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# DISSOLVED AND PARTICULATE TRACE METAL GEOCHEMISTRY IN THE SCHELDT ESTUARY, S.W. NETHERLANDS (WATER COLUMN AND SEDIMENTS)

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**KEYWORDS:** Trace metals; geochemistry; Scheldt estuary.

## ABSTRACT

The geochemistry of dissolved and particulate trace metals has been studied in the water column and the sediments of the Scheldt estuary between 1987 and 1990. A strong seasonal influence on the behaviour of dissolved Cd, Cu and Zn is observed, related to the redox conditions in the upper estuary and phytoplankton activity in the lower estuary (which are both seasonally dependent variables). The dissolved trace metal concentrations in the fresh water end-member are remarkably low during spring and summer, due to metal sulphide precipitation in the anoxic Scheldt river. However, the dissolved concentrations increase rapidly with increasing salinity, due to oxidation of metal sulphides that are present in the suspended matter, accompanied by (*e.g.* chloro-)complexation of the released metals. Readsorption of Cd and Zn occurs in the lower estuary during the spring phytoplankton bloom. During winter, when the Scheldt river is not completely anoxic, much higher dissolved trace metal concentrations are observed in the fresh water end-member since metal sulphide precipitation in the water column is precluded. Rapid trace metal removal is observed in the low salinity, high turbidity zone, due to adsorption onto suspended matter and freshly precipitated iron and manganese oxyhydroxides. Upon further mixing, desorption is apparent, due to a similar oxidation-complexation mechanism as observed during spring and summer. Pore water infusion may also contribute to the enrichment of dissolved Cd, Cu and Zn in the mid-estuarine region. The trace metal contents of the suspended matter and the sediments show a continuous decrease with increasing salinity. This behaviour is to a very large extent due to physical mixing of contaminated fluvial particulates and relatively unpolluted marine particulates. Desorption of Cd, Cu and Zn can be identified but is of minor importance compared to the conservative mixing process. The distribution of dissolved Cd, Cu and Zn in the pore waters of the mid-estuarine region reflects the impact of early diagenetic processes. Trace metal peaks are observed near the sediment-water interface, and at greater depth in the manganese and iron reduction zones. These peaks are attributed to oxidation of reduced trace metal compounds (*e.g.* sulphides) and reduction of the (iron and manganese) oxide carrier phases, respectively. At greater depth, the dissolved trace metal concentrations are much lower due to metal sulphide precipitation in the sulphate reduction zone. Analysis of a large sediment dataset indicates severe trace metal pollution of the Scheldt estuary at the end of the fifties. A major reduction of the pollution by As, Cr, Hg, Pb, and Zn has occurred in the seventies, and of Cd and Cu in the eighties. The Ni pollution has increased over the time period considered. In spite of this improvement, the present-day pollution status of the Scheldt estuary is still reason for concern.

## INTRODUCTION

The Scheldt estuary (Fig.1) is confronted with two major problems. 1) Extensive dredging and dumping operations of (contaminated) sediments to keep the port of Antwerp accessible and 2) large domestic and industrial waste water discharges. A few years ago it was decided to construct a management-oriented transport, biogeochemical and bio-accumulation model to deal with the second problem. The aim of the model is to relate the discharge of pollutants into the estuary to the contents found in some organisms (and in the abiotic compartments as well). An outline of the model is given in VAN ECK and DE ROOIJ (1990). The water quality model developed is described in VAN GILS *et al.* (1993).

In order to provide data and process information for the trace metal routine of the water quality model, the occurrence and behaviour of some trace metals in the abiotic compartments water, suspended matter, bottom sediments and pore waters were studied between 1986 and 1990. The major objectives of this study were to assess the spatial and seasonal trace metal distribution in the water column and the sediments, and to identify the processes which control this distribution. Moreover, the trace metal composition of the sediments was studied in order to assess changes in the 'pollution history' between 1959 and 1989 in a statistically reliable way. Pore waters were studied in order to assess the fate of trace metals during early diagenesis, and for ecotoxicological reasons. Since the dissolved metal fraction is generally considered to be biologically available, the composition of the pore waters may be more important in determining the toxicity of the sediments than is their total metal content (DI TORO *et al.*, 1990).

Related studies supporting the model concern a cohesive sediment balance (VAN MALDEGEM *et al.*, 1993), the behaviour of nutrients (BODERIE *et al.*, 1993) and organic micropollutants (VAN ZOEST and VAN ECK, 1993), and the effects of trace metals and organic micropollutants on the biota of the Scheldt estuary (STRONKHORST, 1993).

## STUDY AREA

The river Scheldt and its tributaries drain some 21600 km$^2$ in northwest France, west Belgium and the southwest Netherlands. The river discharge varies from 20 m$^3$ s$^{-1}$ during summer to 400 m$^3$ s$^{-1}$ during winter, averaging 105 m$^3$ s$^{-1}$ over the period 1949-1987. The estuarine mixing zone is situated between the village Rupelmonde and the North Sea, covering a distance of 90 km (Fig. 1). The Scheldt estuary is a macrotidal coastal plain estuary with a tidal range of 4-5 m and an average water depth of 10 m. The residence time of the water in the estuary ranges from one to three months, depending on the river discharge. Usually, only small vertical gradients are observed in the water column, implying that the water masses are well-mixed (except for extremely high river discharges during winter). The estuary can be divided into two zones with different hydrographical characteristics.

The upper estuary, located in northwest Belgium, is heavily polluted by domestic, industrial and agricultural waste loads (*e.g.* WOLLAST, 1988). One of the most striking features of this area is the presence of an anoxic water column during most of the year (SOMVILLE and DE PAUW, 1982). Previous studies in the Scheldt estuary have suggested that this anoxic zone plays an important role in the behaviour of trace metals (SALOMONS *et al.*, 1981; DUINKER *et al.*, 1982). The sediments of the upper estuary consist of sands, sandy muds and clayey muds (WARTEL, 1977). The finest sediments are found in the so-called high turbidity zone (HTZ) between the city of Antwerp and the Dutch-Belgian border. The HTZ is an important sedimentation area, due to the presence of high suspended matter concentrations, combined with low residual current velocities near the bottom (WOLLAST, 1988). Consequently, the sediments in the HTZ need to be dredged continuously in order to keep the port of Antwerp accessible. The majority of the dredged sediments is disposed in the estuary itself at several dumping locations.

The lower estuary, situated between the Dutch-Belgian border and the North Sea, has a complex morphology with well-defined flood and ebb channels surrounding intertidal sand- and mudflats (Fig. 1). The water column is well-oxygenated, with oxygen saturation increasing from 20-60% at the border to 90-100% at the mouth of the estuary. The bottom sediments consist mainly of medium to coarse sands, while mud deposits are exceptional here (WARTEL, 1977). Much finer sediments can be found in the intertidal areas of the lower estuary, especially in the salt marshes (OENEMA *et al.*, 1988; ZWOLSMAN *et al.*, 1993).

The input of fluvial suspended matter into the upper estuary is about 10 kg s$^{-1}$ or 321$*$10$^6$ kg y$^{-1}$ (VAN MALDEGEM *et al.*, 1993). A second source of suspended matter is marine mud, which accounts for an additional input of 87$*$10$^6$ kg y$^{-1}$. Other major sources of suspended matter include primary production, which is important during spring and summer, and waste water discharges in the highly industrialized Antwerp area. Most of the suspended matter is deposited between Antwerp and the Dutch-Belgian border, and in the intertidal areas of the lower estuary (especially in the Saeftinghe salt marsh, see Fig. 1). According to recent estimates,

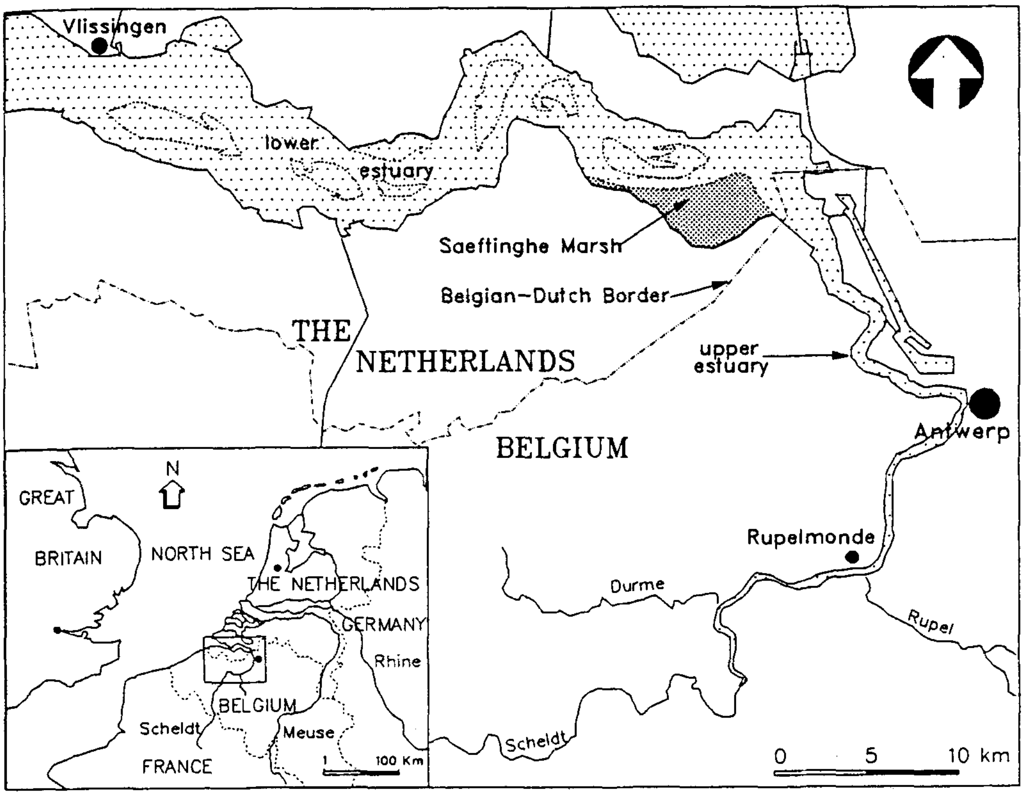

**Fig. 1.** The Scheldt estuary.

about 10-30% of the fluvial suspended matter reaches the coastal zone.

## SAMPLING AND ANALYSIS

### General water quality and dissolved trace metals

Eight surveys were carried out at regular intervals between February 1987 and February 1988. Water samples from the main shipping channel were collected during cruises from the mouth of the estuary (salinity $22\text{-}29*10^{-3}$) up to the Rupel confluent (salinity $0.3\text{-}1.0*10^{-3}$). Salinity, pH, dissolved oxygen and water temperature were monitored continuously during each cruise. At appropriate salinities, water was pumped from a depth of 1 m and subsampled for analysis of trace metals, nutrients and chlorophyll-*a*. Some anoxic water samples were also analyzed for dissolved sulphide.

Special care was taken to avoid contamination during sampling for dissolved trace metals. All materials were acid-cleaned prior to use. Water samples for trace metal analyses were immediately filtered through 0.45 μm cellulose nitrate filters. The filtration was carried out under nitrogen pressure in an all-teflon apparatus, placed on a clean bench. The first 100 ml of the filtrate were rejected. The next 250 ml were collected and adjusted to pH 1-2 with ultra-pure $HNO_3$. The filtered samples were stored at 4°C in the dark until analysis. Dissolved Cd, Cu and Zn were determined in the clean laboratory by atomic absorption spectroscopy after preconcentration in HMDC-DIPK, following the method of DORNEMANN and KLEIST (1979).

Subsamples for analyses of general water quality parameters were filtered immediately after collection and stored at 4°C in the dark. These samples were analyzed within two days, following standard auto-analyzer procedures (GRASSHOFF *et al.*, 1983). Nutrients were determined colorimetrically, chlorophyll-a by reversed-phase HPLC, and sulphide by the methylene-blue method.

### Suspended matter composition (major elements and trace metals)

At each of the stations for dissolved trace metal sampling, suspended matter was collected by means of continuous flow centrifugation. Suspended matter samples were stored at -20°C and freeze-dried within two days. Trace and major elements (except Si) were measured by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) after total decomposition of the samples in HF-$HClO_4$-$HNO_3$, following the method of NAKASHIMA *et al.* (1988). Particulate Si was analyzed by ICP-ES after fusion with $LiBO_2$ at 900°C, followed by dissolution in 0.2 M HCl.

Organic carbon (POC) was determined in HCl-treated samples by combustion and subsequent $CO_2$ analysis. The carbonate content (PIC) of the samples was determined by $CO_2$ analysis after acidification with diluted $H_2SO_4$. Particulate nitrogen was determined spectrophotometrically (as $NH_4^+$) after destruction with $H_2SO_4$. All elemental contents were corrected for the presence of sea salt.

### Pore water trace metals

Sediment cores were collected from an intertidal flat near the Dutch-Belgian border during April 25, 1989 and June 7, 1989. Corresponding pore water salinities were $12 \ast 10^{-3}$ and $16 \ast 10^{-3}$, respectively. The cores were cut into 1-2 cm sections, which were pressure-filtrated in all-teflon Reeburgh-type squeezers in a nitrogen glove-box. Special care was taken to avoid contamination (*e.g.* due to oxidation) during the whole procedure. The pore waters were subsampled for analysis of nutrients. The remaining pore water was acidified to pH 1-2 with ultrapure $HNO_3$. Dissolved Ba, Fe and Mn were analyzed by ICP-ES, Cd and Cu by flameless AAS, and Zn by flame AAS. The AAS measurements were carried out after a preconcentration step, namely HMDC-DIPK complexation (April 1989 core) and Co-APDC coprecipitation (June 1989 core).

### Sediment-bound trace metals

The spatial and temporal distribution of trace metals in bottom sediments was assessed by evaluating a large data set (about 1000 samples) for the period 1959-1990. Most data concern surface sediments taken with a Van Veen grab. The trace metal content of the samples has been determined by various laboratories, using a variety of leaching agents, from solely $HNO_3$ to HF+$HNO_3$+$HClO_4$, and detection methods (AAS, ICP-ES, XRF and INAA). After a profound data evaluation it was decided to use only the data obtained after strong acid leaching. Thus, the results given here can best be defined as the total metal content, excluding the detrital (residual) fraction.

On the basis of the available data, we selected four areas with different percentage marine silt in the sediments (0, 50, 75 and 90%). The percentage marine silt in the sediments was calculated from the stable carbon isotopic ratio ($^{13}C/^{12}C$), which shows a conservative behaviour in the Scheldt estuary (SALOMONS and EYSINK, 1981). For the determination of spatial and temporal trends a correction method was employed in order to eliminate the influence of differences in sediment composition on the measured trace metal contents (*e.g.* KLAMER *et al*, 1990). The grain-size fraction <16 µm was used as a correction variable for sediment composition. For each area and period considered, we expressed the trace metal content at the mean percentage <16 µm of the entire data set (12%), using well-established trace metal-texture relationships. More details on the statistical procedure used will be given elsewhere (ZWOLSMAN *et al.*, in prep.).

## RESULTS AND DISCUSSION

### General estuarine chemistry

The results of a typical 'winter', 'spring' and 'summer' cruise are shown in Fig. 2, from which the following generalisations can be made. Winter conditions (February 1987) are characterized by low water temperatures and high river discharges. Under these favourable conditions an anoxic zone does not develop in the upper estuary, though the water column is highly undersaturated with respect to oxygen at low salinities. A rapid increase in dissolved oxygen concentrations with increasing salinity is observed, due to reaeration and dilution by sea water. A turbidity maximum is present in the low salinity, high turbidity zone. Phytoplankton activity is very low in the entire estuary, as reflected by the chlorophyll-*a* profile.

During spring and summer (May and August 1987 in Fig. 2) the river water entering the upper estuary is usually anoxic and also depleted in nitrate, indicating highly reducing conditions. Nitrate is rapidly regenerated in the upper estuary due to nitrification, but the anoxic water column extends over a length of about 30 km, in spite of reaeration and dilution by sea water. This feature reflects the intense nitrification and organic matter decomposition in the upper estuary. Further downstream, dissolved oxygen reappears in the

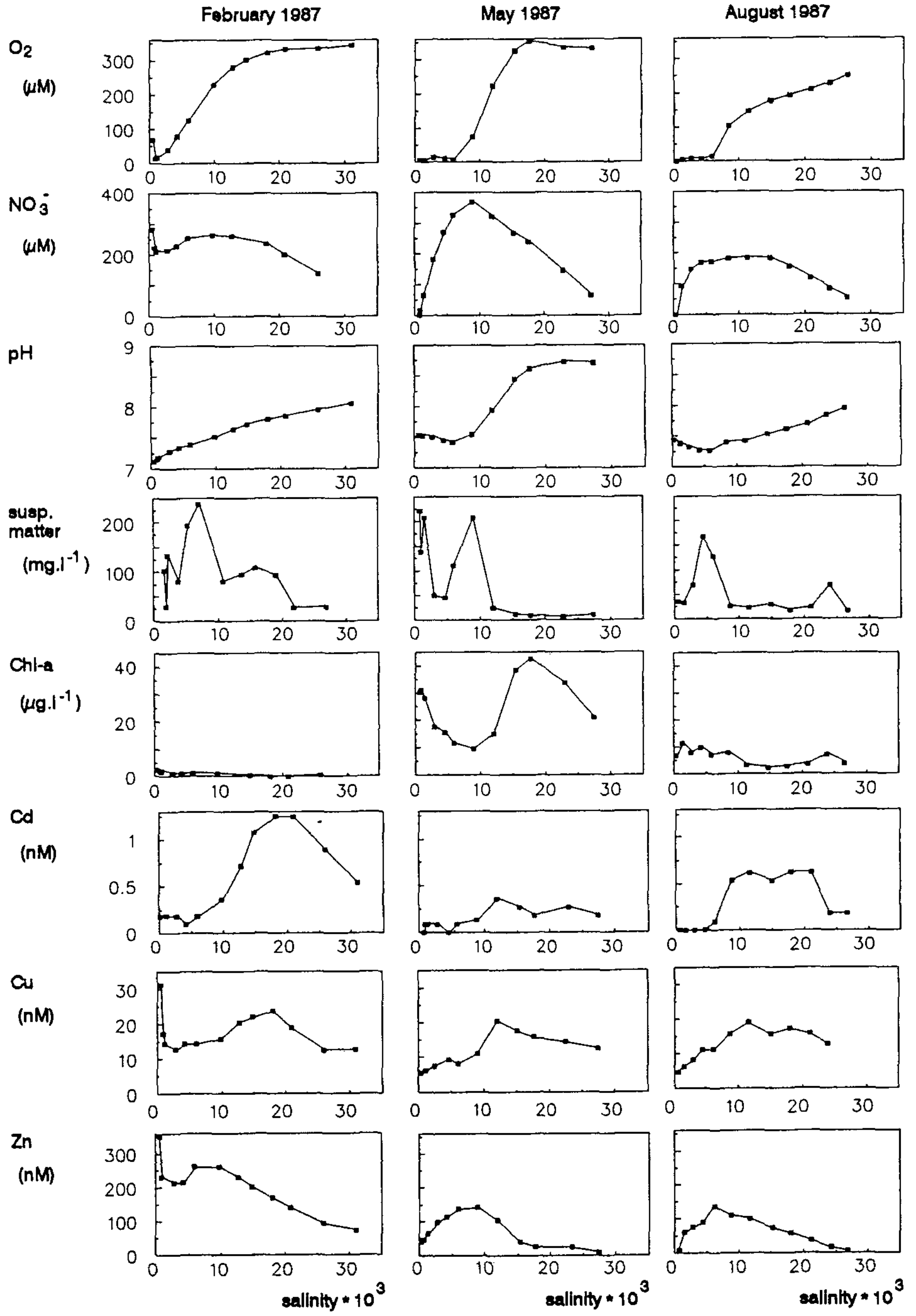

**Fig. 2.** Typical winter, spring and summer profiles of dissolved oxygen, nitrate, pH, suspended matter, chlorophyll-a and dissolved Cd, Cu and Zn in the Scheldt estuary.

water column, and the oxygen concentrations are restored just near the mouth of the estuary. The pH profiles show a transient minimum in the upper estuary, which appears to be caused by the high rates of nitrification. The suspended matter concentrations in the lower estuary are much lower during spring (typically 10 mg $l^{-1}$) than during winter (25-100 mg $l^{-1}$). The sudden drop in suspended matter concentration causes an increase of the light penetration depth from 40-50 cm during winter to 100-150 cm during spring. The improved light climate allows phytoplankton blooms to develop, which explains the observed supersaturation of dissolved oxygen (up to 150%) and the high pH values in the lower estuary during spring.

**Dissolved trace metal geochemistry**

Just like the general water quality parameters discussed so far, the distributions of dissolved Cd, Cu and Zn in the Scheldt estuary depend on the season. In fact, three fundamentally different dissolved metal profiles have been recorded (Fig. 2).

The 'winter' profiles of dissolved Cu, Zn and (less obvious) Cd show high concentrations in the fresh water end-member (the river water). In the very low salinity zone (the HTZ area), a sudden decline of dissolved Cu and Zn is apparent, whereas dissolved Cd tends to decrease towards the detection limit. At higher salinities, a gradual increase in dissolved Cd, Cu and Zn is observed, leading to concentration maxima at well-defined salinities ($6\text{-}9{\ast}10^{-3}$ for Zn, $12\text{-}18{\ast}10^{-3}$ for Cu, and $15\text{-}21{\ast}10^{-3}$ for Cd). Further seawards, a continuous decrease of dissolved Cd, Cu and Zn occurs due to dilution with coastal sea water.

The dissolved metal concentrations in the fresh water end-member are much lower during spring and summer than during winter. Mid-estuarine maxima for dissolved Cd, Cu and Zn are found within approximately the same salinity ranges as those observed during winter. Differences between the spring and summer profiles are apparent in the lower estuary for Cd and Zn, while the spring and summer profiles for Cu are much more similar. Dissolved Cd and Zn reach much lower concentration levels in the lower estuary during spring than during summer, suggesting an additional removal process is active in the lower estuary during spring.

The seasonal variability in the dissolved trace metal concentrations in the fresh water end-member is related to the anoxic nature of the river water during spring and summer, resulting in the precipitation of metal sulphides. This relation has also been suggested in previous studies (SALOMONS *et al.*, 1981; DUINKER *et al.*, 1982), but the hypothesis is now confirmed by our observation that dissolved sulphide is present in trace quantities (0.20-0.94 μM) in anoxic river water samples. Further evidence for metal sulphide formation comes from an electron microprobe study of suspended matter from the anoxic water column, in which discrete zinc sulphides have been identified (BERNARD, pers. comm.).

The decrease in dissolved metal concentrations in the low salinity zone can be attributed to several geochemical removal processes. The first removal process involves the dissolved metal fraction that is strongly complexed with organics, because of the flocculation of dissolved organic matter at low salinity (SHOLKOVITZ, 1978; KRAMER and DUINKER, 1984). Since the fresh-water speciation of Cu is dominated by organic complexes (*e.g.* BOURG, 1983), significant removal of dissolved Cu may be expected in the low salinity zone. The concentrations of dissolved Zn and Cd will be less affected, however. The second removal process is adsorption onto suspended matter in the HTZ area, enhanced by the (increasing) pH gradient. The third and probably most important removal process is adsorption onto freshly precipitated Fe and Mn oxyhydroxides. Infusion of reduced pore water, rich in dissolved $Fe^{2+}$ and $Mn^{2+}$, occurs in the HTZ area (ZWOLSMAN, 1993). After release to the water column, $Fe^{2+}$ is immediately reoxidized and precipitated, whereas reoxidation of $Mn^{2+}$ occurs more gradually with increasing salinity (see next section). The oxidation leads to formation of highly reactive Fe and Mn oxyhydroxide coatings on mineral grains, which are effective scavengers of trace metals (*e.g.* TESSIER *et al.*, 1985).

The most likely process causing dissolved metal concentration maxima in the Scheldt estuary is desorption from suspended matter. It is well known, that trace metals, stable under reducing conditions, can be mobilized upon oxidation, due to dissolution of metal sulphides or decomposition of organometal compounds (PRAUSE *et al.*, 1985; HOLMES, 1986). Mobilization of trace metals in the Scheldt estuary proceeds via an oxidation-complexation mechanism. Firstly, metal sulphides are oxidized along the longitudinal redox gradient (see dissolved oxygen profiles), followed by complexation of the released metals with *e.g.* chloride. In this way, readsorption onto the suspended matter is limited. A second source of dissolved trace metals to the water column may be diffusion from the pore waters in the mid-estuarine region, as will be discussed later.

Biological processes (primary production) cause additional uptake of dissolved Cd and Zn in the lower estuary, as suggested by the coincidence of phytoplankton blooms and trace metal removal during spring (Fig. 2). The involvement of trace metals in biological cycles is a well-known fact for estuaries (*e.g.* CHURCH, 1986). Phytoplankton activity may also indirectly affect the behaviour of trace metals. The near depletion of dissolved Cd and Zn, observed in the lower estuary during spring, is at least partially related to the very high pH values associated with the phytoplankton bloom. Trace metal adsorption is strongly pH dependent within the pH range 6-9 (BOURG, 1983; TESSIER *et al.*, 1985). Presumably, the lack of Cu uptake is due to the strong association between dissolved Cu and humic acids, which apparently limits utilization by phytoplankton. Furthermore, adsorption of Cu-humic acid complexes is suppressed at increasing pH, whereas adsorption of (inorganic forms of) Cd and Zn is enhanced (BOURG, 1983; DAVIS, 1984).

## Suspended matter geochemistry

The first part of this section deals with the geochemistry of 'inorganic' (algae-free) suspended matter. The effect of the spring phytoplankton bloom on the suspended matter composition will be discussed afterwards.

The composition of inorganic suspended matter of the Scheldt estuary can be described as follows (see Fig. 3):

(1) Contents largely independent of salinity are observed for Al and Al-related elements such as Si, K, Ti, Li, V and Be (not shown).

(2) Particulate Ca and Sr contents increase with increasing salinity. The increasing Ca content of the suspended matter in seaward direction reflects primarily physical mixing of fluvial and marine suspended matter, having carbonate contents of 10 and 25%, respectively. In addition, precipitation of carbonates may occur in the estuary, since the water column is generally supersaturated with respect to calcite (WOLLAST *et al.*, 1973). The similar distributions of Ca and Sr (not shown) suggest that Sr is incorporated in the carbonate fraction to a major extent.

(3) Maximum contents at intermediate salinities are observed for Fe, S and Mn. The enrichment of S in the suspended matter is due to resuspension of bottom sediments rich in ferrous

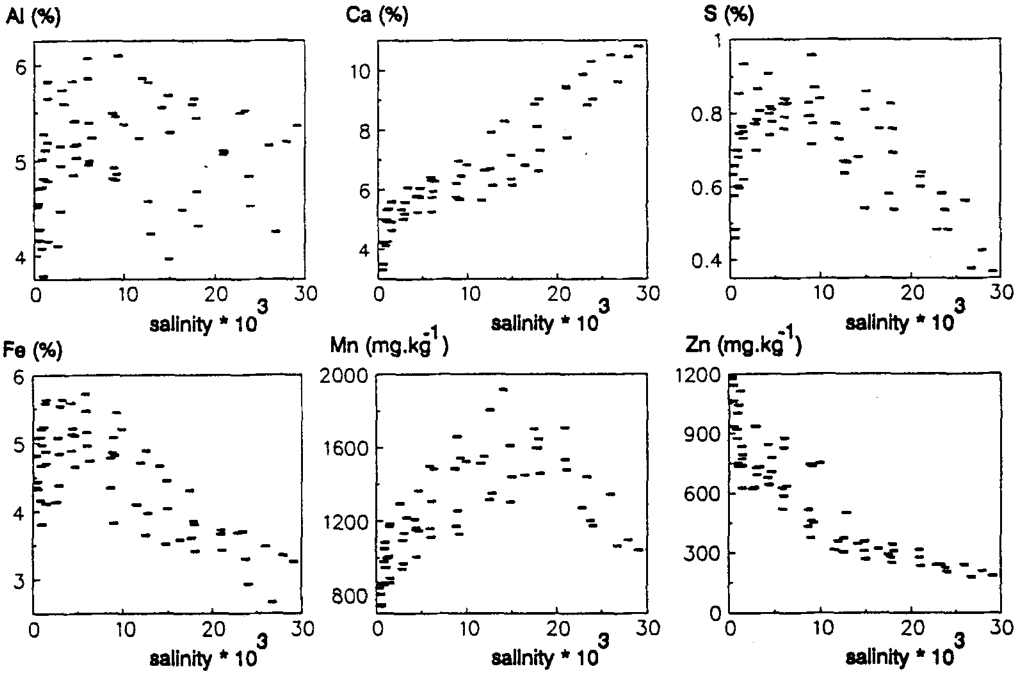

**Fig. 3.** Composition of inorganic (algae-free) suspended matter in the Scheldt estuary (data from five surveys carried out in 1987).

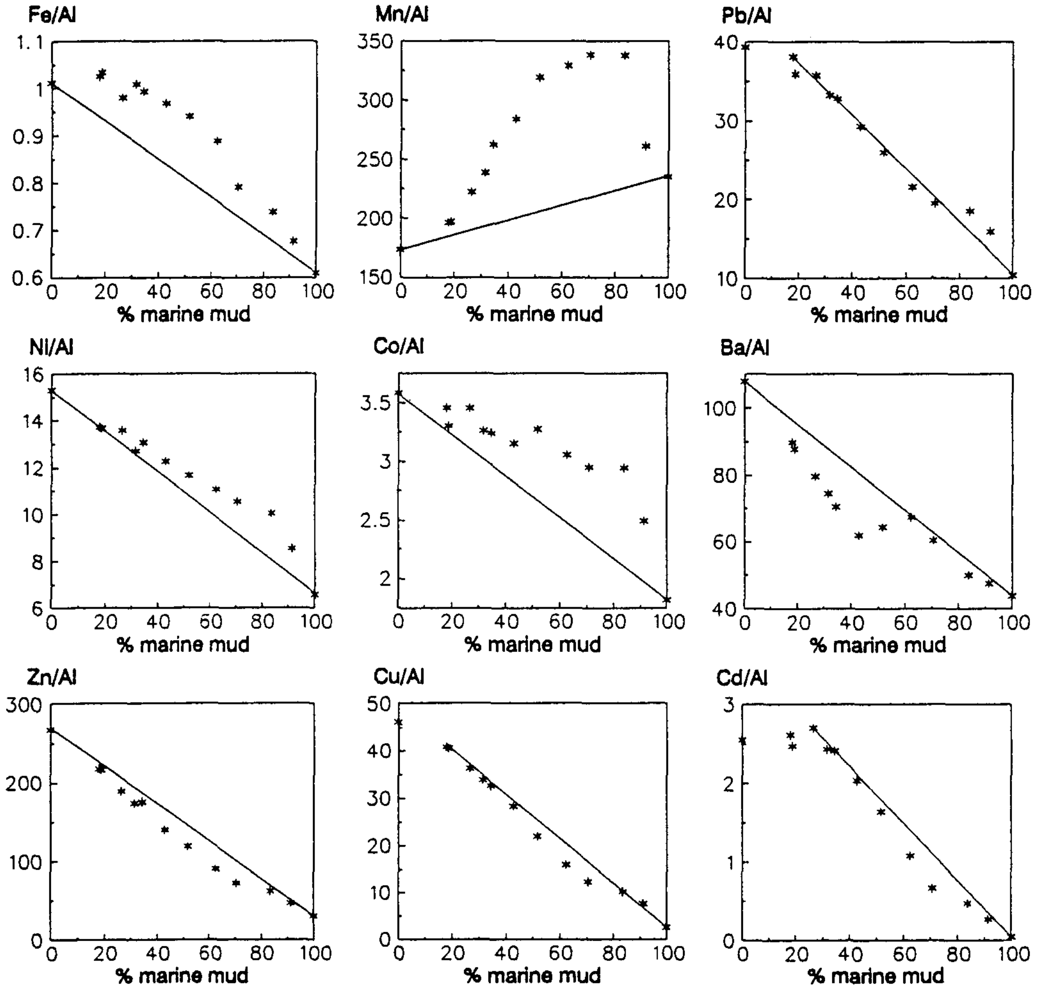

Fig. 4. General relationship between trace metal content (normalized on Al) and percentage of marine mud in the suspended matter. Units are $\mu g\ g^{-1}$ for trace elements, and % for Fe and Al. The theoretical dilution lines in the plots predict the suspended matter composition if particle mixing were the only process occurring in the estuary (data from February 1987 cruise).

sulphides. Resuspension is most important in the HTZ area, due to the unconsolidated nature of the bottom sediments, and the large-scale dredging activities occurring there. The increase of particulate Fe in the HTZ area is partly caused by resuspension of ferrous sulphides, and partly by instantaneous oxidation of reduced Fe derived from the pore waters (see previous section). Dissolved Mn, on the other hand, escapes from reoxidation in the upper estuary due to the suboxic nature of the water column and the slow kinetics of Mn oxidation. In the oxic lower estuary, however, dissolved Mn is reoxidized, leading to a Mn maximum in the suspended matter. Similar conclusions on the geochemistry of Mn in the Scheldt estuary were reached previously by DUINKER *et al.* (1979, 1982).

(4) An exponential decrease with increasing salinity is observed for Zn and other 'anthropogenic' elements such as Ag, Ba, Cd, Cr, Cu, Pb, Sn and P (only shown for Zn). Particulate Ni and Co show a more or less linear decrease with increasing salinity (not shown). For a proper interpretation of these distribution patterns it is necessary to distinguish geochemical reactivity from physical mixing processes. Knowledge of the mixing ratio between fluvial and marine suspended matter is therefore

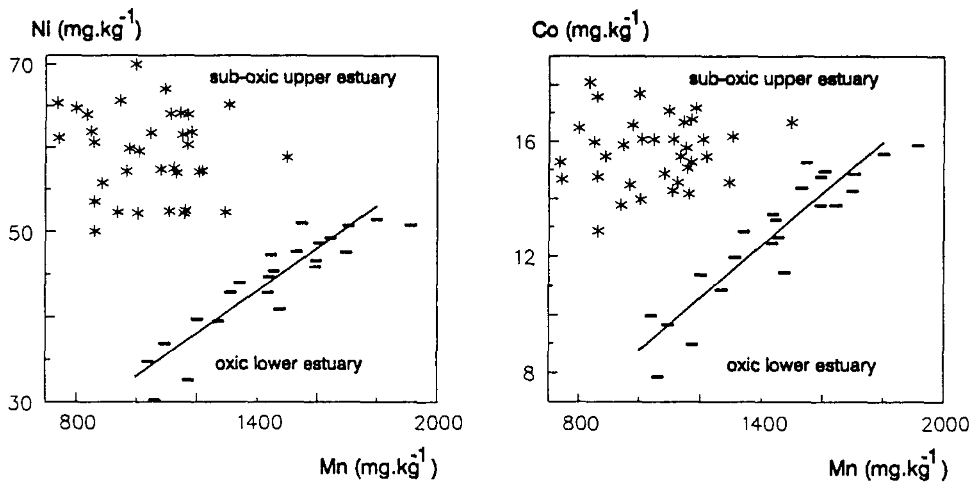

**Fig. 5.** Ni-Mn and Co-Mn relationships in suspended matter of the suboxic upper estuary (asterisks) and the oxic lower estuary (dashes).

essential. In this work, the Cr/Al ratio has been used as a tracer for particle mixing. Conservative behaviour of this parameter in the Scheldt estuary has been demonstrated previously (SALOMONS and EYSINK, 1981).

The behaviour of particulate trace metals in the Scheldt estuary can be assessed from Fig. 4 (February 1987 survey), showing Al-normalized trace metal contents as a function of marine suspended matter content which was determined from the Cr/Al ratio. Normalization on Al was done to eliminate the influence of the varying sand fraction on the trace metal content. The theoretical dilution lines indicated in the plots represent the composition of estuarine suspended matter if particle mixing were the only process occurring in the estuary (conservative behaviour).

Particulate Pb shows conservative behaviour in Fig. 4, in agreement with the very high affinity of Pb for suspended matter all over the estuary. The profile of particulate Ba suggests that desorption takes place in the upper estuary, in agreement with dissolved Ba measurements in the Scheldt estuary (BAEYENS, pers. comm.) and elsewhere (LI *et al.*, 1984). The particulate Fe and Mn profiles show large enrichment in estuarine suspended matter due to *in situ* precipitation of Fe and Mn oxyhydroxides. Suspended matter from the lower estuary appears to be enriched in Ni and Co, due to coprecipitation with Mn oxides as suggested by the Ni-Mn and Co-Mn relationships found in the oxic lower estuary (Fig. 5). Similar coprecipitation of Ni and Co with $MnO_2$ has also been observed in salt marsh sediments of the Scheldt estuary (ZWOLSMAN *et al.*, 1993). Particulate Cd, Cu and Zn contents tend to fall below the theoretical dilution lines, indicating some mobilization from suspended matter. This behaviour is confirmed by the dissolved Cd, Cu and Zn profiles shown in Fig. 2. Still, the deviations of the particulate trace metal contents with respect to the theoretical dilution lines are quite small, showing that the suspended matter composition is primarily controlled by physical mixing of uncontaminated marine suspended matter and contaminated fluvial suspended matter. Similar conclusions were reached previously by SALOMONS and EYSINK (1981).

The spring phytoplankton bloom drastically alters the suspended matter composition in the lower estuary (ZWOLSMAN, 1993). The contents of POC, N, P, S and Ba in the suspended matter show a major increase during the bloom, due to production of organic matter and barite (DEHAIRS *et al.*, 1987). The trace metal content of the suspended matter decreases during the bloom, due to dilution of (polluted) mineral particles by autochthonous organic matter. Thus, phytoplankton appears to have lower trace metal levels than mineral particles, similar to observations in other estuaries (SIGLEO and HELZ, 1981; BALLS, 1990).

### Pore water trace metals

The intertidal sediment cores collected near the Dutch-Belgian border are fairly typical of the mid-estuarine zone, but not of the estuary as a

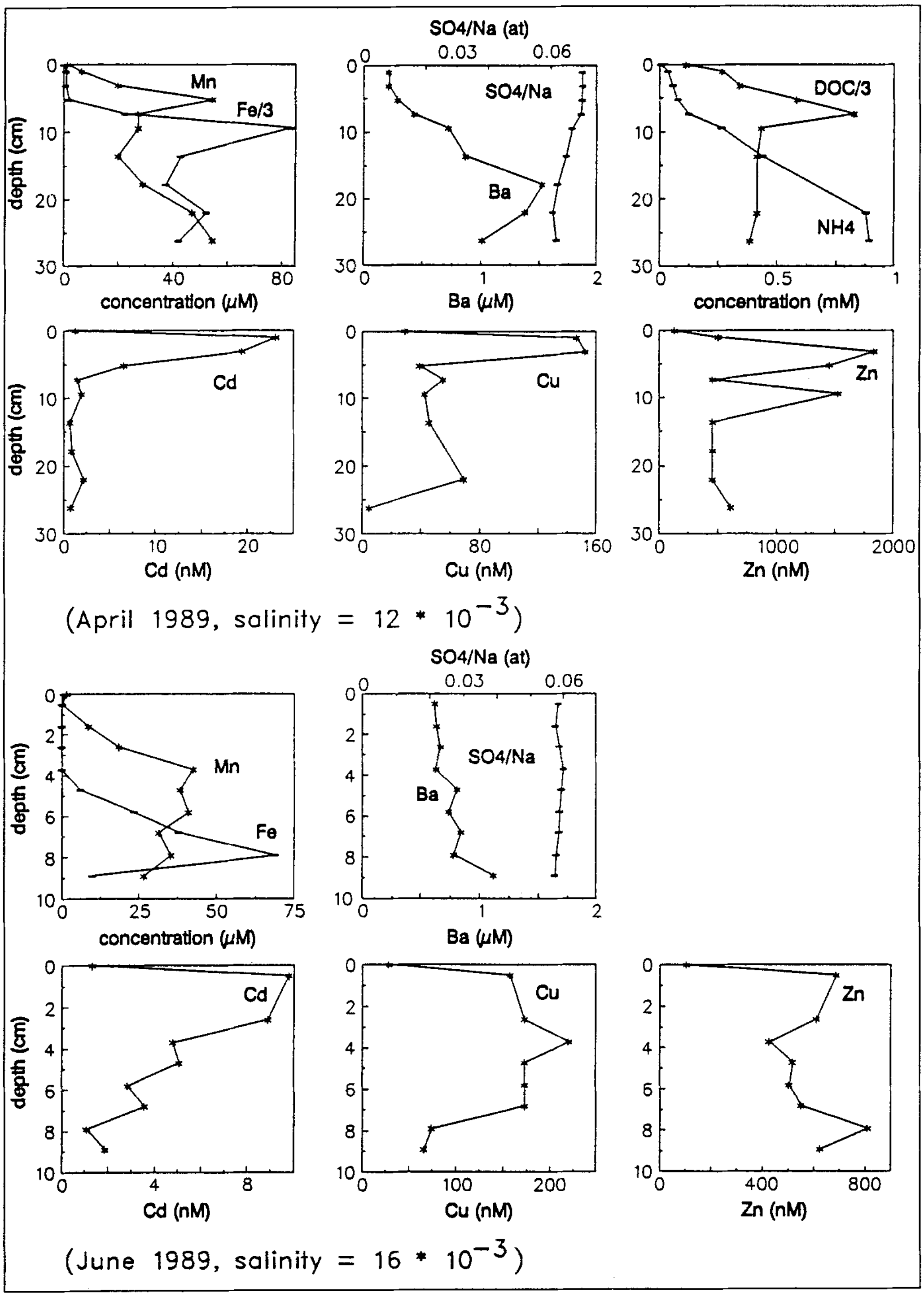

**Fig. 6.** Pore water composition of brackish intertidal sediments near the Dutch-Belgian border. Note that the near-surface maxima of Cd, Cu and Zn are located above the Mn and Fe reduction zones.

whole (WARTEL, 1977). The sediments consist of sandy silt, heavily bioturbated in the top 5 cm by shrimps, worms and molluscs. The top 15 cm of the cores showed a gradual transition from oxidized (brown) to reduced (grey-black) conditions. The vertical distribution of redox species in the pore waters is in agreement with this observation (Fig. 6). Thus, Mn reduction occurs in the top few cm of the sediments, while Fe reduction starts below a depth of 4 cm. Below 10 cm, sulphate reduction becomes important, as shown by decreasing sulphate/sodium ratios (April 1989 core), increasing Ba concentrations (due to dissolution of barite) and the sudden decrease of dissolved Fe (due to precipitation of iron sulphides). This redox sequence is in accordance with thermodynamic predictions (FROELICH *et al.*, 1979).

The profiles of dissolved Cd, Cu and Zn show pronounced maxima near the surface of the cores, located well above the maxima of dissolved Mn and Fe (Fig. 6). Additional peaks of Cu and (more obvious) Zn occur at greater depths, coinciding with elevated Mn and Fe concentrations, respectively. The near-interface maxima of Cd, Cu and Zn, which have been recorded in other pore waters as well (EMERSON *et al.*, 1984; GIBLIN *et al.*, 1986), are derived from oxidation of organic matter and metal sulphides in the top layer of the sediments (BAEYENS *et al.*, 1986). By contrast, the trace metal peaks at greater depth result from reduction of Mn and Fe oxyhydroxides, which are important 'host' phases of trace metals in suboxic sediments (TESSIER *et al.*, 1985; SHAW *et al.*, 1990). An important consequence of the near-interface maxima of Cd, Cu and Zn is that the sediments will act as a source of dissolved trace metals to the water column (while being a sink for particulate trace metals). Thus, the observed enrichment of dissolved Cd, Cu and Zn in the mid-estuarine zone (Fig. 2) may partly be due to pore water infusion. From an ecotoxicological point of view, the near-interface maxima are an important but usually overlooked feature which may be more important in determining sediment toxicity than is the total metal content of the sediments. Since the top few cm of the sediments is the habitat of a great number of burrowing animals, the infaunal population is exposed to very high levels of dissolved (bioavailable) trace metals.

## Sediment-bound trace metals and pollution record

The trace metal content of the bottom sediments decreases in seaward direction, as noted previously by WOLLAST *et al.* (1985). This may indicate that the composition of the sediments is controlled by physical mixing of contaminated fluvial and relatively uncontaminated marine particulates (as found previously for the suspended matter). This hypothesis has been tested by calculating the average trace metal content during 1978-1986 for

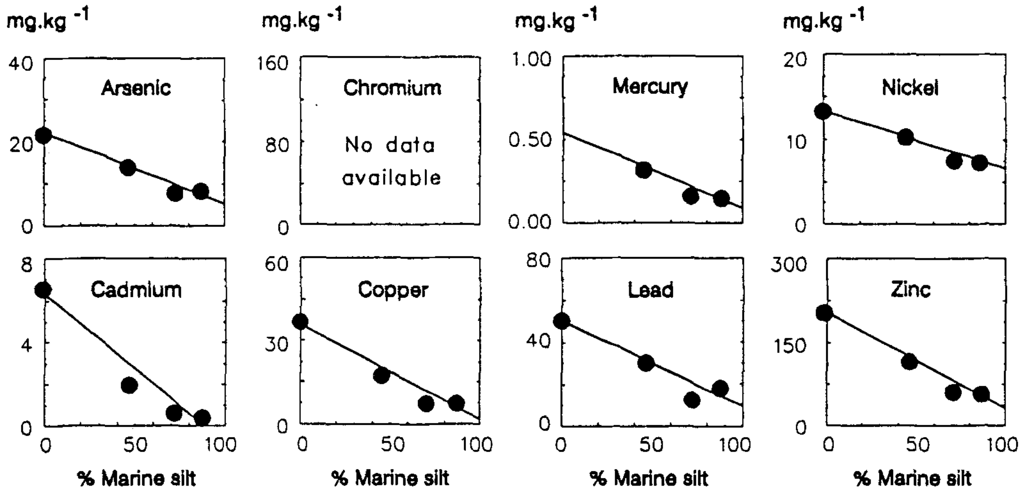

Fig. 7. Relationship between average trace metal content and percentage marine silt in the bottom sediments of the four selected areas of the Scheldt estuary (period 1978-1986). The sediment trace metal content has been corrected for grain-size differences between the four areas (standardization at a grain-size of 12% <16 µm).

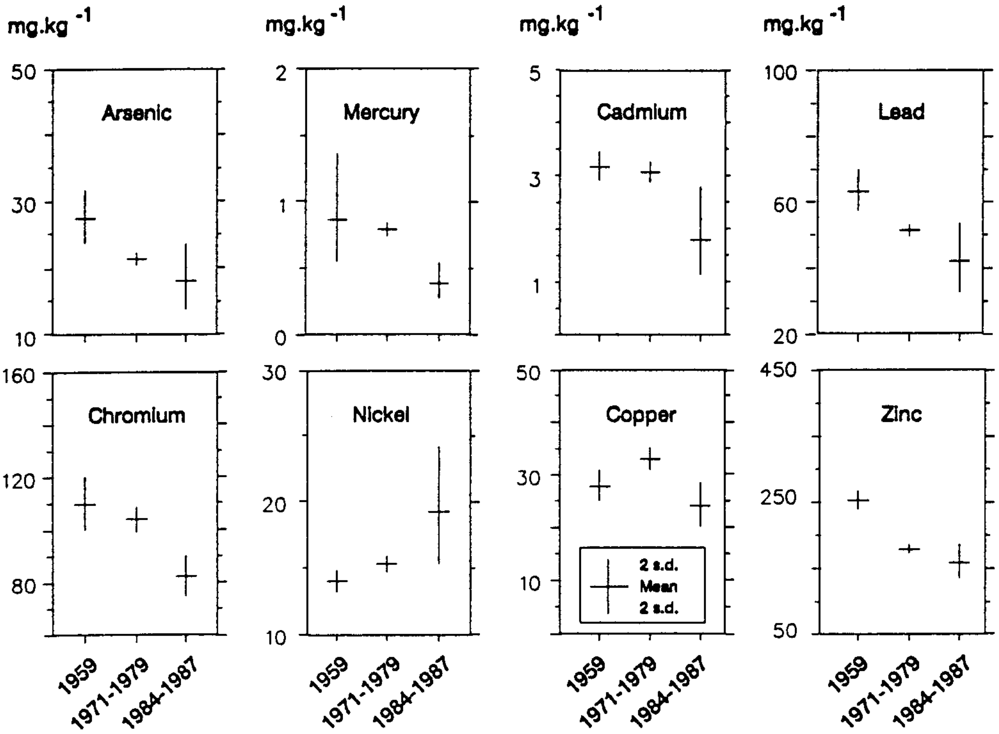

Fig. 8. Average trace metal content of the sediments at the Dutch-Belgian border between 1959 and 1987, expressed at a grain-size of 19% <16 μm.

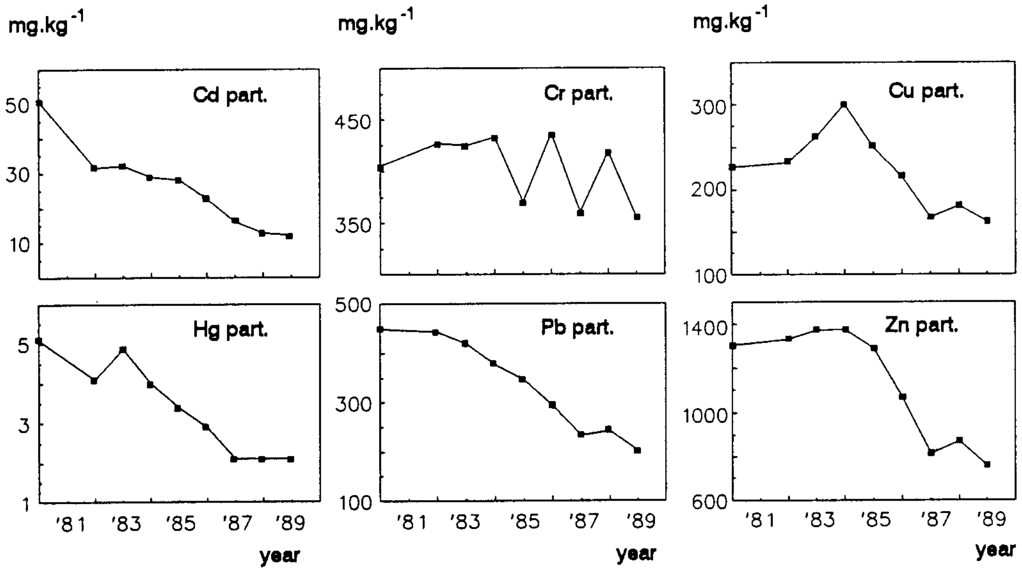

Fig. 9. Calculated trace metal content of fluvial suspended matter during 1980-1990. Data from the routine monitoring program at the Dutch-Belgian border (TIDAL WATERS DIVISION, unpubl.), extrapolated to fluvial salinity.

the four selected areas (containing 0, 50, 75 and 90% marine silt), expressed at the average grainsize fraction <16 µm for the entire estuary (12%). This grain-size correction is necessary since the four areas show great differences in sediment texture. The grain-size corrected trace metal content of each of the four areas lies close to the theoretical dilution line (Fig. 7), indicating that particle mixing is the dominant process that controls the sediment composition. However, Cd seems to be mobilized from the sediments, as indicated by the negative Cd content at 100% marine silt (when extrapolated).

The trace metal pollution history of the Scheldt estuary was assessed by calculating the trace metal content for the area around the Dutch-Belgian border during 1959, 1971-1979 and 1984-1987, expressing the results at the average grain-size fraction <16 µm of this area (19%). The results show that the Scheldt estuary was already severely polluted by trace metals in 1959 (Fig. 8). However, a trend towards decreasing trace metal pollution is apparent afterwards for As, Cr, Pb and Zn, and more recently for Cd, Cu and Hg. Only the pollution by Ni seems to have increased since 1959. These conclusions are fully supported by a study on trace metal distributions in radiodated sediment cores, in which two pollution maxima were identified, occurring in the mid sixties and at the end of the seventies (ZWOLSMAN *et al.*, 1993). Monitoring data of the water quality near the Dutch-Belgian border confirm that the trace metal content of the suspended matter has decreased considerably in the eighties (Fig. 9). Nevertheless, the trace metal contents found in the Scheldt estuary are still high compared to the contents found in most other European estuaries, and are certainly well above the global average. The present-day pollution status of the Scheldt estuary gives therefore still reason for concern.

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