
- Danielsson L.-G., B. Magnusson, S. Westerlund, & K. Zhong, 1982. Trace metal determinations in estuarine waters by electrothermal atomic absorption after extraction of dithiocarbamate complexes into freon. *Analytica Chimica Acta* 144: 183–188.
- Dewolf, H., T. Backeljau & R. Blust, 2000. Heavy metal accumulation in the periwinkle *Littorina Littorea*, along a pollution gradient in the Scheldt estuary. *Science Total Environment* 262: 111–121.
- Duinker, J. C., R. F. Nolting & D. Michel, 1982. Effects of salinity, pH and redox conditions on the behaviour of Cd, Zn, Ni and Mn in the Scheldt Estuary. *Thalassia Jugoslavica* 18 (1–4): 191–202.
- Leermakers, M., S. Galetti, S. De Galan, N. Brion & W. Baeyens, 2001. Mercury in the Southern North Sea and Scheldt Estuary. *Marine Chemistry* 75(3): 229–248.
- Martin, J. M., D. M. Guan, F. Elbaz-Poulichet, A. J. Thomas & V. V. Gordeev, 1993. Preliminary assessment of the distributions of some trace elements (As, Cd, Cu, Fe, Ni, Pb and Zn) in a pristine aquatic environment: the Lena River estuary (Russia). *Marine Chemistry* 43: 185–199.
- Ouddane, B., J.-C. Fischer & M. Wartel, 1992. Evaluation statistique de la repartition des metaux en traces Cd, Pb, Cu, Zn et Mn dans la Seine et son estuaire. *Oceanology Acta* 15(4): 347–354.
- Parmentier, K., 2003. Biogeochemical behaviour of trace metals in the Scheldt estuary and the Southern Bight of the North Sea. PhD thesis, Vrije Universiteit Brussel, Belgium, 254 pp.
- Paucot, H. & R. Wollast, 1997. Transport and transformation of trace metals in the Scheldt estuary. *Marine Chemistry* 58: 229–244.
- Srinetr, V., 1997. Metal bioavailability to macrobenthic species of the Western Scheldt: adverse effect, source and exposure. PhD thesis, Vrije Universiteit Brussel, Belgium, 299 pp.
- Valenta P., E. K. Duursma, A. G. Merks, H. Rützel & H. W. Nürnberg, 1986. Distribution of Cd, Pb and Cu between the dissolved and particulate phase in the eastern Scheldt and western Scheldt estuary. *Science Total Environment* 53: 41–76.
- Zwolsman, G. & G. T. M. Van Eck, 1993. Dissolved and particulate trace metal geochemistry in the Scheldt estuary, S. W. Netherlands (water column and sediments). *Netherlands Journal of Aquatic Ecology* 27: 287–300.