

## **Geochemical composition of sediments in the Scheldt estuary with emphasis on trace metals**

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### **Abstract**

Superficial sediments of the Scheldt estuary were collected with a Van Veen grab at 57 stations between Temse and Vlissingen. They were analysed for major elements (Si, Al, Fe, Ca, Mg, Na, K, Cinorg and Corg) and trace metals (Cd, Pb, Cu, Zn, Cr, Ni, Co, Mn and Li). Factor analysis indicates that 44% of the variance can be explained by one factor which exhibits a high saturation for trace metals, organic matter, Al and Fe, all variables typical of fine mud. The high scores of this first factor are almost exclusively present in the upper estuary except for one area in front of Terneuzen. The second factor, which explains 23% of the variance, is typical of the carbonates and the third one (19% of the variance) is representative of the clay minerals. These two factors are more evenly distributed over the estuary. As usual, a strong influence of granulometry on the distribution of trace elements in the sediments was observed. Intercomparison of their composition within the Scheldt or with those of other aquatic systems requires thus a normalization procedure. This problem has been studied in detail by analysing various size fractions (63-16, 16-8, 8-4, <4  $\mu\text{m}$ ) obtained by elutriation of the sample or by using a parameter characteristic of the fine fraction such as the concentration of a typical element (Al, Fe, Li, Corg). The normalization of trace metals allowed us to evaluate an enrichment factor of the trace elements in the estuarine deposits due to man's activities. In addition, it demonstrates the decrease of the anthropogenic impact on the composition of sediments by comparing the composition of sediments collected in 1976 and in 1994.

**Key words:** trace metals, major elements, sediments, estuary, Scheldt

### **Introduction**

Estuaries are well known to act as filters that prevent compounds transported by rivers to reach the sea. Sedimentation, favoured by flocculation of the fine particles carried by fresh water, constitutes one of the main processes responsible for trapping material in the estuarine system. Flocculation and coagulation occur as soon as the salinity increases in the upper part of the estuary. Furthermore, the hydrodynamic conditions generated by tides and the existence of salt wedges are also favourable to the deposition and upward transport of sediments along the bottom boundary layer. With a tidal amplitude of 4 m at the mouth and an annual fresh water discharge of 3.8 km<sup>3</sup>/y, the Scheldt is a strong tidal estuary, fairly well mixed vertically. The existence of a turbidity maximum at low salinities and upward residual currents along the bottom in the brackish zone, favour the accumulation of sediments in the upper estuary (Wollast, 1988). Most of the particulate contaminants transported by the heavily polluted river Scheldt are therefore trapped in the upper part of the system and do not reach the sea, except during intense flood events. This process is however complicated by successive deposition and resuspension events of the solid phase, which are enhancing exchanges between the deposited sediments and the water column. A detailed description of the geochemical composition of the sediments is of great interest for various reasons. The composition of the deposited material allows to detect and quantify anthropogenic perturbations and represents a valuable indicator of the environmental quality of the estuarine system. In addition, due to its integration properties, the sediments constitute an archive of the past which reflects the historical evolution of the estuary. The accumulation of elements in the sediments is also a fundamental parameter to evaluate their budget and in particular to estimate the amount of material trapped in the estuary which is not transported to the sea. Finally, the knowledge of the contamination of the sediments is very useful to predict what may be the future situation of the system, if for example a better quality of the overlying water is restored.

Most of the studies of the composition of the solid phase in the Scheldt estuary were devoted to suspended matter and many of them were restricted to the concentration of a limited number of particulate trace metals (Duinker et al., 1982; Regnier and Wollast, 1993; Van Alsenoy et al., 1989; Paucot & Wollast, 1997; Baeyens et al., 1998; Zwolsman & Van Eck, 1999). Only a few investigations were carried out on the geochemical composition of deposited sediments (Wollast, 1976; Beefink et al., 1982; Wollast et al., 1985; Zwolsman et al., 1996). A rather detailed study of the estuarine sediments including the distribution of the major and minor elements, was performed in 1976 (Wollast, 1976) and constitutes the first well-documented historical reference.

These sediments were collected in a period during which the Scheldt estuary exhibited a heavy contamination with strong anaerobic conditions in the upper estuary (Van Damme et al., 1995). The anthropogenic perturbations were reflected among others by the excessive concentrations of trace metals in the sediments accumulating in the upper part of the estuary. Various studies of the composition of sediments were performed since then, mainly by management authorities and are not available in the scientific literature. They have however, been compiled and interpreted statistically by Zwolsman et al. (1996). As pointed out by the authors the data must be utilized carefully due to the variety of analytical procedures used during the various studies. Nevertheless, they show a high degree of contamination of the sediments by trace elements of anthropogenic origin. The temporal evolution of the composition of the Scheldt sediments demonstrates also unambiguously that the inorganic contamination load has significantly decreased from 1959 to 1989.

The aim of the present study was to determine the distribution of major (Si, Al, Fe, Ca, Mg, Na, K, inorganic and organic carbon) and trace elements (Cd, Pb, Cu, Zn, Cr, Ni, Co, Mn and Li) in 57 sediments collected in the area corresponding to the mixing zone of fresh water and seawater. The mineralogical composition was also evaluated semi-quantitatively by X-ray diffraction, on a restricted number of samples. In order to investigate the influence of the particle size on the distribution of the elements, a detailed analysis of five granulometric fractions comprised between 63  $\mu\text{m}$  and less than 4  $\mu\text{m}$ , was also performed on a few selected samples. Normalization of the composition of the sediments with respect to grain size or to reference elements will be discussed.

The large number of samples analysed allowed us to perform a robust statistical analysis and to evaluate correlation coefficients between 18 compositional parameters. In addition, a factorial analysis was performed in order to determine the principal components controlling the distribution of chemical elements in the sediments. A comparison of the normalized composition of the sediments collected during this study in 1994 with those sampled in 1974 (Wollast, 1976) will be used to evaluate the evolution of the environmental quality of the estuary.

## **Material and methods**

A total of 57 sediment samples were collected with a Van Veen grab in August 1994, along the axial channel of the Scheldt estuary from the Rupel confluence down to the mouth (Fig. 1). This covers the area of mixing of fresh water with seawater under normal discharge conditions. The position and the macroscopic sediment characteristics were noted for each sample. The bottom sediments consist of sand, sandy mud and mud. Based on the collected sediments, the estuary can be divided into two principal zones: (1) the brackish upper estuary, situated from the Ruppel confluence to Doel, (2) the lower marine area, situated between Doel and the mouth near Vlissingen. The brackish zone is characterised by the presence of a turbidity maximum leading to local of fine material. This area corresponds also to intensive industrial and harbour activities. In the marine area, mainly sands were encountered with only exceptional mud deposits, particularly in front of the mouth of the Gent-Terneuzen channel.

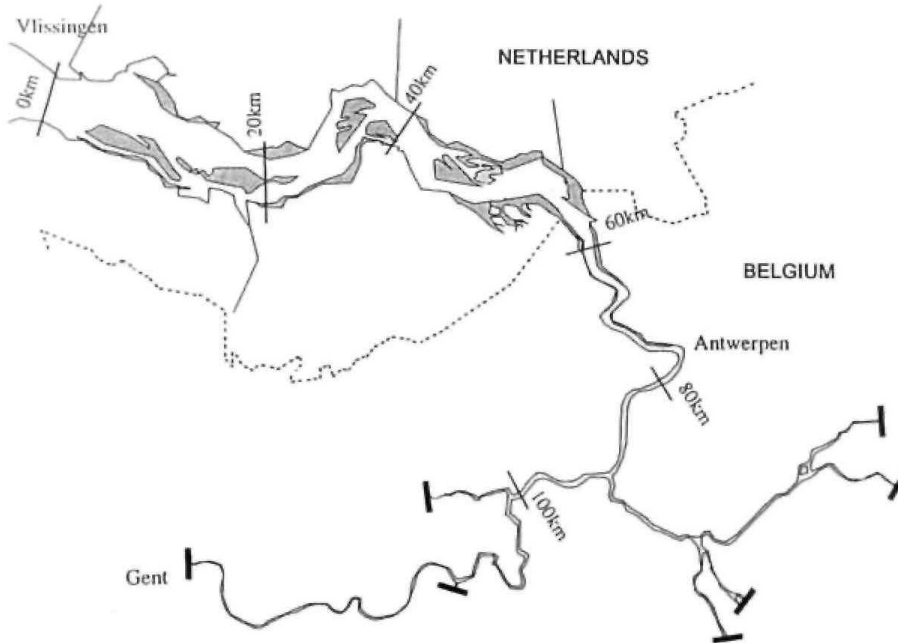
About 100 g of the surficial layer of each sediment was collected from the grab, dried overnight at 80 °C. A sub-sample of a few grammes was finely grinded to less than 10  $\mu\text{m}$  to reduce the heterogeneities of the sediment. On the other hand, size fractionation was performed on a few selected samples using the elutriation method (Blangeaud, 1938), in order to evaluate the influence of granulometry on the elemental distribution. In this method, based on Stokes law of sedimentation, the solid sample is initially dispersed by sonication in a 1 % solution of polyphosphate. The suspension is submitted to a vertical water current whose velocity is adjusted to remove selectively all the particles with a size fraction less than a given Stokes diameter. In our experimental device, the vertical water flow has been adjusted to obtain the five following fractions: 63-32, 32-16, 16-8, 8-4 and < 4  $\mu\text{m}$ .

The chemical analysis was performed on a sub-samples (50-100 mg) totally decomposed in closed Teflon vessels by a mixture of 2 ml HF and 2ml of regal water ( $\text{HNO}_3$  and  $\text{HCl}$ ) (Loring & Rantala, 1992). After digestion, 0.62 g of  $\text{H}_3\text{BO}_3$  was added to neutralize the fluorhydric acid. Resulting solutions and reagent blanks were analysed for major elements and trace metals. Cd, Pb, Cu, Cr, Ni and Co were analysed by Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Si, Al, Fe, Ca, Mg, Na, K, Li, Mn and Zn were analysed by inductive coupled plasma (ICP). A detailed description of the analytical method used can be found in Paucot (1997).

Particulate organic carbon (POC) was determined by catalytic combustion in  $\text{HCl}$ -treated samples and subsequent analysis of  $\text{CO}_2$ . The particulate inorganic carbon (PIC) content of the samples was calculated by

subtracting POC from total carbon measured on the untreated samples. X-ray diffraction was performed on a few representative samples of clay and sand as well as on the various size fractions obtained by elutriation.

**Figure 1.** Map of the Scheldt estuary. The brackish upper estuary is situated between km 100 and 50, the lower marine estuary between km 50 and 0.



## Results and discussion

### Major elements

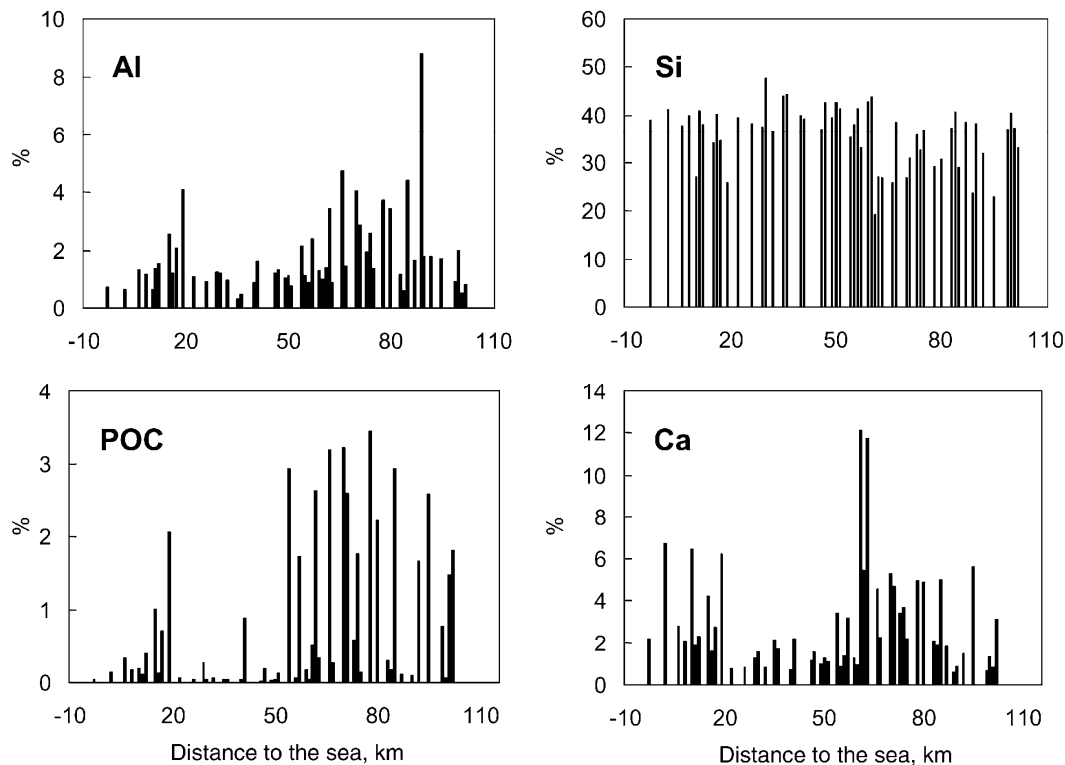
The minimum, maximum and mean content (in weight per cent) of major elements in the 57 sediments are reported in Table 1. We have also calculated mean values for the muddy (20 samples) and sandy (37 samples) deposits distinguished by their macroscopic properties. The longitudinal distribution of the major elements is shown in Figure 2.

The Si content is very high, even in the muddy fraction, Figure 2 confirms that this element is very evenly distributed all along the estuary. Ca and inorganic carbon are the second most abundant elements. This is not surprising because of the presence of calcareous sands, which are abundant near the mouth of the estuary, but also upstream where the river bed is constituted by quaternary marine carbonaceous deposits in the process of erosion. There are even higher concentrations of  $\text{CaCO}_3$  in the muddy deposits, especially up-stream, which is less usual in a temperate estuary. This aspect will be discussed later. Al and Fe are in very comparable amounts in the Scheldt deposits. They are usually representative of the muddy sediments (Bruland et al., 1974; Loring & Rantala, 1988; Windom et al., 1989) and are effectively three times more concentrated in mud than in sand. The highest Al contents (Fig. 2) are encountered in the brackish zone and in front of the Gent-Terneuzen channel (between km 15 and 20), both areas where mud is accumulating preferentially. The organic matter constitutes also a very good indicator of muddy deposits and the concentration of POC in muds is about 10 times higher than in sands. The distribution of this parameter (Fig. 2) shows a marked difference between the brackish zone (above km 50) and the marine area (below km 50). Here again, it is possible to detect the muddy deposits in front of the channel Gent-Terneuzen.

**Table 1.** Composition of major elements expressed in weight % of superficial sediments of the Scheldt estuary collected in 1994

%	Minimum	Maximum	Mean	Muds	Sands
Si	19	47.7	35.4	29.3	38.4
Al	0.34	4.75	1.8	3.22	1.09
Fe	0.39	8.11	1.86	3.05	1.26
Ca	0.57	12.14	3.07	4.39	2.41
Mg	0.08	0.89	0.34	0.61	0.2
Na	0.06	1.19	0.5	0.74	0.37
K	0.31	1.62	0.98	1.28	0.83
PIC	0.14	5.15	1.01	1.32	0.85
POC	0.02	3.97	0.98	2.4	0.28

**Figure 2.** Longitudinal distribution of Si, Al, Ca and POC in bottom sediments as a function of the distance to the sea.



X-ray diffraction (Table 2) shows that quartz is the dominant mineral even in the muddy deposits where it is present as very fine particles. This explains the rather uniform distribution of Si shown in Figure 2. Calcium carbonate is often abundant in sand as well as in mud. In calcareous sand,  $\text{CaCO}_3$  is present as calcite and aragonite in comparable amounts and related to the occurrence of numerous shell debris. In the muddy sediments, only calcite is observed and microscopic examination indicates that  $\text{CaCO}_3$  is often present there as small rhombohedral crystals. In the sandy sediments, small amounts of feldspars are also detected by X-ray diffraction, as microcline and albite. In the muddy sediments, illite and kaolinite are the most abundant clay minerals with smaller amounts of muscovite, glauconite and montmorillonite.

#### Minor elements

The minimum, maximum and mean content of minor elements for 57 samples analysed are reported in Table 3, where we have, as previously, also distinguished between the sandy and muddy sediments. Their distribution

along the estuary is shown in Figure 3. There are very large fluctuations of the concentration of trace metals in the Scheldt sediments. As usual, there is a marked enrichment of all the trace metals in the muddy samples where the maximum values demonstrate highly contaminated sediments. The distribution of all the minor elements along the estuary is very similar (Fig. 3) with high contents in the upper brackish part and in the area in front of the Gent-Terneuzen channel (km 15-20). On the contrary, concentration of the trace metals in sandy deposits looks relatively low but remains nevertheless high for pure sand. This may be explained by the presence of small pellets of mud mixed with the sands all along the estuary, as described by Wartel (pers. comm.). The occurrence of glauconite in sandy sediments, which is known to fix by adsorption trace metals, contribute also to their high content in coarse sediments.

**Table 2.** Semi quantitative X-ray diffraction analysis of sands, mud and various size fractions

	Quartz	Albite-Microcline	Calcite-Aragonite	Muscovite-Illite	Kaolinite
Sand	XXX	XX	X		
Mud	XX	X	XX	XXX	XX
Size fractions ( $\mu\text{m}$ )					
63-32	XXX	XX	X		
32-16	XXX	XX	X		
16-8	XXX	XX	X	XX	X
8-4	XXX	X	X	XXX	XX
<4	XX	X	XXX	XXX	XXX

**Table 3.** Composition of minor elements expressed in  $\mu\text{g/g}$  of superficial sediments of the Scheldt estuary collected in 1994

$\mu\text{g/g}$	Minimum	Maximum	Mean	Muds	Sands
Cd	0.03	21.9	2.38	5.40	0.86
Pb	0.06	271	38.2	87.6	13.5
Cu	0.24	121	22.3	51.6	7.60
Zn	17.4	1143	210	446	92
Cr	6.36	388	47.9	101	21.5
Ni	0.12	36.4	10.1	20.7	4.84
Co	0.48	12.7	4.02	7.70	2.18
Mn	25	1120	317	665	143

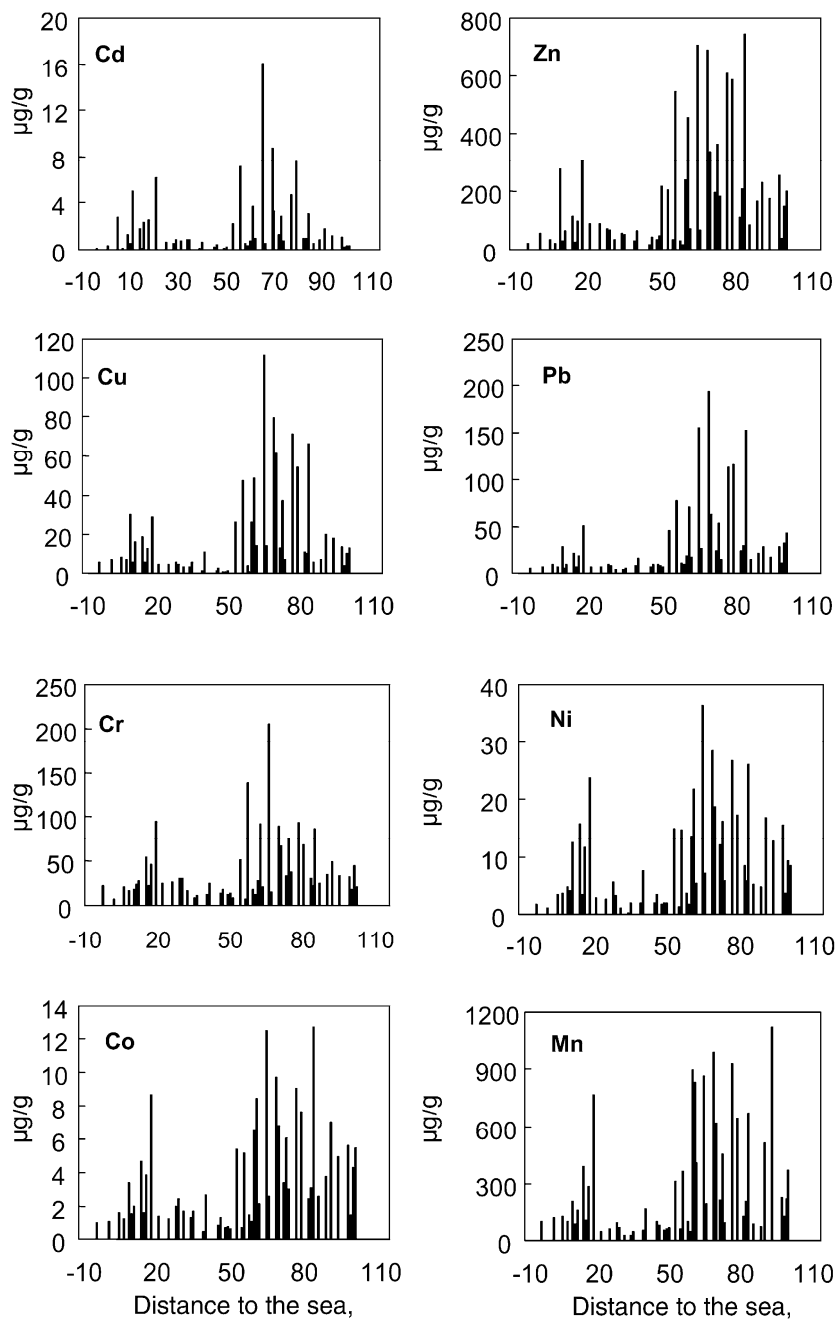
#### Size fractionation

The results of Tables 1-3 confirm that there is a strong influence of the size distribution of the particles on the composition of the sediments. We have therefore selected four muddy samples which were elutriated and subdivided into five sub-samples of decreasing granulometry from 63 to  $< 4 \mu\text{m}$ . The sub samples were analysed for major and minor elements following the same procedure as for the total sample. The results of this fractionation are given in Table 4 and Figures 4 and 5.

The Si content in the sub-samples decreases continuously with decreasing particle size, except for the  $< 4 \mu\text{m}$  fraction where Si is increasing again. This is mainly due to a diminution of the abundance of quartz and feldspar (see also Na) content in the finer fractions. The increase of the concentration of silica in the finest fraction ( $< 4 \mu\text{m}$ ) may be due to the presence of silica rich clay minerals such as chlorite but also to debris of diatom skeletons. There is on the contrary, a rapid increase of Al and Fe concentration in the finer size fractions due to the abundance of clay minerals and iron oxi-hydroxides in the muddy sediments. The calcium remains rather constant except for the finest fraction where it increases in three of the four samples analysed. The presence of rhombohedral crystals, detectable by microscopy, suggests that precipitation of calcite is occurring in the sediments due to diagenetic processes and in particular in relation to sulfato-reduction (Morse & Mackenzie,

1990). There is also an increase of Mg in the fine part, which may be attributed to the presence of chlorites poorly crystallized in the clay fraction. The Na distribution reflects the complexity of the silicate minerals presents in the Scheldt. The sodium content in the smaller size fraction is due to the presence of Na-montmorillonite. The increase of Na in the large size fraction up to 63  $\mu\text{m}$  may be attributed to albite. In the sands, the feldspars are diluted by coarse quartz ( $>100 \mu\text{m}$ ) which leads to the decrease of the Na content. This situation is classically observed in the case of sediments derived from glacial erosion (Loring & Rantala, 1988). Finally, the element K is present among others in feldspars, muscovite, glauconite and illite and its distribution is therefore not significantly influenced by the granulometry.

**Figure 3.** Longitudinal distribution of trace metals in bottom sediments collected in 1994, as a function of the distance to the sea.



The trace element content is strongly affected by the particle size of the sub samples (Fig. 5). The concentration of all the elements considered is rapidly decreasing with increasing particle size. The trace metals are practically absent in the 32-63  $\mu\text{m}$  fraction which is often the most abundant in our samples. The X-ray diffraction analysis indicates that this coarse fraction contains only quartz, calcite, feldspar, and no thus minerals presenting a high affinity for trace metals.

There is a striking analogy between the distribution of Mn, Co, Ni, Cr and Cu in the various size fractions. Manganese is known to precipitate as oxi-hydroxides in the upper layer of anoxic sediments near the sediment-water interface, when oxygen is restored (Wollast et al., 1979). These Mn oxi-hydroxides have a strong affinity for the above metals, which can be co-precipitated or adsorbed. Finally, there is also a nice similarity between the distribution of Cd, Zn and Pb, which all present a regular and systematic decrease of concentration with particle size and a maximum content in the finest fraction (<4  $\mu\text{m}$ ). This is not surprising because of the close geochemical properties of these elements. This observation may nevertheless also reflect a common origin of the three elements.

#### *Normalisation and enrichment factor*

Due to the fluctuations of the concentration of the trace elements in the sediments with the particle size, it becomes difficult to compare deposits occurring in different areas of the estuary characterized by a large granulometric spectrum. This reflects also the selective settling of the suspended solids of riverine or marine origin within the system. For the same reason, it is also difficult to compare sediments corresponding to different periods, or collected in different estuaries. On the other hand, the analysis of the granulometric fractions shows clearly that it is difficult to define one characteristic size fraction, which could be used to compare the concentration of contaminants present in different samples. Therefore, it has been generally recommended to use a normalization factor which is constituted by an element characteristic of the fine fraction and which behave conservatively, especially during early diagenesis (Loring, 1988; Windom et al., 1989). The most currently elements used are Al (Hirst, 1962a, b; Bruland et al., 1974; Kemp et al., 1974; Windom et al., 1989; Schropp et al., 1990; Hanson et al., 1993; Cho et al., 1999), Fe (Rule, 1986; Morse et al., 1993; Schiff & Weisberg, 1999), organic matter (Cato, 1977; Windom et al., 1989; Daskalakis & O'Conner, 1995) and Li (Loring, 1988).

We have tested each of these elements by estimating the value of their linear correlation coefficient with the various trace elements (Table 4). The four elements give high correlation factors, but we have selected to use Al as the normalization factor because of its conservative behaviour. It is also often used in the literature, which allows to compare the composition of the Scheldt estuary sediments to those of other environments, natural or polluted. Figure 6 illustrates the good correlations obtained between Al and trace metals. However, in the future, it would be interesting to use Li as normalized element in particular in areas where feldspar are present in the detrital phase.

The normalization procedure allowed us to calculate an enrichment factor (Ef) of the mean concentration of each element in the Scheldt sediments compared to the mean global concentration in crustal rocks (Martin and Withfield, 1983), both normalized with respect to Al:

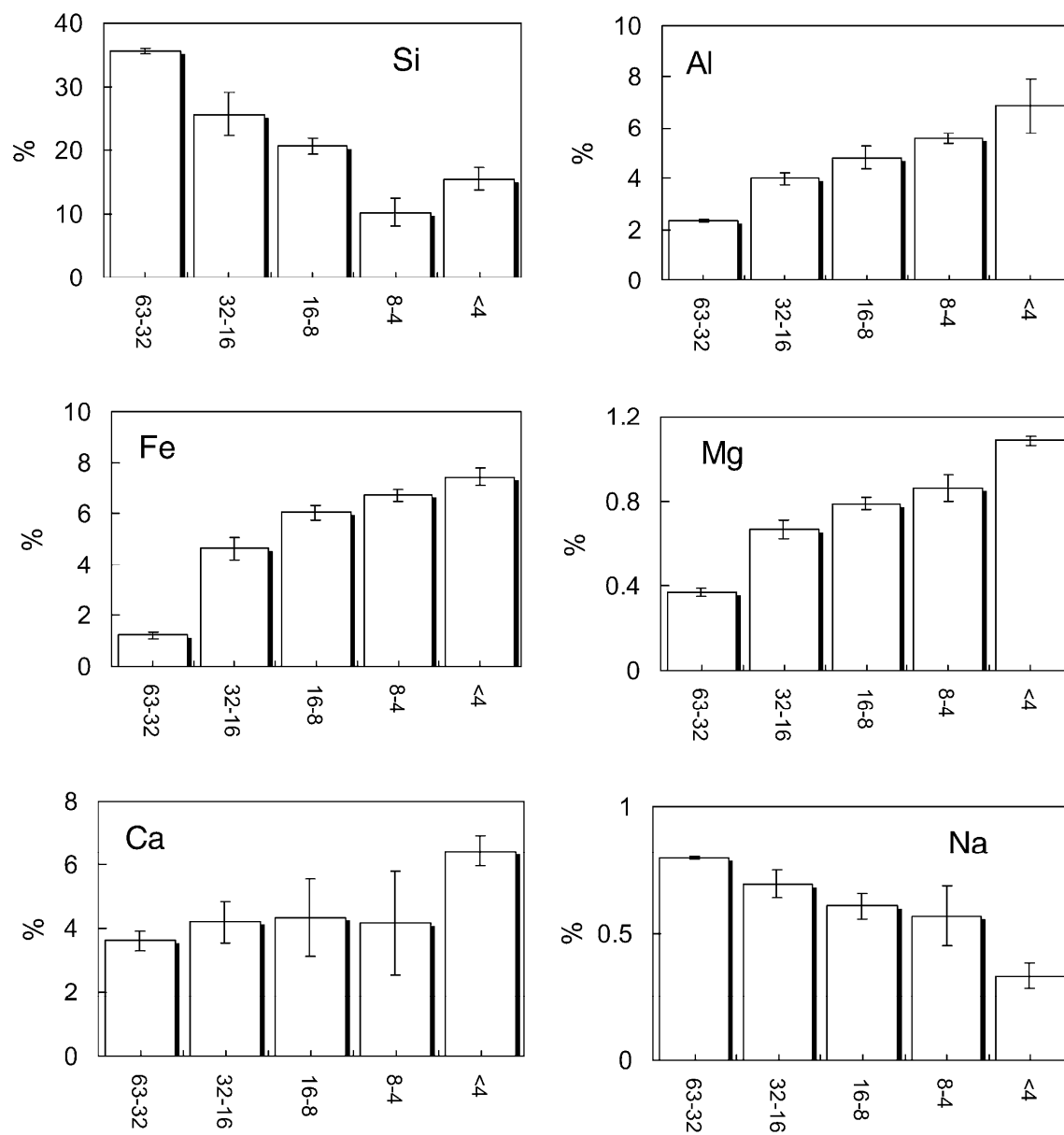
$$Ef = \frac{\text{Me/Al in sediments}}{\text{Me/Al in crustal rocks}}$$

The results of the comparison of the Scheldt sediments with crustal rocks are shown in Table 5. Only Cd, Pb and Zn are strongly enriched in the surficial muddy deposits of the Scheldt compared to the mean crustal composition. These metals are however among the most toxic elements present in the sediments.

**Table 4.** Correlation coefficients between trace metals and respectively Li, Al, Fe and POC for all sediments

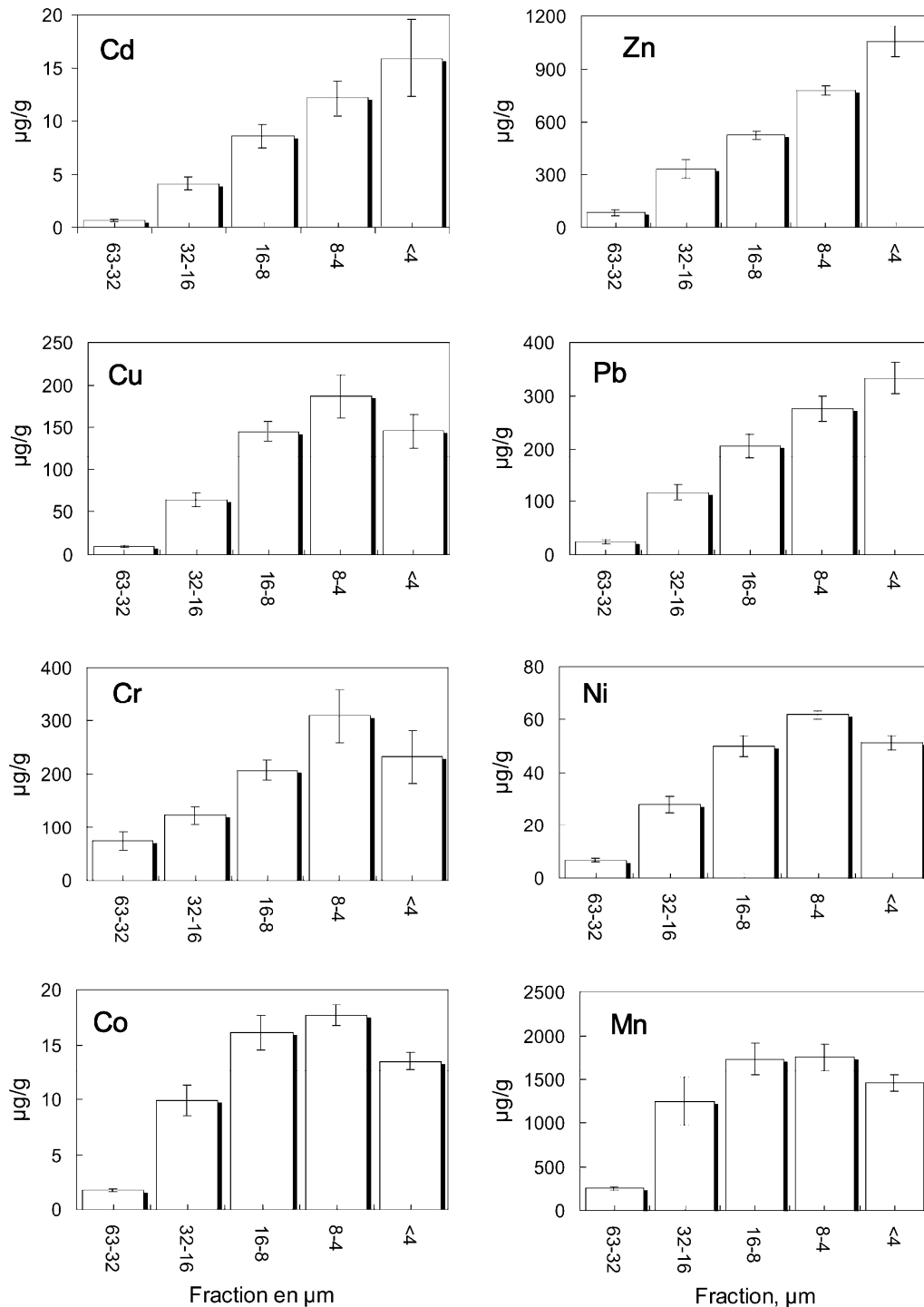
	Mn	Zn	Ni	Pb	Cu	Co	Cr	Cd	Mean
Li	0.91	0.85	0.95	0.83	0.90	0.92	0.76	0.71	0.85
Al	0.86	0.84	0.94	0.84	0.89	0.89	0.77	0.70	0.84
Fe	0.87	0.79	0.85	0.73	0.82	0.85	0.70	0.63	0.78
POC	0.88	0.89	0.95	0.88	0.92	0.92	0.79	0.71	0.87

**Figure 4.** Distribution of the major elements in the different size fractions obtained for selected muddy sediments.



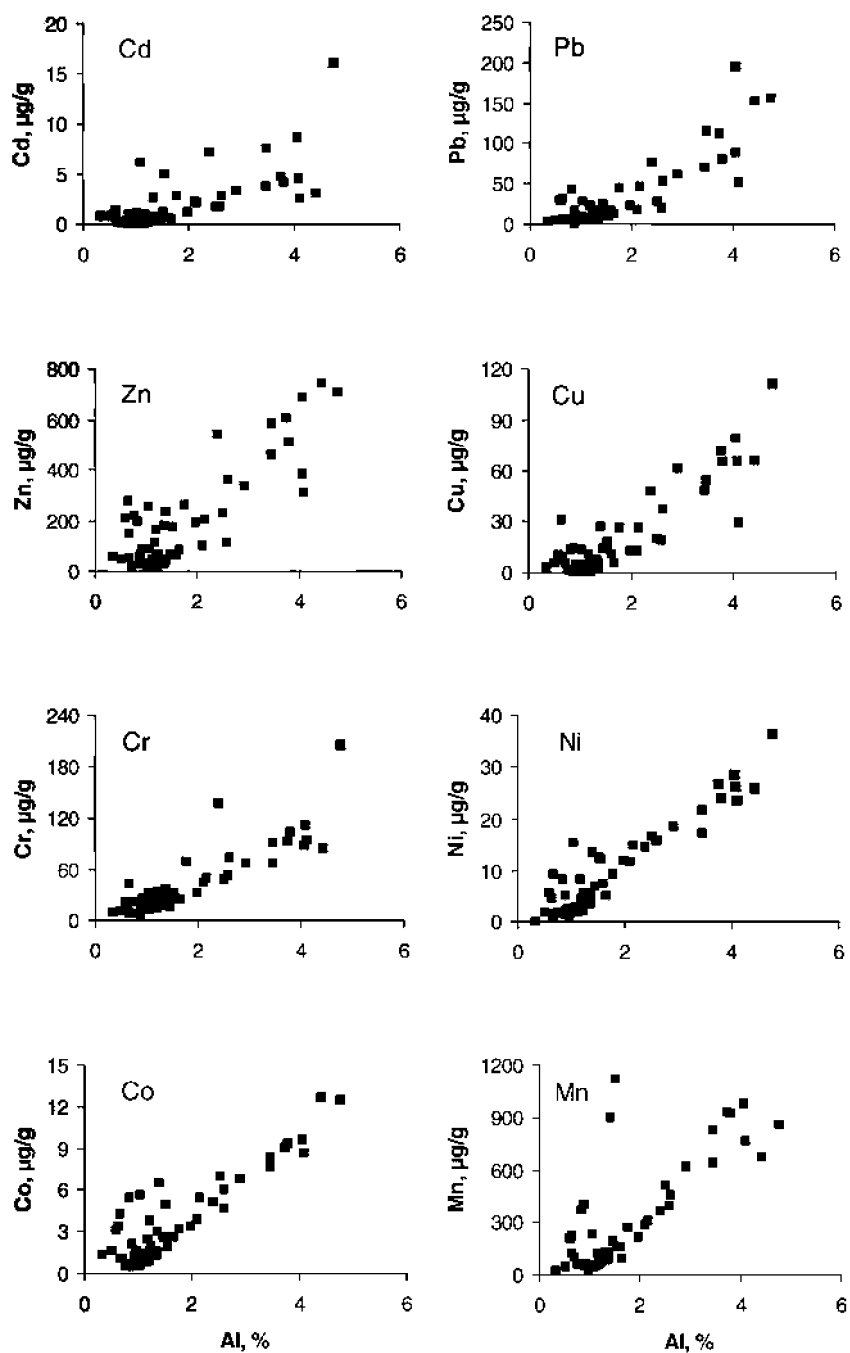


**Figure 5.** Distribution of the minor elements in the different size fractions obtained for selected muddy sediments.



The normalization allows also to evaluate the evolution of the composition of the sediments with time. We have compared in Figure 7a, the normalized content of trace metals in the superficial muddy sediments collected in 1994 to those collected in 1974 (Wollast, 1976). The values calculated for all the elements, except Mn, have decreased very significantly during that period. As shown in Figure 7b, a decreasing trend has also been observed for the normalized composition of the suspended matter between 1987-1988 and 1995-1996 by Zwolsman (1999). Using a box model of metal flows through the Scheldt estuary, Baeyens et al. (1998) have demonstrated that the fluxes of dissolved and particulate Cd, Pb, Zn and Cu have decreased by more than a factor of 5 for Cd and about 2 for Pb, Zn and Cu from 1985 to 1995.

**Figure 6.** Concentration of trace metals as a function of the Al content.



**Table 5.** Concentrations of trace metals normalized with respect to Al in the muddy sediments of the Scheldt estuary

	Me/Al, mg/g		Enrichment factor Ef
	Escauts	Roches crustales	
Cd	0.13	0.003	45
Pb	2.12	0.23	9.2
Zn	11.6	1.83	6.3
Cu	1.24	0.46	2.7
Cr	2.66	1.02	2.6
Mn	17.6	10.4	1.7
Co	0.22	0.19	1.2
Ni	0.56	0.71	0.8

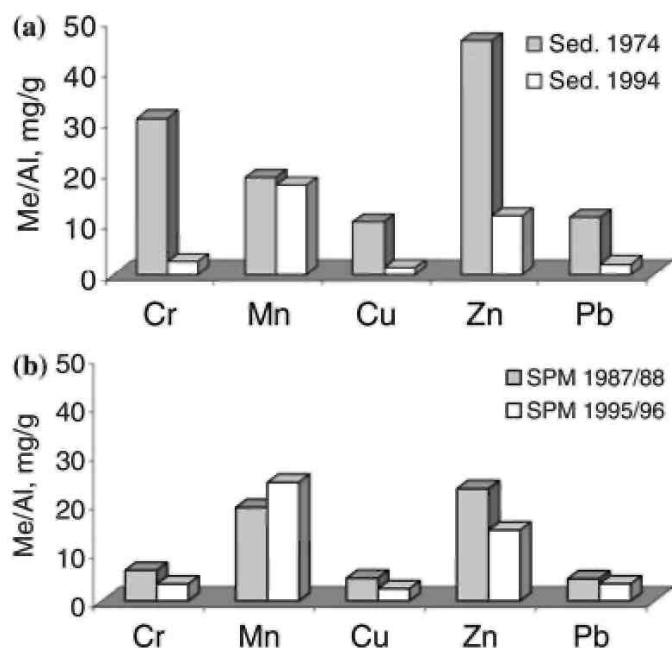
The last column gives the calculated enrichment factor of the estuarine deposits versus crustal rocks.

### Statistical analysis

Each of the 57 analysed sediments has been characterized by 18 chemical parameters, which follow nicely a log-normal distribution. A factorial analysis was performed on the logarithm of the characteristic parameters in order to determine the principal components controlling the distribution of chemical elements of these sediments (Herbosh, 1975). The results of the statistical analysis are reported in Table 6. About 87% of the variance in the dataset can be explained by only 3 common factors, all are anticorrelated to Si. The first one, which explains 44.4%, is characterised by the trace metal group (Co, Zn, Pb, Cr, Ni, Cu, Cd, Li and Mn) but comprises also POC and the major elements presenting a strong affinity for the fine particles such as Fe, Al and Mg according to the size fractionation test. The longitudinal distribution of the values of the factor 1 in the estuarine Scheldt sediments is shown in Figure 8. It is positive and large in the area of mud accumulation corresponding to the brackish zone and in front of the Gent-Terneuzen channel. As shown above, trace metals are preferentially associated with the fine particles, which are flocculated and coagulated when salinity increases, and are finally deposited in the upper part of the Scheldt estuary. The second factor, explaining 23.3% of the variance of the dataset, is highly saturated by Ca and PIC, which are typical of the carbonate fraction, and less but significantly saturated by Mn. This factor is positive near the mouth of the Scheldt estuary, where carbonate skeletons of marine origin are abundant. It is also favoured in the brackish zone where old marine carbonaceous deposits are presently eroded. In this area, there are also high concentrations of CaCO<sub>3</sub> in the organic rich mud (Table 1), especially in the finest particles (Fig. 4), due likely to carbonate precipitation during early diagenesis processes in anaerobic deposits. Under anoxic conditions, the rhodochrosite (MnCO<sub>3</sub>) is a typical mineral precipitated during diagenesis which explains the saturation of this factor for Mn, (Wollast et al., 1979, Saulnier & Mucci, 1999). The third factor explains 19.2% of the data variance and is highly saturated by Na, K, Al and Mg, characteristic of aluminosilicate minerals (clays and feldspars).

It is interesting to note that a principal component analysis carried out by Zwolsman & van Eck (1999) on 90 samples of suspended matter collected in the Scheldt in 1987-1988 gave very similar results, with 90% of the variance explained by four factors. The first factor comprised the trace metal group, the second the detrital elements typical of the clay fraction, the third the organic components only partially analysed by us in the sediments and finally the last factor consisting of the carbonate group. The individual component loadings in each factor were similar to those obtained for the sediments although systematically higher in the suspended matter. This may be attributed to the fact that the sandy sediments results from a bed load transport and are not present in the suspended matter collected in surface water.

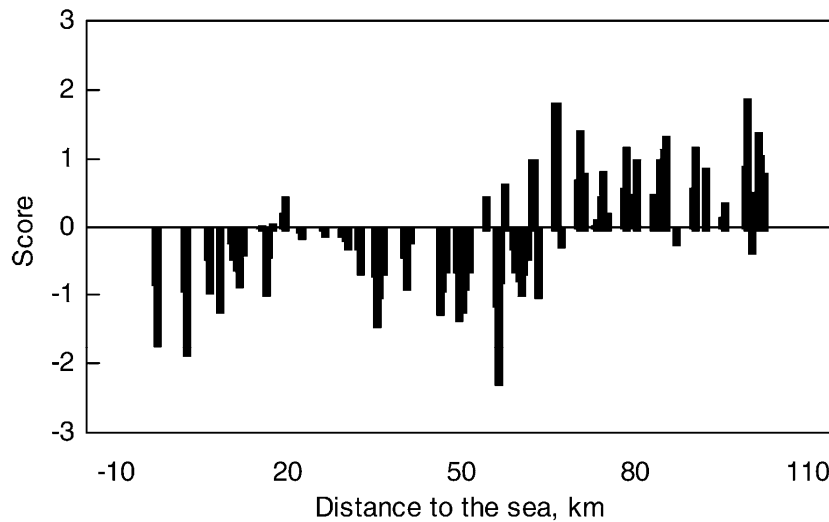
**Figure 7.** (a) Normalized mean content of trace metals in superficial muddy sediments collected in 1974 and 1994. (b) Normalized mean composition of the fluvial end member of suspended matter collected respectively in 1987-1988 and 1995-1996 (after Zwolsman, 1999).



**Table 6.** Results of factorial analysis showing for each factor the percentage of variance explained and the individual component loadings

Factor	1	2	3
% variance	44	23	19
Co	0.856	0.406	0.172
Zn	0.854	0.335	0.093
Pb	0.842	0.284	0.157
Cr	0.835	0.205	0.428
Ni	0.816	0.327	0.305
Cu	0.770	0.513	0.215
Cd	0.717	0.295	0.342
POC	0.700	0.511	0.203
Mn	0.684	0.631	0.221
Li	0.673	0.527	0.437
Fe	0.669	0.418	0.351
Ca	0.250	0.912	0.223
PIC	0.385	0.807	0.023
Si	-0.531	-0.691	-0.188
Na	-0.049	0.337	0.901
K	0.431	-0.114	0.850
Al	0.628	0.204	0.700
Mg	0.646	0.307	0.661

**Figure 8.** Longitudinal distribution of the values of the principal component 1 in the estuarine Scheldt sediments.



## Conclusions

A statistical analysis of the chemical parameters characterizing the Scheldt sedimentary deposits confirms previous studies which indicated that the sediments of the estuary can be subdivided, according to their composition, into two well-characterized areas. The deposits of the brackish zone, located between km 50 and km 100 from the mouth, are mixtures of fine sand and organic rich mud. They contrast with those of the marine zone (km 0-km 50 from the mouth) where sand and coarse calcium carbonate debris are predominant. In this area, mud is sometimes present as small pellets, except in front of the Gent-Terneuzen channel where muddy deposits are locally observed. This distribution can be explained by the fact that there is a twofold origin of the sediments (Wollast, 1988; Regnier & Wollast, 1993; Zwolsman, 1999). First, fine suspended matter, carried by riverine fresh water, which flocculates and coagulates as soon as the salinity increases and is deposited in the upper part of the estuary. On the other hand, sand and calcareous debris of shells of marine origin are transported upward along the bottom by density currents, in the area of mixing of fresh water and seawater.

The separation of the  $<63 \mu\text{m}$  fraction of the sediments into five granulometric sub-samples by elutriation, shows that the trace elements are mainly present in the fraction  $<32 \mu\text{m}$ . The analysis of the finer fractions gives additional interesting information on accumulation of trace metals in the sediments. Some elements (Mn, Co, Ni, Cr, Cu) exhibit a maximum concentration in the 4-8  $\mu\text{m}$  fractions more likely associated with Mn oxo-hydroxide. Their presence in the sediments may be related to co-precipitation with Mn minerals during redox diagenetic processes. Other elements (Pb, Cd, Zn) seem to be preferentially associated with clay minerals in the very fine fraction ( $<4 \mu\text{m}$ ). Interestingly, this finest fraction contains also an excess of calcite and silica. The calcite can be formed during sulfato-reduction in anoxic sediments and the high values of silica may be either due to some clay minerals such as chlorite or to debris of diatom skeletons. The concentration of Cd, Zn and Pb, which are among the most toxic metals, remains however very high especially in the fraction less than 4  $\mu\text{m}$ . This fraction is easily consumed by benthic organism and can be preferentially resuspended and transported downward. Comparison of the actual Al normalized composition of the superficial sediments with those collected in 1976 confirms a decrease of all trace metals observed previously for the suspended matter (Zwolsman, 1999). This may be due to a reduction of their discharge in the hydrographic basin as suggested by the model calculations of Baeyens et al. (1998). However, the recent dredging of highly contaminated deposits in the estuarine zone contributes also to the decrease of the trace element concentration in the sediments.

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