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THE POTENTIAL USE OF SEDIMENTS AND SUSPENDED MATTER AS A MONITORING  
TOOL FOR POLLUTION IN ESTUARIES AND COASTAL REGIONS.

by

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ABSTRACT

The use of sediments and suspended matter as a monitoring tool for pollution in estuaries and coastal regions is a matter of preoccupation of various national and international authorities. The sediments have obviously the advantage to integrate on a long time scale (depending on the sedimentation rate) modifications of the quality of the water column. Since many contaminants, organic and inorganic, are preferentially transferred from the aqueous phase to the suspended solid phase in the aquatic environment, sediments become thus rapidly the final depository for these contaminants.

Sedimentation in the estuarine and coastal regions is a very complicated process influenced by the local hydrodynamical conditions. Deposited sediments may be further affected by physical and biological perturbations or early diagenetic reactions. The evaluation of background levels of contaminants prior to the disturbances due to human activities as a reference level constitutes also a delicate problem.

Many of these problems can be solved by the use of adequate normalizing techniques. Our contribution is an attempt to use the analysis of the fraction less than 20  $\mu\text{m}$  or to normalize the concentrations of trace metals with respect to Al in the case of suspended matter and sediments collected in the Scheldt in order to evaluate the degree of contamination of the estuary. Various original methods of collection of suspended matter, of size fractionation and of chemical analysis have been therefore developed and tested.

Furthermore, a method based on the introduction of the solid sample previously dispersed in a viscous medium (slurry sampling) has been developed and applied to the analysis of suspended matter collected in the Scheldt estuary.

## THE POTENTIAL USE OF SEDIMENTS AND SUSPENDED MATTER AS A MONITORING TOOL FOR POLLUTION IN ESTUARIES AND COASTAL REGIONS

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The use of sediments and suspended matter as a monitoring tool for pollution in estuaries and coastal regions is a matter of preoccupation of various national and international authorities. The sediments have obviously the advantage to integrate on a long time scale (depending on the sedimentation rate) modifications of the quality of the water column. Since many contaminants, organic and inorganic, are preferentially transferred from the aqueous phase to the suspended solid in the aquatic environment, sediments become thus rapidly the final depository for these contaminants.

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Furthermore, a method based on the introduction of the solid sample previously dispersed in a viscous medium (slurry sampling) has been developed and applied to the analysis of suspended matter collected in the Scheldt Estuary.

### INTRODUCTION

The use of sediments and suspended matter as a monitoring tool in relation to pollution has been a subject of concern and discussion at various national and international levels since several years (ICES, 1981).

In general, most contaminants show high affinity to particulate matter and preferentially to the fine grained fraction of the suspended solids. These particles tend then to be accumulated by sedimentation in areas of low hydrodynamic energy. One of the main advantages of sediments is that they tend to concentrate many contaminants and they integrate, over rather long time scales, the usually fluctuating input of many industrial pollutants such as toxic metals. However, sediments are submitted to various physical, chemical and biological processes which renders their use as a monitoring tool often difficult, especially in estuaries and in the coastal zones, characterized by strong hydrodynamical and physico-chemical gradients (Larsen et al., 1988, Eisma et al., 1989).

It is therefore essential to take into account the physical and chemical characteristics of the sediments and to understand their distribution and origin in order to evaluate the extent of their

possible anthropogenic contamination.

Many of these problems can be simplified if an adequate normalization procedure is used in order to characterize the origin of the sediments and their ability to accumulate pollutants of interest (Loring, 1988). The most commonly normalization factors that have been suggested are grain size and the use of elements characteristic of the fine fraction of sediments like Al, Fe and organic matter (ICES, 1988).

We will discuss here briefly the application of these normalization techniques in the case of the sediments of the Scheldt.

In a second part of this report, we will describe a method that we have developed to analyze trace metals in small amounts of suspended matter, collected by filtration in the estuary. Due to the great affinity of trace elements to the particulate phase it is often primordial to characterize the composition of the suspended matter in a river if a realistic and complete assessment of the potential pollution is to be performed (Wollast, 1982). The distribution of elements between the dissolved and the particulate phase is also an essential factor for the understanding of the geochemical behaviour of the element considered. There are however only a few systematic studies of the composition of the particulate matters in aquatic systems because the sampling and the analytical procedures are often tedious or require sophisticated equipments like the neutron activation analysis. The method presented here is based on the direct analysis of a solid sample by atomic absorption.

#### UTILISATION OF NORMALIZATION FACTORS FOR THE SEDIMENTS OF THE SCHELDT

A detailed distribution of major and trace elements as a function of particle size has been performed on two typical mud sediments of the Scheldt estuary collected in the harbour of Antwerp.

The sediments were ultrasonically dispersed in a solution of sodium polyphosphate in distilled water and separated by elutriation in 6 granulometric fractions. The granulometric fractions were further filtered and dried.

Two digestion methods were used :

- a total dissolution using a mixture of HF + HClO<sub>4</sub> in a platinum crucible ;
- a strong acid digestion using reflux boiling of a mixture of concentrated HCl + HNO<sub>3</sub> (3+1) during 2 hours.

The major elements (Al, Ca, Mg, K, Na, Fe, Mn) were measured by inductively coupled plasma emission spectrometry and the minor elements (Zn, Cu, Pb, Cr, and Ni) by flame atomic absorption spectrometry or graphite furnace atomic absorption spectrometry (Co, Cd).

The results for the distribution of Pb, Cr and Al in the various granulometric fractions after total decomposition of the samples are shown as selected examples in figure 1.

The results are very similar for the two samples and demonstrate very clearly the increase of concentration of trace elements in the fine fractions. Similar results have been obtained for all the trace metals investigated. These results indicate that most of the trace metals are present in

the fraction smaller than 20  $\mu\text{m}$ . The relative amount of the fraction less than 20  $\mu\text{m}$  may thus constitute a good normalizing parameter in the case of the Scheldt sediments.

It can also be seen in figure 1 that there is a constant increase of the Al content with decreasing particle size. The Al content of the sediment represents thus a good indication of the amount of fine material present in the sample.

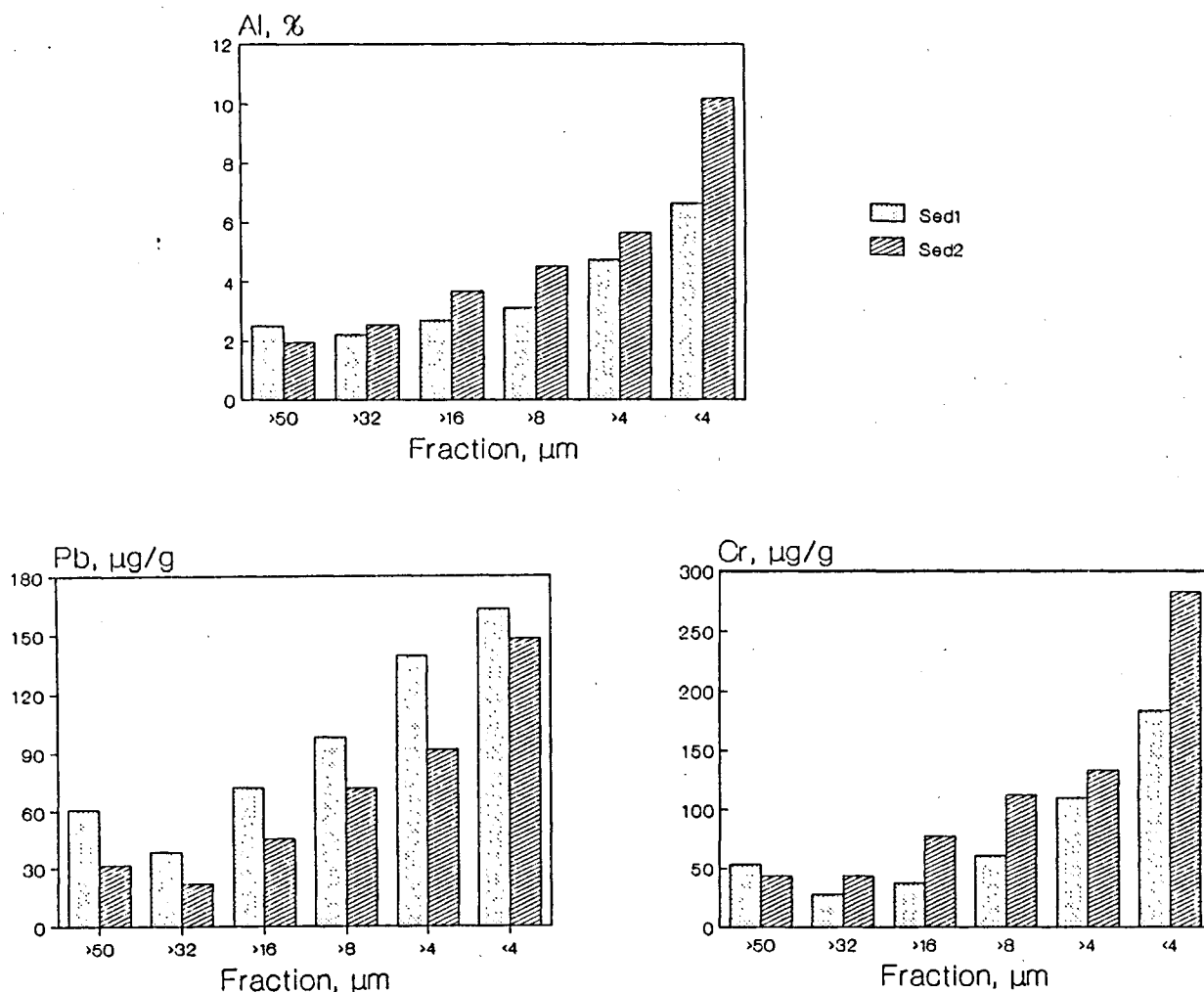


Fig. 1. Granulometric distribution of Pb, Cr and Al in the case of two typical muddy sediments of the Scheldt estuary.

It is of course much easier to measure the Al content of a sediment than to perform the tedious size fractionation necessary to recover the less than 20  $\mu\text{m}$  fraction. We have also calculated the regression coefficient between the concentration of all the trace elements measured and the aluminium content of the sediments. The results of these calculations are represented in table 1. Since there is also an excellent correlation between Al and Fe, iron can also be used as a good normalizing factor in the case of Scheldt sediments. It is not the case for Mn which is strongly affected by remobilization processes due to the very reducing condition existing in the Scheldt estuary (Wollast, 1982).

Manganese exhibits however a significant positive correlation ( $r = 0,72$ ) with Ca which is representative of the carbonate fraction of the sediments.

The results obtained with the strong acid extraction are much less satisfactory due to partial mobilization of Al and of many trace elements even in the fraction less than  $4 \mu\text{m}$ .

The normalization technique with respect to size fraction and Al content has been applied to compare the results obtained for a few typical sediments and for suspended matter of the Scheldt estuary (Fig. 2).

TABLE 1. Correlation coefficients of elements in the various size fractions of two sediments of the Scheldt.

	Zn	Cu	Cd	Pb	Cr	Ni	Co	Fe	Mn
Al	0.82	0.83	0.73	0.93	0.99	0.79	0.88	0.98	0.29

Two sediments were collected in the marine part of the estuary dominated by sandy deposits mainly of marine origin which were transported upward the estuary by bottom currents generated by the salinity gradient.

Three samples of sediments were collected in the muddy area of the estuary located between km 50 and 100 where intensive shoaling occurs. Most of the fine material transported by the river is flocculated and deposited in that area. This fine fraction is however mixed and partially diluted with coarse sands of marine origin transported upwards by bottom currents. At these three stations we have also collected continuously the suspended matter during four months by taking one instantaneous sample of 2 liters per tide. The suspended matter accumulated during one month period was then carefully homogenized. The composition of the suspended was found to be remarkably constant at each station.

We have also collected in the same area a sample of a quarternary clay deposit (Rupelian) which is presently being eroded by the river.

The granulometric fraction less than  $20 \mu\text{m}$  was extracted by elutriation from both sediments and suspended matter, and was analyzed for major and minor elements. The results are presented in tables 2 and 3.

The analyses of the suspended matter normalized with respect to the size fraction are very constant and normalization appears to be very satisfactory. Since the Al content is rather constant in the less than  $20 \mu\text{m}$  fraction both criteria reflect well the accumulation of the trace elements in the fine fraction. It is remarkable to see that for all the elements considered there is a systematic decrease of the concentration of trace elements with decreasing distance to the sea. There may be two explanations for this observation : the fine fraction rich in trace elements is preferentially removed by sedimentation in the lower salinity area of the estuary and/or the highly contaminated suspended matter of fresh water origin is progressively diluted by less contaminated and more marine suspensions.

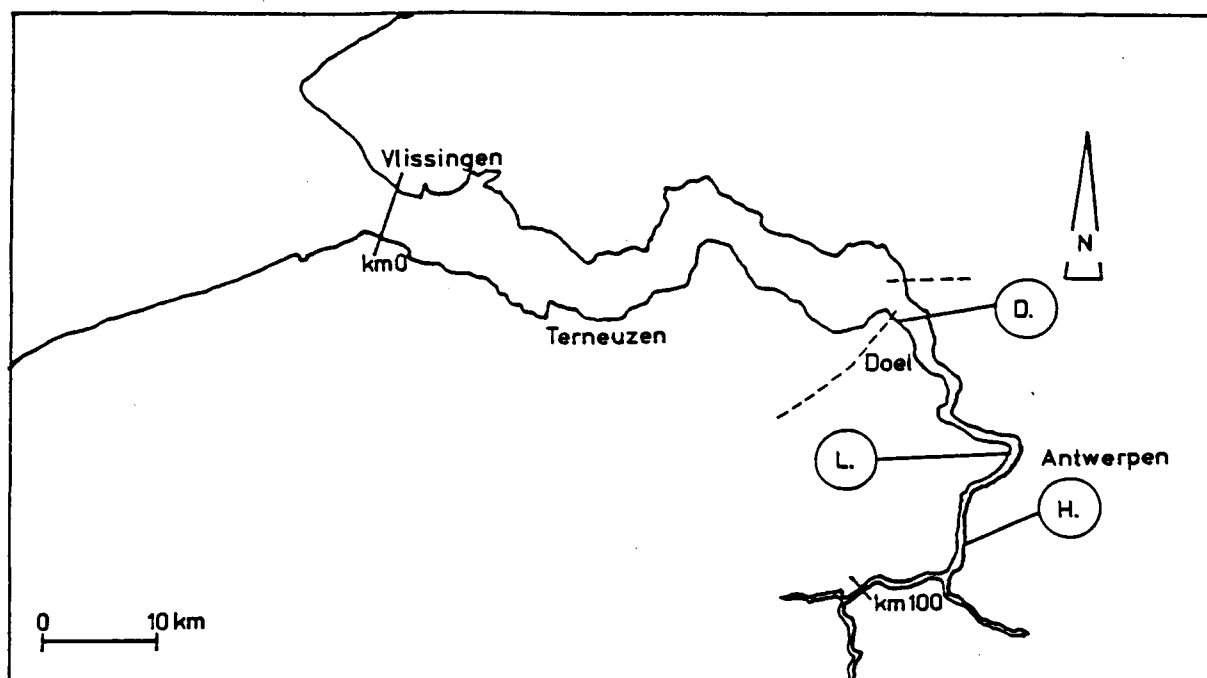


Fig. 2. The Scheldt estuary ; location of the suspended matter samples (D : Doel, L : Linkeroever and H : Hemiksem)

				Normalization with respect to Al		
	(1) D.	(2) L.	(3) H.	D.	L.	H.
Al	6.48	6.90	6.75	—	—	—
P	4910	5880	6590	75.7	85.2	97.6
Zn	834	1000	1130	12.9	14.5	16.7
Cu	144	178	200	2.22	2.58	2.96
Cd	12	13	14	0.18	0.19	0.21
Pb	230	276	328	3.55	4.00	4.86
Cr	200	235	255	3.09	3.41	3.78
Ni	67	97	100	1.03	1.40	1.48
Co	19	24	24	0.29	0.35	0.38

(1) Doel, km 61.5  
(2) Linkeroever, km 78.0  
(3) Hemiksem, km 87.5

TABLE 2 Composition of the less than 20  $\mu\text{m}$  fraction of suspended matter collected in the Scheldt (in ppm except for Al in %).

The use of normalization techniques appears more powerful in the case of sediments because of the much larger spectrum of their particle size. The distribution of contaminants in the total sediment gives only very broad information and selective dissolution techniques obscure the distribution pattern rather than enlight it (Wollast et al., 1985).

The use of the less than 20  $\mu\text{m}$  fraction allows not only to distinguish clearly the considerable enrichment of some trace elements in the fine fraction of the sediments but also to compare with an uncontaminated sediment (sed6) to evaluate the level of contamination of the area. The number of samples considered here is not sufficient to discuss in detail the sources and sinks of contaminants in the estuary. But it gives nevertheless some general ideas about the degree of pollution in the upper part of the estuary.

With no doubt such a preliminary investigation can lead to the development of a very powerful monitoring strategy based on the use of sediments.

	sed1	sed2	sed3	sed4	sed5	sed6
Distance km	4	45	57.5	76	87.5	82.8
Al	5.76	7.02	6.74	6.39	9.70	10.44
P	1923	1481	5157	5143	4815	1517
Zn	250	142	682	909	1798	141
Cu	35	28	157	172	1981	93
Cd	<1	<1	10	14	NA	<1
Pb	87	32	200	251	208	29
Cr	92	85	210	200	124	117
Ni	33	48	65	68	76	60
Co	12	14	20	19	12	12
Normalization with respect to Al						
P	33	21	77	80	50	15
Zn	4.3	2.0	10.1	14.2	18.5	1.4
Cu	0.61	0.40	2.33	2.69	20.4	0.89
Cd	<0.1	<0.1	0.15	0.22	NA	<0.1
Pb	1.51	0.46	2.97	3.93	2.14	0.28
Cr	1.60	1.21	3.12	3.13	1.28	1.12
Ni	0.57	0.68	0.96	1.06	0.78	0.57
Co	0.21	0.20	0.30	0.30	0.12	0.13

TABLE 3 Composition of the less than 20  $\mu\text{m}$  fraction of the sediments collected in the Scheldt (in ppm except for Al in %)

#### ANALYSIS OF TRACE METALS IN SUSPENDED MATTER COLLECTED BY FILTRATION

We have recently developed an analytical procedure especially adapted for the determination of trace metals in small quantities of solids, generally 1 to 10 mg. This method is based on the direct analysis of solid samples using electrothermal atomic absorption where the particles are first dispersed in a viscous medium ("slurry sampling") (Hoenig et al., 1986).

This technique is similar to the solution analysis and can be easily automated for routine use. It allows sequential multi-elements analyses of Cd, Cu, Co, Cr, Ni and Pb on the same sample (Hoenig et al., 1989). The performance of this method has been investigated by calibrating four international soil and sediment standards (Table 4). Different tests of the reproducibility of the calibration curve and of the analysis itself have been conducted in the case of the suspended matter collected in the Scheldt. Figure 3 shows the stability of the absorbance signals for Co, Ni and Cr, indicating the stability of the slurried sample.

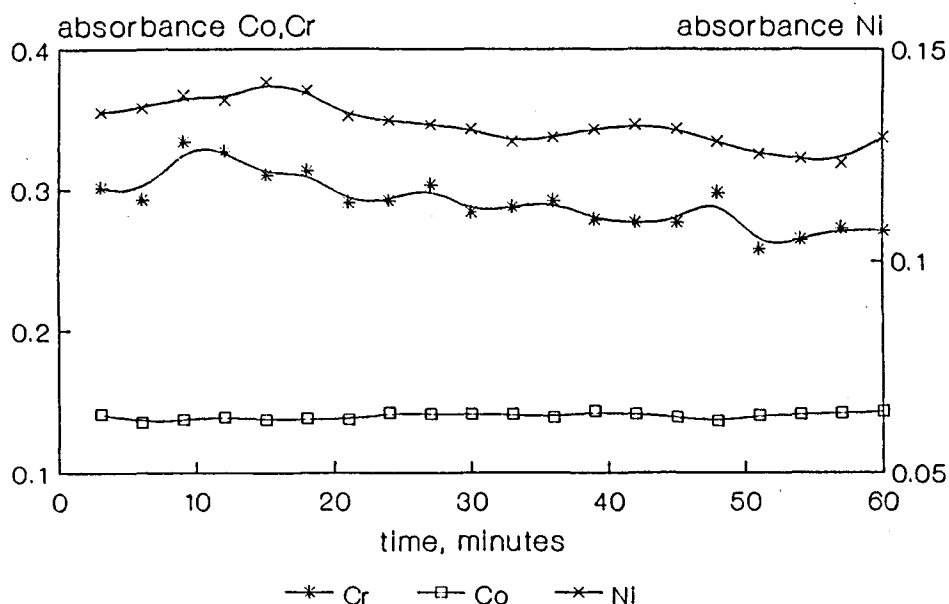


Fig. 3. Stability of the slurries with time : successive absorbance signals of Ni, Cr, and Co (suspended matter sample of the Scheldt estuary).

#### RESULTS AND DISCUSSION

Suspended matter has been sampled at various locations of the Scheldt estuary on 29/03/88 and from 1 to 3/11/88. The particles were recovered by filtration through 0.45  $\mu\text{m}$  membrane filters.

The ability of this method to record rapidly a longitudinal profile of the composition of the suspended matter is demonstrated in figure 4 where the distribution of the concentrations of Cu is presented for March and November 88. Particulate copper behaves obviously not like a conservative component in the upper estuary.

In March, characterized by a high river discharge, the concentration of copper in the suspended matter is relatively low in the fresh water part which may be due to dilution of the contaminants. The maximum observed in the upper estuary may simply reflect departures from steady-state conditions due to a rapid increase of the fresh water discharge also characterized by a lower level of contamination of the suspended matter.

At higher salinities, the mixing curves presented in figure 4 indicate mainly a decrease of the concentration of copper in the suspended matter. Similar trends are observed for the other trace metals (Fig. 5).

This decrease may be due either to desorption and solubilization of particulate metals when the salinity increases or to the dilution of highly contaminated particulate matter of continental origin by marine suspended matter with rather low levels of trace metal contents.

A simple dilution process of suspended matter of terrestrial and marine origin should give a straight line in figures 4 and 5, which seems to be the case for most metals. Positive or negative deviations from the straight line indicate either uptake or release of trace metals by the particulate phase. Alternatively local input of particulate metals or removal by preferential sedimentation



of contaminated particles may lead to the same effect. Ideally concentration in both dissolved and particulate phases should be performed along longitudinal profiles.

Until now, the particulate phase has been very much neglected, mainly because of the difficulties encountered in sampling large representative quantities of suspended matter required for the chemical analysis.

Element	SRM	Recommended value, ppm	Found value, ppm	% RSD (n = 4)
Cu	SOIL-7 <sup>1)</sup>	11	13.5	3.9
	ESTUAR. SED. <sup>2)</sup>	18+3	20.3	5.5
	LAKE SED. <sup>1)</sup>	30+5	32.3	6.8
	MARINE SED. <sup>1)</sup>	72.2	76.3	2.8
Cd	SOIL-7 <sup>1)</sup>	(1.3)	1.14	1.5
	ESTUAR. SED. <sup>2)</sup>	0.36+0.07	0.35	5.0
	LAKE SED. <sup>1)</sup>	0.26+0.05	0.28	5.0
	MARINE SED. <sup>1)</sup>	11	9.0	2.1
Pb	SOIL-7 <sup>1)</sup>	60	62.1	1.8
	ESTUAR. SED. <sup>2)</sup>	28.2+1.8	26.8	8.6
	LAKE SED. <sup>1)</sup>	37.7+7.4	34.1	2.9
	MARINE SED. <sup>1)</sup>	120	120	5.4
Cr	SOIL-7 <sup>1)</sup>	60	62.1	4.7
	ESTUAR. SED. <sup>2)</sup>	76+3	72.5	3.2
	LAKE SED. <sup>1)</sup>	104+9	95.1	21.1
	MARINE SED. <sup>1)</sup>	149	135	4.3
Co	SOIL-7 <sup>1)</sup>	8.9	9.0	1.0
	ESTUAR. SED. <sup>2)</sup>	10.5+1.3	10.7	5.5
	LAKE SED. <sup>1)</sup>	19.8+1.5	22.3	18.1
	MARINE SED. <sup>1)</sup>	12.1	12.8	8.3
Ni	SOIL-7 <sup>1)</sup>	(26)	29.5	6.2
	ESTUAR. SED. <sup>2)</sup>	32.0+3.0	33.5	10.1
	LAKE SED. <sup>1)</sup>	44.9+8.0	40.3	17.5
	MARINE SED. <sup>1)</sup>	31	29.3	3.0

1) : International Atomic Energy Agency (IAEA) ; SRMs : SOIL-7, SL-1 and SD-N1/2  
 2) : National Bureau of Standards (NBS) ; SRM 1646.

TABLE 4 Analytical results on standard reference materials obtained by graphite furnace atomic absorption spectrometry using "slurry" sampling technique (Hoenig et al., 1989).

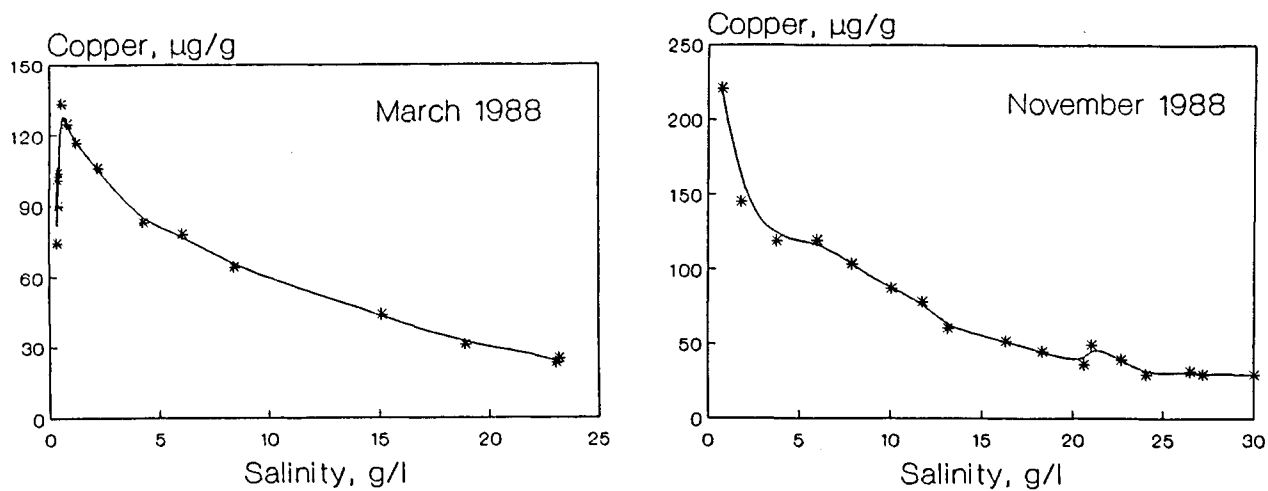


Fig. 4. Longitudinal profile of the concentration of copper in the suspended matter collected in the Scheldt in March and November 1988.

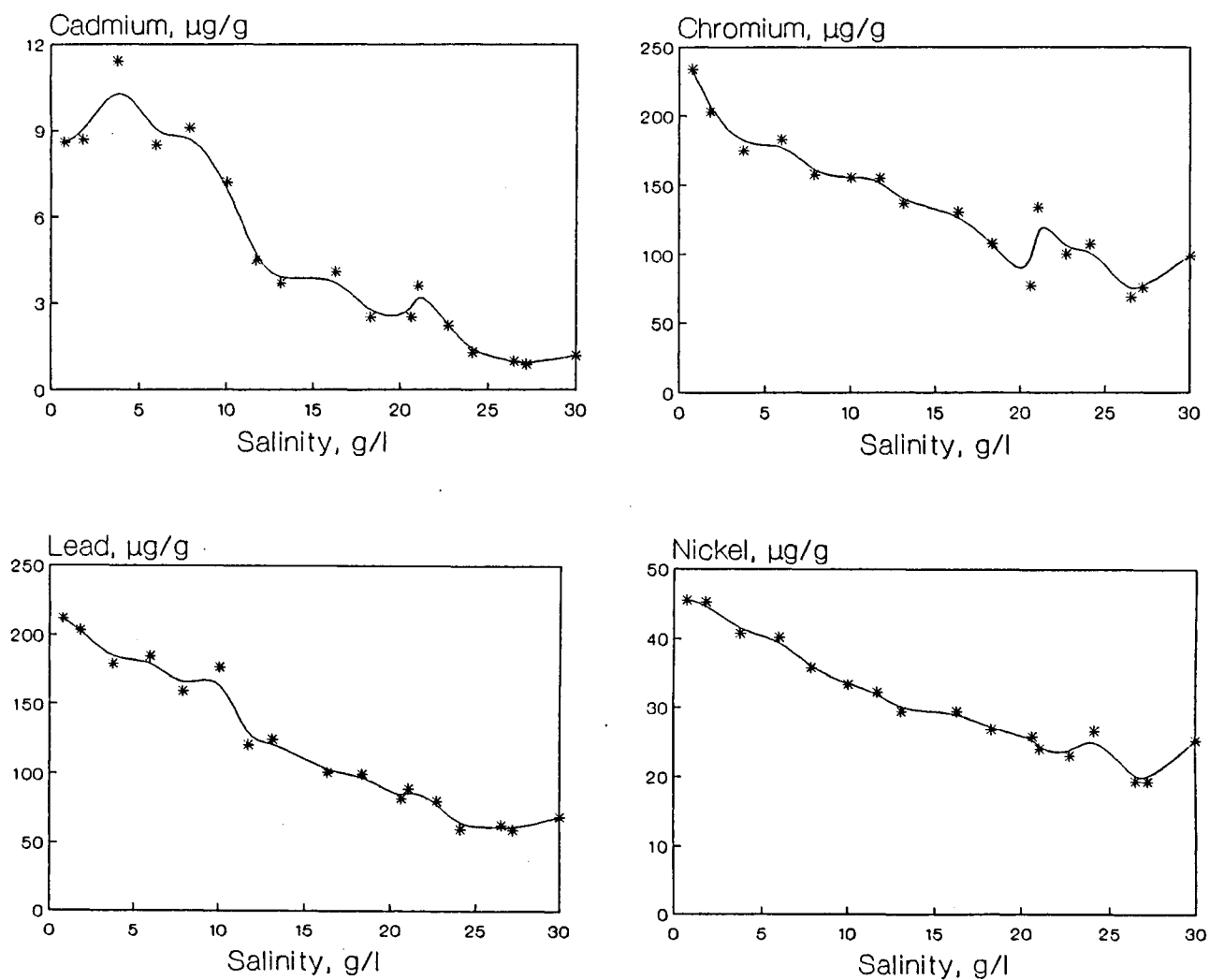


Fig. 5. Longitudinal profile of the concentration of Cd, Cr, Pb and Ni in the suspended matter collected in the Scheldt estuary (November 1988).

## CONCLUSIONS

Our recent work on the Scheldt estuary has been mainly devoted to the development of sampling strategies and analytical procedures in order to use sediments and particulate matter as monitoring tools in pollution studies.

We have shown that normalization of the trace metal content in sediments and suspended matter can be carried out either by analysing the fraction less than 20  $\mu\text{m}$  or by expressing the results of the analysis of trace metals with respect to the Al content of the solid phase. Small but consistent fluctuations in composition can be detected when such normalization is performed and can give interesting indications concerning the origin behaviour and fate of contaminants.

We have on the other hand developed a rapid method of analysis of particulate matter requiring only a few mg of sample. This method allows to consider the use of the composition of suspended matter as a water quality indicator. It would be of major interest to develop more systematically simultaneous measurement of both the particulate and dissolved fraction of trace elements in order to gain a better understanding of their behaviour in the aquatic systems.

## ACKNOWLEDGEMENTS

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## REFERENCES

- Eisma, D., Berger, G.N., Chen Wei-Yue and Shen Jian, 1989. Pb-210 as a tracer for sediment transport and deposition in the Dutch-German Waddensea. In : Proceedings KNGMG Symposium "Coastal Lowlands, Geology and Geotechnology", Kluwer Academic Publishers, Dordrecht, pp. 237-253.
- Hoenig, M. and Van Hoeyweghen, P., 1986. Alternative to solid sampling for trace metal determination by platform electrothermal atomic absorption spectrometry : direct dispensing of powdered samples suspended in liquid medium. *Anal. Chem.* 58 : 2614-2617.
- Hoenig, M., Regnier, P. and Wollast, R., 1989. Automated trace metals analyses of slurried solid samples by GFAAS with application to sediments and suspended matter collected in natural waters. *J. Anal. Atom. Spectrom.*, in press.
- ICES, 1981. Report on the first meeting of the Working Group on marine sediments in relation to pollution. ICES Publ., Copenhagen, 20 pp.
- ICES, 1988. Report of the 75th statutory meeting of the Working Group on Marine Sediments in relation to pollution. ICES Publ., Copenhagen, 86 pp.
- Larsen, B., Madsen, P.P. and Jensen, A., 1988. Sensitivity of sediments in pollution monitoring. In : Report of the 75th statutory meeting of the WGMS in relation to pollution, annex ICES Publ., Copenhagen, pp. 61-68.
- Loring, D.H., 1988. Normalization of heavy metal data. In : Report of the 75th statutory meeting of the WGMS in relation to pollution, annex 2. ICES Publ., Copenhagen, pp. 19-42.
- Wollast, R., 1982. Methodology of research in micropollutants - heavy metals. *Wat. Sci. Tech.*, 14 : 107-125.
- Wollast, R., Devos, G. and Hoenig, M., 1985. Distribution of heavy metals in the sediments of the Scheldt Estuary. In : Van Grieken R. and Wollast R. (Editors). Proceedings Progress in Belgian Oceanographic Research. Royal Academy of Sciences, Brussels, pp. 147-159.