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Trace metals
Analyses
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Mer du Nord

Trace metals in the eastern part of the North Sea. I : Analyses and short-term distributions

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ABSTRACT

Advanced analysis procedures for dissolved and particulate trace metals in sea water have been developed and tested in international intercalibration exercices. Since these tests gave evidence that reliable data could be produced with such methods, trace metal distributions in the coastal waters of the eastern North Sea were studied.

The spatial distributions of most dissolved and particulate trace metals are, at least qualitatively, similar. Their concentrations decrease with distance from the coast and the mouth of the Scheldt estuary (particulates much stronger than dissolved species). The salinity gradient is similar (but opposite) to the trace metals and turbidity gradients. The five trace metals studied can be subdivided into two groups on the basis of their K_D ratios (particulate metal concentration to dissolved metal concentration). Hg and Pb are strongly associated with particulate matter (K_D from 0.5 to 1.5 offshore and from 7.9 to 40 in the coastal area), while Cd, Cu and Zn are predominantly in the dissolved phase (K_D from 0.1 to 0.2 offshore—up to 0.5 for Zn—and from 1 to 1.7 in the coastal area).

The distributions of the metal concentrations in suspended solids ($mg.kg^{-1}$) are much more complex. Only the Pb distribution is similar to that of the turbidity, but also to those of the major inorganic elements in suspended sediments (Al, Fe, Mn) and the chlorophyll *a* content. However, the chlorophyll *a* content is, like the salinity, inversely correlated to the concentrations of the major inorganic elements.

High X/Al (X = Cd, Cu, Hg, or Zn) ratios in suspended matter are observed at low suspended matter concentrations. Detrital organic matter is probably the main carrier of these trace metals. At high suspended matter concentrations, these ratios decrease and approach the reference soil value. Both the Scheldt estuary and resuspended bottom sediments may be the source of those high suspended matter concentrations. Fe/Al and Mn/Al ratios are high at high suspended matter concentrations and decrease at low turbidity. These particles enriched in Fe and Mn are supplied by the Scheldt estuary. Pb/Al and Fe/Al ratios appear to be correlated.

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RÉSUMÉ

Métaux en traces dans la partie orientale de la Mer du Nord. I. Analyses et répartitions à court terme

Des méthodes analytiques de pointe ont été développées pour doser les métaux en traces dissous et particulaires dans l'eau de mer. Ces méthodes ont été testées dans le cadre d'exercices internationaux d'intercalibration. Comme ces tests ont fourni la preuve que des résultats fiables peuvent être obtenus par ces méthodes, ces dernières ont été utilisées pour étudier la répartition de métaux en traces dans les eaux côtières de la Mer du Nord orientale.

Les répartitions spatiales de la plupart des métaux en traces, dissous et particulaires, sont fort semblables, du moins qualitativement. Leurs concentrations diminuent lorsque l'on s'éloigne de la côte et de l'embouchure de l'estuaire de l'Escaut (les formes particulaires beaucoup plus rapidement que les formes dissoutes). Le gradient de salinité est semblable (mais opposé) aux gradients de métaux en traces et de turbidité. Les cinq métaux en traces étudiés peuvent être subdivisés en 2 groupes sur la base de leur K_D (rapport entre la concentration particulaire et la concentration dissoute). Le Hg et le Pb sont associés à la matière particulaire (K_D de 0,5 à 1,5 en haute mer et de 7,9 à 40 en zone côtière), tandis que le Cd, le Cu et le Zn sont principalement présents sous forme dissoute (K_D de 0,1 à 0,2 en haute mer — jusqu'à 0,5 pour le Zn — et de 1 à 1,7 en zone côtière).

Les répartitions de la concentration des métaux en traces dans les matières en suspension ($mg.kg^{-1}$) sont beaucoup plus complexes. Seule la répartition du plomb est semblable à celle de la turbidité, mais également à celles des éléments inorganiques majeurs présents dans les sédiments en suspension (Al, Fe, Mn), ainsi qu'à la répartition de la chlorophylle *a*, compte tenu du fait qu'il s'agit ici, comme dans le cas de la salinité, d'une corrélation inverse par rapport aux éléments inorganiques majeurs.

Pour des concentrations faibles en matières en suspension des rapports X/Al (X = Cd, Cu, Hg et Zn) élevés sont observés. Les matières organiques détritiques sont probablement les vecteurs principaux de ces métaux en traces. Pour des concentrations élevées en matières en suspension (celles-ci peuvent provenir de l'estuaire de l'Escaut ou de la remise en suspension des sédiments de fond) ces rapports diminuent et tendent vers la valeur de référence du sol. Pour des concentrations faibles en matières en suspension des rapports Fe/Al et Mn/Al faibles sont observés, mais ceux-ci croissent quand la turbidité augmente. Les particules enrichies en Fe et Mn proviennent de l'estuaire de l'Escaut. Les valeurs obtenues pour le plomb sont à corréler avec celles obtenues pour le fer.

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INTRODUCTION

Biological productivity in coastal waters is often very high owing to the high levels of nutrients supplied via coastal inputs or through upwelling. In Belgian coastal waters, for example, the daily primary production ranges from 10 to 280 mg $N.m^{-2}\ d^{-1}$ corresponding to an annual primary production of about 25 g $N\ m^{-2}a^{-1}$ (Baeyens *et al.*, 1983; Mommaerts *et al.*, 1984; Baeyens *et al.*, 1984). Shellfish and fish thus find there excellent spawning, nursing and feeding grounds. Coastal ecosystems are very sensitive to pollution which can perturb severely the biological processes. Heavy metals are amongst the major potential pollutants because of their toxicity.

Obtaining reliable, accurate trace metal data in sea water is still a cumbersome operation. In many areas, values are at or below the detection limits of most methods. Topping *et al.* (1980) reviewed the distribution of trace metals in waters of the Atlantic including the shelf seas. The aim of this exercise was to assemble the trace metal data submitted by the various institutes into a composite picture of their distribution around the British Isles. His conclusion at that time was that data from different areas measured by different analysts cannot be compared owing to the diversity of methods used for sample collection and analysis, and to inadequate intercalibration.

A fundamental point is then the reliability of our trace metal data. In order to evaluate our analysing procedures, we participated in several intercalibration exercises: 1) the intercalibration exercises for the analysis of cadmium and mercury in sea water requested by the Joint Monitoring Group of the Oslo and Paris Commissions and conducted by ICES, results of which have been reported by Thibaud (1981) for cadmium and Olafsson (1981) for mercury; 2) the intercalibration exercise of trace metals in sediments conducted by the Centre Océanologique de Bretagne (CNEXO), results of which have been reported by Joanny *et al.* (1980); 3) the analysis of mercury in botanical substrates (BCR reference materials), involving comparison of several mineralization-digestion methods, results of which have been reported by Dehairs *et al.* (1982).

Participation in these intercalibration exercises offered us the possibility to demonstrate that the analysing procedures in use in our laboratories for Cd, Cu, Hg, Pb and Zn produce reliable data, at least on samples similar to those that served for the intercalibration exercises. Another encouraging fact is that our trace metal data obtained in the English Channel (Baeyens *et al.*, 1987), the Southern Bight of the North Sea (*see* Tab. 2), the northern North Sea (Baeyens *et al.*, 1987) and the Mediterranean Sea (our data are given in the section "Sampling of heavy metals", this paper; for example Mart *et al.*, 1982 report data for the Western

Mediterranean Sea) compare favourably with these obtained by other investigators in the same areas.

Besides the analytical techniques, short-term distributions of trace metals observed during two cruises in the Southern Bight, which present quite different physicochemical conditions, are discussed in this paper. Since short-term processes (tidal current, wind field, fluctuating river inputs, phytoplankton patchiness,...) may affect the small-scale metal distribution observed during a cruise of a few days, some aspects such as the dilution of a metal input can only be dealt with in a qualitative manner. The analyses of particulate Al, Fe and Mn during one of the cruises allow, on the other hand, to discuss particulate trace metal contents in terms of different suspended matter fractions.

METHODS AND MATERIALS

Sampling of heavy metals

To increase the spatial and temporal representativity of our samples, we continuously collected small subsamples from a much larger flow of sea water, the whole system being screened from atmospheric contamination. A peristaltic pump continuously draws 6 $l.min^{-1}$ sea water from 5 m depth through a PVC tube. When sampling, the ship is left adrift and the sampling tube is on the lee side so that it meets water masses not polluted by the vessel. A second peristaltic pump continuously draws 0.5 $l.min^{-1}$ from the main flow into a 5 l polyethylene bottle, equipped with a magnetic stirrer. The filtration apparatus, a stirred system pressurized with purified nitrogen, is connected directly to the 5 l polyethylene bottle. The water drained from the 5 l polyethylene bottle is replaced by pure nitrogen. Filtration is carried out on 0.45 μm MF-Millipore membranes. The filtered sea water is collected in a polyethylene flask. Before use, the sampling and filtration device was soaked in 6N HCl and abundantly rinsed with ultrapure water. Concerning mercury, specific tests showed that a pretreatment of the polyethylene container with a solution of $KMnO_4$ (2%) in H_2SO_4 (50%) during 24 h made them completely mercury-free (Decadt, 1986). Pyrex bottles soaked in boiling 3N HNO_3 during 24 h, rinsed several times with Milli-Q water and baked at 500°C during 24 h can also be used. The filters were decontaminated in a 10^{-2} M DTPA (Diethylenetriaminepentaacetic acid) solution and then abundantly rinsed with ultrapure water.

The performance of the sampling and filtration system was tested on the Mediterranean Sea (Corsica, Calvi) in an area considered as uncontaminated (Gillain, Brihaye, 1985). Dissolved levels for Cd in the range 0.005-0.02 $\mu g.l^{-1}$, for Pb in the range 0.015-0.08 $\mu g.l^{-1}$, for Cu in the range 0.04-0.10 $\mu g.l^{-1}$ and for Zn in the range 0.05-0.18 $\mu g.l^{-1}$ were obtained. All these data are much lower than those measured in Belgian coastal waters and reinforce our confidence in the sampling and filtration system designed to minimize contamination.

Storage of solution and solid matter

For the analysis of total dissolved Zn, Cd, Pb or Cu, samples are acidified to pH 1, using suprapure HNO_3 (Merck). For speciation studies, samples were deep-frozen (—20°C) immediately after collection and filtration without any additive. Storage of these samples over a long time period (6 months) showed no significant changes in trace metal concentrations. For the total dissolved mercury analysis, we opted for a sample storage at —20°C after acidification to pH 1. For speciation of dissolved mercury forms, analysis immediately after sampling and filtration seems necessary.

Suspended matter samples collected on Millipore membranes are stored in acid-cleaned Petri dishes and maintained at —20°C prior to analyses.

Analysis procedure of dissolved metals

To transform all Cu, Pb, Zn and Cd complexes (chelates, inorganic complexes,...) into free ions, samples were acidified to pH 1 and irradiated overnight with ultraviolet light. These free ions are determined by differential pulse anodic stripping voltammetry (DPASV). Thirty ml of filtered sea water are placed in an electrolysis cell. The sample is stirred and oxygen is removed by bubbling with pure nitrogen. Electrolysis is carried out at —1 200 mV (v.s.SCE) for 10 to 20 minutes while nitrogen is introduced into the space above the solution. One minute before the end of the electrolysis, stirring is stopped and the current-potential curve is then recorded from —1 200 to 0 mV with a scan rate of 2 $mV.s^{-1}$ and a pulse of 50 mV (Gillain *et al.*, 1979). Detection limits are 0.01 $\mu g.l^{-1}$ (Zn), 0.005 $\mu g.l^{-1}$ (Cd), 0.03 $\mu g.l^{-1}$ (Pb), 0.1 $\mu g.l^{-1}$ (Cu) and the coefficient of variation is estimated at 7% for a concentration of 1 $\mu g.l^{-1}$ Zn, 14% for 0.05 $\mu g.l^{-1}$ Cd, 13% for 0.1 $\mu g.l^{-1}$ Pb and 12% for 0.5 $\mu g.l^{-1}$ Cu. Speciation of Cu, Pb, Zn and Cd is carried out as follows: 1) the ionic and very labile metal fraction corresponds to the amount measured at the natural pH of sea water; 2) the sum of the moderately mobile fraction and the former fraction corresponds to the amount measured at pH = 1 through addition of HCl; 3) the total amount of dissolved metals is measured according to the procedure described hereabove. It includes the very labile, the moderately labile and the strongly bound fractions.

All dissolved mercury compounds are transformed into metallic mercury by a digestion procedure. To 150 ml sample, 5 ml of $KMnO_4$ (5%), 5 ml of H_2SO_4 (1:1 v/v) and 5 ml of HNO_3 (1:2 v/v) are added. The solution is then heated to 60°C for 16 hours. Excess $KMnO_4$ is reduced with 1 ml hydroxylamine (5%) and the sample volume brought to 180 ml. After reduction with 1 ml of $NaBH_4$ (1%), mercury is determined with flameless absorption spectrophotometry. The coefficient of variation is about 15% for a concentration of 5 $ng.l^{-1}$ Hg, and the detection limit 1 $ng.l^{-1}$ Hg.

Analysis procedure of total particulate metals

Zn, Cd, Cu, Pb

The filter, dried at 50°C, is inserted into a PTFE bomb. Four ml of concentrated HNO_3, 4 ml of H_2O_2 (30%) and 1 ml of concentrated HF were added to the solid material. The bomb was then closed and heated to 160°C for 6 hours. The solution was subsequently evaporated to dryness and an additional ml of concentrated HCl was added. This solution stood overnight and was then brought to 100 ml at a pH = 1. Thirty ml of this solution was transferred to the polarographic cell for DPASV analysis.

Hg

To a Millipore membrane filter in a PTFE bomb, 3 ml concentrated HF and 10 ml concentrated HNO_3 were added. This solution was heated to 110°C for 5 hours. The volume was then brought to 100 ml. To 25 ml of this solution, 2 ml H_2SO_4 (1:1 v/v) and 10 ml $KMnO_4$ (5%) were added. After shaking the sample during 16 hours at 60°C, the excess $KMnO_4$ is reduced with 5 ml of NH_4OCl, and the sample diluted to 150 ml. Mercury is measured on a 100 ml aliquot of this solution, after reducing it to Hg (0) with $NaBH_4$ (1%).

Fe, Al, Mn

The filter was mineralized with HF-HNO_3 like for Hg. The solution was subsequently evaporated to dryness and the residue redissolved in diluted HNO_3. Analysis was performed with FAAS.

Apparatus

DPASV is carried out with a Brucker E310 modular polarographic analyser and a Hewlett-Packard 7040 A X-Y recorder. A three electrode system was employed with a Methrom E410 hanging drop mercury electrode (HMDE) as the working electrode. Potentials were measured in reference to a saturated calomel electrode (SCE). An auxiliary platinum electrode was used to minimize I.R. drop effects across the electrolysis cell.

To detect mercury a modified Coleman MAS-50 spectrophotometer was used. This spectrophotometer is equipped with a second detector, correcting for baseline fluctuations. The characteristics of this double beam system are: 1) diameter and length of the cell respectively 1 and 30 cm; 2) excitation lamp: Hg penlamp (UV products). For low mercury concentrations, <5 ng.l^{-1}, a reduction aeration Au-amalgamation procedure, described in Dedeurwaerder *et al.* (1982), is used.

Salinity

Salinity data are provided by the Management Unit of the Mathematical Model of the North Sea (Ministry of Public Health). They are measured with a Plessey 9400 automated sensor. Calibration of the instrument is regularly performed.

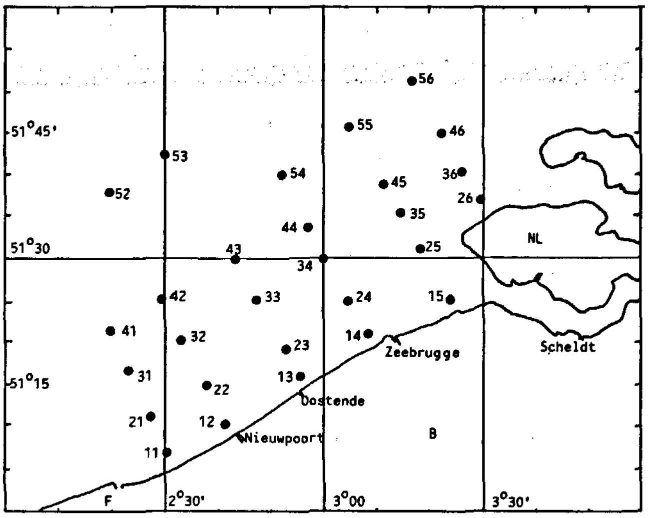

Figure 1

Sampling stations in the Belgian coastal waters.

Sampling

The Belgian coastal waters are fairly shallow (between 15 and 30 m) and under the direct influence of the river Scheldt. Surface samples for the determination of trace elements in solution and suspension were taken in 28 sampling stations off the Belgian coast (Fig. 1), during eleven cruises in the period 1981-1983.

RESULTS AND DISCUSSION

Salinity

Spatial distribution patterns of salinity, observed during the cruises of October 1982 and March 1983, are shown in Figures 2 and 3.

The October 1982 cruise corresponds to a situation of high salinity in the coastal waters and a low fresh water supply by the river Scheldt during the preceeding months [a freshwater flow of 45, 52 and 44 m^3.s^{-1} measured at Schelle (about 80 km from the mouth of the river) respectively in July, August and September 1982], while the March 1983 cruise corresponds to a situation of low salinity in the coastal waters and a high fresh water supply by the river Scheldt during the preceeding months (a freshwater flow of 111, 155 and 188 m^3.s^{-1} measured at Schelle respectively in December 1982 and January, February 1983).

Offshore (salinity$>$34) isohalines are oriented northeasterly and run parallel to the coastline. Inshore (salinity$<$33) isohalines are clearly created by the outflow of the river Scheldt. The northeasterly-flowing watermass coming from the Channel encounters the more coastal and southwesterly oriented Scheldt outflow. As a result, the less saline coastal Scheldt outflow is deviated to the north where it mixes progressively with the more saline northeasterly-flowing watermasses (*see* for further details Baeyens *et al.*, 1987). Isohalines up to

33 all show the same pattern: from the northeast to the southwest they are first parallel to the coast, then bend towards the coastline and finally become perpendicular to it.

Dissolved metals

Comparison with literature data

In Table 2 a summary of previous determinations in the area is given together with relevant data from the west coast of the Southern Bight. These comparisons should be carried out with care, however, for reasons mentioned in the introduction. The range of dissolved copper concentrations we observed compares favourably with those observed by Duinker and Nolting (1982) and by Mart (1976), if we do not consider his stations 4 and 8 which show very high copper concentrations (8.5 and 15.05 $\mu g.l^{-1}$ respectively). The minimum values reported by Duinker and Kramer (1977) are a factor three to four higher than these observed during this study. For the west coast of the North Sea Basin, Taylor (1979) reports a mean dissolved copper concentration (2.1 $\mu g.l^{-1}$) which approaches our maximum values, while Balls (1985) observed a concentration range that is from two to four times lower than the concentration range in the Belgian coastal zone.

The dissolved lead values reported by Mart (1976) (with or without stations 4 and 8) and Duinker and Kramer (1977), for the present study area, are substantially higher than the values we observed. Duinker and Kramer (1977) attributed these high concentrations to particulate lead (lead oxide) passing the 0.45 µm pore size filters. This lead is released to solution following acidification. However, at the western side of the Southern Bight, Balls (1985) found dissolved lead concentrations comparable to our values. The dissolved lead concentrations show a tendency to decrease with increasing salinity (*see* also Fig. 2 and 3). This is in contrast

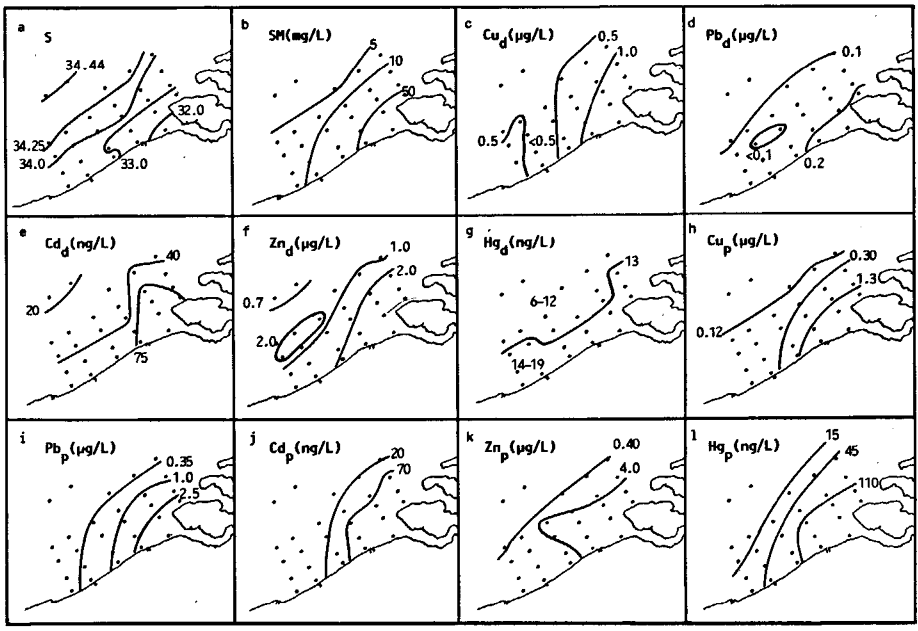

Figure 2

Distribution patterns of dissolved and particulate metals observed during the October 1982 cruise.

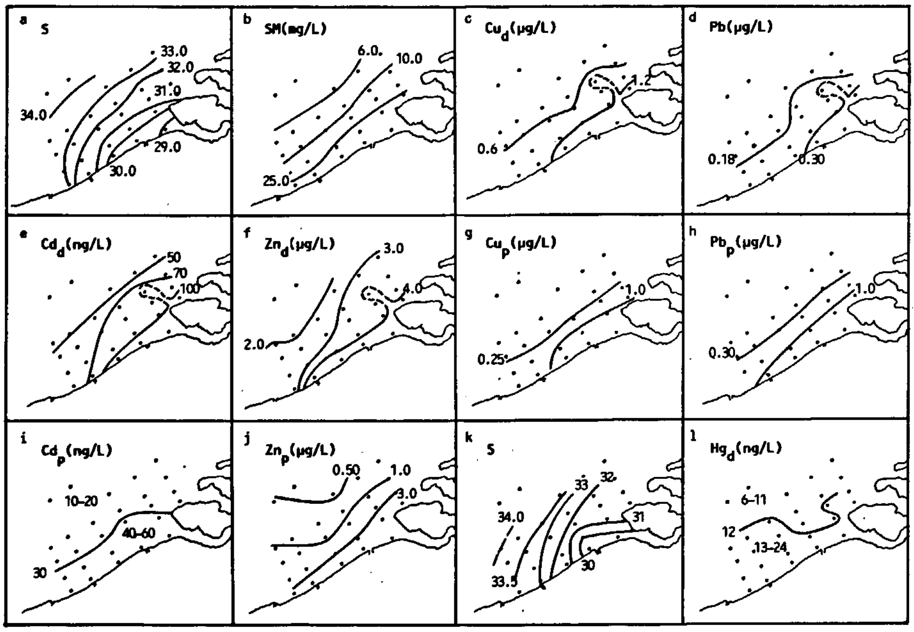

Figure 3

Distribution patterns of dissolved and particulate metals observed during the March 1983 cruise.

with the findings of Balls (1985), who observed lower dissolved lead concentrations in the Humber estuary (0.01-0.055 µg.l^{-1}) than in the coastal zone (0.015-0.135 µg.l^{-1}).

Dissolved cadmium values reported by Mart (1976) and Duinker and Nolting (1982) for the present study area are of the same magnitude, the minimum values reported by Duinker and Kramer (1977) are substantially higher. Taylor (1979) found a mean dissolved Cd concentration of 0.39 µg.l^{-1} off the west coast of the Southern Bight, which is about three times higher than our maximum values, but Balls (1985) found still lower concentrations than the ones we observed off the Belgian and Dutch coasts.

Dissolved zinc concentrations reported by Duinker and Kramer (1977) are substantially higher than our results but in a more recent study Duinker and Nolting (1982) observed a similar range. At the western side of the Southern Bight basin, Taylor (1979) observed much higher values (mean value of 25.2 µg.l^{-1}).

Dissolved mercury data in the North Sea are scarce. Burton and Leatherland (1971) reported values between 14 and 21 ng.l^{-1} in the English Channel on non-filtered samples. Baker (1977) who measured reactive mercury in the Southern Bight reported values between 2.0 and 7.7 ng.l^{-1} with some individual high spots of 12 and 18 ng.l^{-1}. These values compare favourably with our offshore data (6 ng.l^{-1}) and coastal-estuarine data (19-22 ng.l^{-1}).

The dissolved metal concentrations observed in March 1983 in the mouth of the Sheldt estuary are of the same magnitude as those observed in the coastal water-mass off the Scheldt mouth (coastal stations 14 and 15).

Spatial distributions patterns

October 1982: the resemblance between the salinity and the heavy metal concentration patterns, if we make abstraction of the fact that they are inversely correlated, is quite good for Cd and Pb, differs partly for Cu and Zn and strongly for Hg (Fig. 2). The dissolved Cu distribution shows a kind of depleted zone in front of Nieuwpoort, while for Zn an area of increased concentrations is observed around the light-vessel West-Hinder. Mercury shows a somewhat different distribution: its concentration range is by far the smallest of all metals. Moreover, two separate zones can be distinguished, parallel to the coast: concentrations between 14 and 19 ng.l^{-1} are found in the inshore zone, between 6 and 12 ng.l^{-1} in the offshore zone (one station excepted).

March 1983: dissolved metal concentrations observed at station 45 are higher than at surrounding stations (Fig. 3); we do not at present have enough information to attribute these high levels to any specific activity such as dredging or dumping of industrial wastes. Isolating this point from the other sampling stations (in the Figures 3*c* to 3*f* the station is linked to the high concentration area by a dashed line) we recognize a strong resemblance between the concentration patterns of salinity and all metals measured during this cruise (Zn, Pb, Cu, Cd), with the understanding that salinity and metal concentrations are inversely correlated. Mercury was not measured during this cruise, but the May 1981 cruise is very similar to that of March 1983 as regards the salinity distribution. The mercury concentration pattern (Fig. 3) is almost identical to the pattern observed in October 1982 and thus shows no resemblance to the salinity pattern.

The dissolved metal distributions are, however, only qualitatively similar to the salinity distribution (in addition of their opposite gradients). Considering for example Cd and Cu concentrations versus salinity (Fig. 4), a zone of high concentrations at low salinity and vice versa are observed, but the concentrations fluctuate rather strongly, especially in the low salinity range.

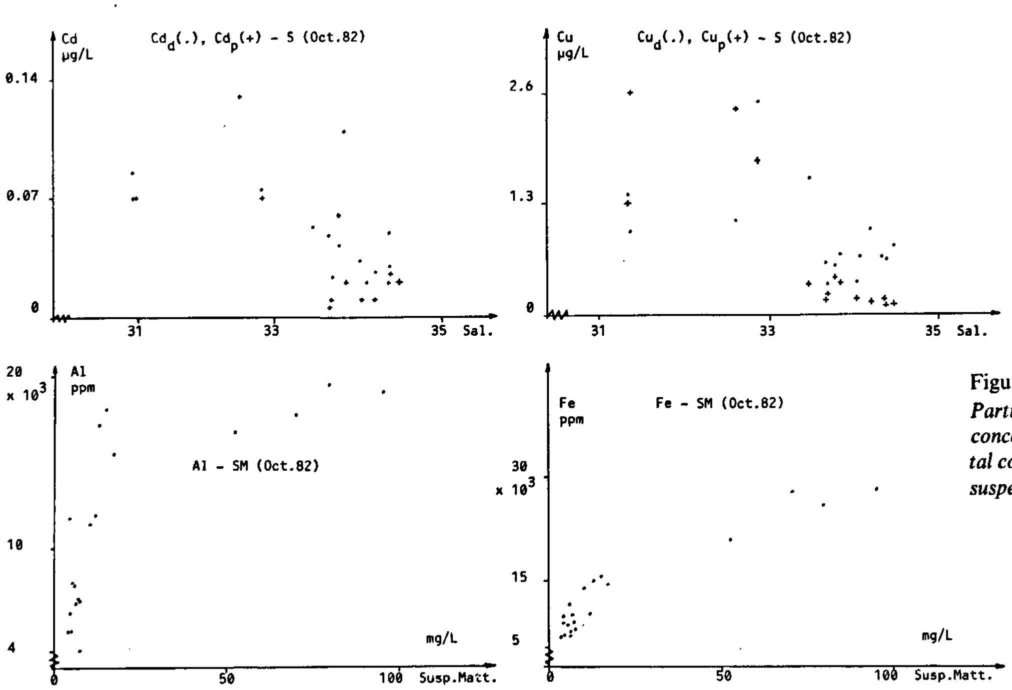

Figure 4

Particulate and dissolved Cd and Cu concentrations versus *salinity. Elemental contents of Al and Fe (ppm)* versus *suspended matter concentration.*

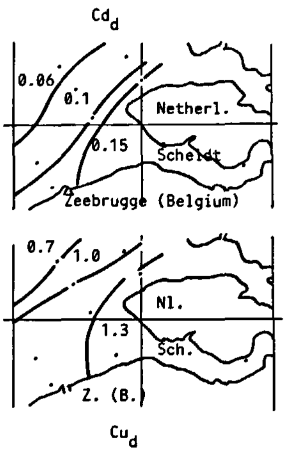

Figure 5
High water (left side) and low water (right side). patterns of dissolved metals at the mouth of the Scheldt estuary.

These fluctuations can be attributed to: 1) irregular, discontinuous discharges of trace metals into the estuary; and 2) the influence of the tide on the dispersion of the metal supply. The patterns at the mouth of the Scheldt estuary are quite different at low and at high water (Fig. 5).

Speciation of the dissolved metals

The concentrations of organically-bound dissolved metals, being the difference between the total dissolved concentration and the concentration measured at pH = 1, decrease with distance from the mouth of the Scheldt estuary and from the coast like the total dissolved concentration. The behaviour of the organically-bound fraction (ratio of organically-bound concentration to total concentration) is more complex (Tab. 1). Between 80 and 95% of dissolved Zn is organically bound. The organically-bound Zn fraction is not only high, but also fairly constant over the whole area. This is not the case for the organically-bound Cd, Cu and Pb fractions which vary between 20 and 80%. The fluctuations are less for Cu, especially in the offshore area (stations 41 to 56), than for Cd and Pb. The average organically-bound Cd and Pb fractions are higher in the vicinity of the Scheldt mouth (stations 14 to 26) than in the remaining part of the study area; the opposite is true for Cu.

Tableau 1
Speciation of dissolved metals: the average organically bound fraction.

Stations	Coastal zone	Coastal-estuarine zone	Offshore zone
	11, 12, 13, 21, 22, 23	14, 15, 24, 25, 26	31-36, 41-46, 52-56
Metal:			
Zn	0.87	0.85	0.91
Cd	0.43	0.49	0.38
Pb	0.56	0.59	0.54
Cu	0.63	0.53	0.61

Particulate metals

Comparison with literature data

The range of particulate copper concentrations we have measured compares favourably with those reported by Mart (1976) and Duinker and Nolting (1977), the range of zinc concentrations with those reported by Duinker and Nolting (1977). Mart (1976) observed significantly higher minimum values of particulate Cd and Pb, and a much narrower range of values for Pb.

Spatial distribution patterns

Turbidity values offshore from the Belgian coast range typically between 4 and 10 mg.l^{-1}. Only close to the coast and the Scheldt estuary are higher values observed: up to 95 mg.l^{-1} in October 1982 and to 57 mg.l^{-1} in March 1983. The turbidity pattern corresponds to the salinity pattern offshore and in the northeastern part of the area covered by this study, but is divergent in the southwestern part (Fig. 2 and 3). The origin of these particulates (riverine input or resuspension of bottom sediments) is discussed in the "Elemental partition" section.

October 1982 cruise: the distribution patterns of all metals correspond closely to that of the turbidity. Only the highest isoconcentration line of particulate Zn (4.0 µg.l^{-1}) deviates slightly from that picture. The concentration gradients, which are perpendicular to the isoconcentration lines, are much larger for particulate metals than for dissolved metals. A five to tenfold drop of the turbidity corresponds to an almost equal drop in particulate metal concentrations. Metal concentrations in suspended solids (mg.kg^{-1}) were calculated from the suspended solids weight data and particulate metal analysis. In this case, only Pb shows a distribution pattern similar to that of the turbidity (Fig. 6).

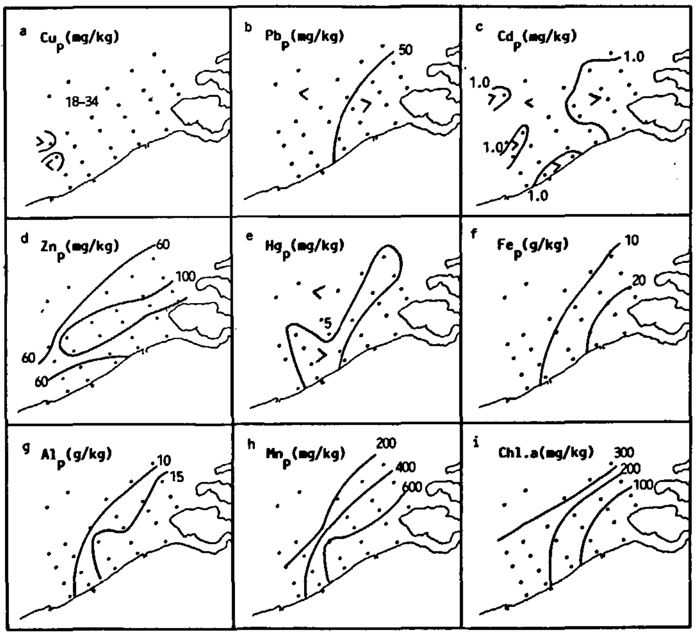

Figure 6
Distribution patterns of metal concentrations in suspended solids observed during the October 1982 cruise.

Table 2
Trace metal data reported for the eastern and western side of the Southern Bight of the North Sea.

	Zn ($\mu g.l^{-1}$)	Cu ($\mu g.l^{-1}$)	Cd ($\mu g.l^{-1}$)	Pb ($\mu g.l^{-1}$)	Hg ($ng.l^{-1}$)
	Dissolved phase				
Belgian and Dutch coasts					
Mart, 1976:					
— all stations	—	0.34-15.05	0.022-0.390	0.079-7.50	—
— all stations minus stations 4 and 8	—	0.34- 2.20	0.022-0.110	0.079-2.60	—
Duinker and Kramer, 1977	3.00-20	1.00- 2.50	0.100-0.300	1.700-3.30	—
Duinker and Nolting, 1982	0.30-12	0.20- 2.40	0.020-0.120	—	—
This study:					
— October 1982	0.25- 8.8	0.28- 2.50	0.014-0.110	0.045-0.260	6-19
— March 1983	0.90- 7.2	0.38- 1.80	0.030-0.170	0.090-0.660	6-24(a)
Mouth of the Scheldt					
This study:					
— March 1983: 25.8 Salinity	4.4	1.6	0.13	0.35	—
— March 1983: 18.7 Salinity	7.1	1.4	0.17	0.26	—
East coast of Britain					
Taylor, 1979 b	(25.2)	(2.1)	(0.39)	(—)	—
Balls, 1985	—	0.12— 0.58	0.010-0.060	0.015-0.135	—
	Particulate phase				
Belgian and Dutch coasts					
Mart, 1976	—	0.11- 1.4	0.023-0.086	0.47 -3.86	—
Duinker and Nolting, 1977	0.3 -10(c)	0.11- 3.0	—	—	—
This study:					
— October 1982	0.07- 9.0	0.08- 2.6	0.002-0.13	0.03 -8.3	4-160
— March 1983	0.16- 8.3	0.06- 1.8	0.010-0.060	0.07 -4.2	—
Mouth of the Scheldt					
This study:					
— March 1983: 18.7 Salinity	9.3	2.6	0.13	3.6	—

a) May 1981 cruise results; b) Taylor, 1979, reports total mean values. The mean dissolved concentrations presented here are calculated after the percentages of dissolved metals reported in his paper: 85% for Zn and Cd, 74% for Cu; c) the particulate Zn values presented here are only between 60 to 90% of the total particulate Zn amount (Duinker, Nolting, 1977).

Major metals Fe, Mn, and Al, often used as reference elements for the fine inorganic suspended solids fraction (Al-silicates and iron-manganese oxydes/hydroxydes), follow also the turbidity pattern. Chlorophyll *a* (marine origin) is inversely correlated with turbidity and the inorganic suspended sediment fraction. This agrees with the land-based origin of the inorganic compounds.

March 1983 cruise: the isoconcentration patterns obtained during this cruise also correspond closely to that of the turbidity. In the case of Cd, this pattern reduces to a zone of high concentrations (40-60 $ng.l^{-1}$) close to the coast and a zone of low concentrations (10-20 $ng.l^{-1}$) offshore.

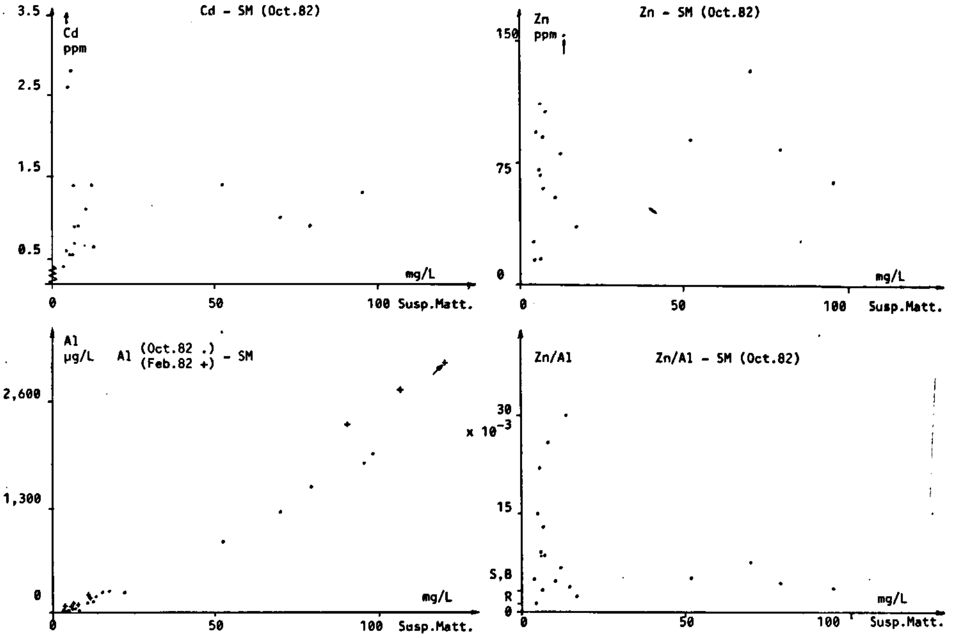

Figure 7
Elemental contents of Cd and Zn (ppm) versus suspended matter concentration. Concentration of particulate Al ($\mu g.l^{-1}$) versus suspended matter concentration. Zn/Al ratio versus suspended matter concentration, with S = Scheldt value; B = bottom value; R = reference soil value.

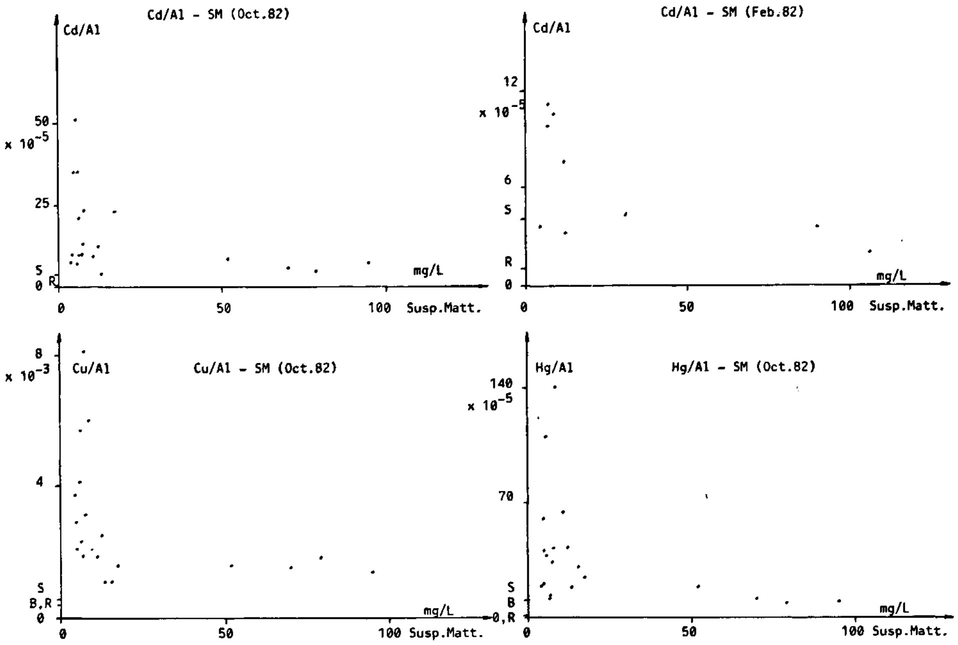

Figure 8
Elemental/Al ratios for Cd, Cu, and Hg versus *suspended matter concentration, with S = Scheldt value; B = bottom value; R = reference soil value.*

In Figure 4 particulate Cd and Cu concentrations are also plotted versus salinity. As for the dissolved metals, a zone of high concentrations at low salinity and vice versa is observed. No quantitative treatment is possible due to the strong scattering of the concentration values.

Elemental partition

High Al and Fe contents of suspended matter expressed in $mg.kg^{-1}$ are associated with high suspended matter concentrations (Fig. 4), but particulate trace metals behave differently: for example Cd and Zn contents at high suspended matter concentrations fall in the range of values observed at low suspended matter concentrations (Fig. 7). These results suggest that there exist different suspended matter fractions at different suspended matter concentrations. These fractions can have different settling properties and different contents of metals and organic matter. Al is often used as the reference element for small sized particles (Duinker, 1983). It may be considered as almost entirely associated with Al-silicates, mainly clay minerals.

The Al concentration ($\mu g.l^{-1}$) is closely related to the total suspended matter concentration (Fig. 7) with a slightly higher slope at higher suspended matter concentrations (>20 $mg.l^{-1}$). At low suspended matter concentrations Al-silicates may thus be diluted by other small-sized components, containing no Al; e.g. detrital organic matter. At high suspended matter concentrations, bottom-derived or terrigenic supplied material, showing a fairly constant Al content, dominates. To correct the content of an element X, altered by mixing of fine grained material, with higher contents of X, with coarse material such as quartz, containing almost no X, use is made of X/Al ratios. These ratios are not altered in such a case. Indeed, we observed almost constant X/Al ratios at higher suspended matter concentrations, lead and iron showing the largest variability (Fig. 7-9). The X/Al ratios above 20 $mg.l^{-1}$ of suspended matter differ little from the mean X/Al ratio of estuarine suspended matter, of coastal bottom sediments and of soil reference value (Bowen, 1977) for Zn, Cd, Cu, and Hg (Fig. 7 and 8). Both the Scheldt estuary and resuspended bottom sediments may be the source of these particulate metals. The high Mn/Al ratio at high suspended matter concentration reflects the average Mn/Al ratio at the mouth of the Scheldt estuary, and is substantially higher than the average value of bottom sediments and the soil reference value (Bowen, 1977). Pb/Al and Fe/Al ratios at high suspended matter concentrations are much higher than the average ratios at the mouth of the Scheldt estuary, the bottom sediments and the soil reference value (Bowen, 1977). Pb/Al and Fe/Al ratios in February 1982, however, are substantially lower and approximate the average ratios at the mouth of the Scheldt estuary. These results agree with more recent findings: 1) Fe/Al ratios vary seasonally (probably related to biological processes); and 2) a good correlation between particulate Fe and Pb is observed. Fe/Al ratios observed in June 1985 are still lower than those observed in February 1982, with the highest ratios found in the plumes of the Rhine and Scheldt estuaries and in the two dumping zones of TiO_2-waste (the two dumping sites correspond to our sampling station 34 and a point 10 km north of sampling station 55 respectively). Mn/Al, Fe/Al and Pb/Al ratios at high suspended matter concentrations can thus not be explained by a large contribution of bottom sediments, but must result from river inputs. The Scheldt estuarine suspended matter is strongly enriched in Fe and Mn hydrous-oxides due to the transition from reducing (upstream) to oxidizing (downstream) conditions in the estuary. These particles appear not to reach the open sea zone.

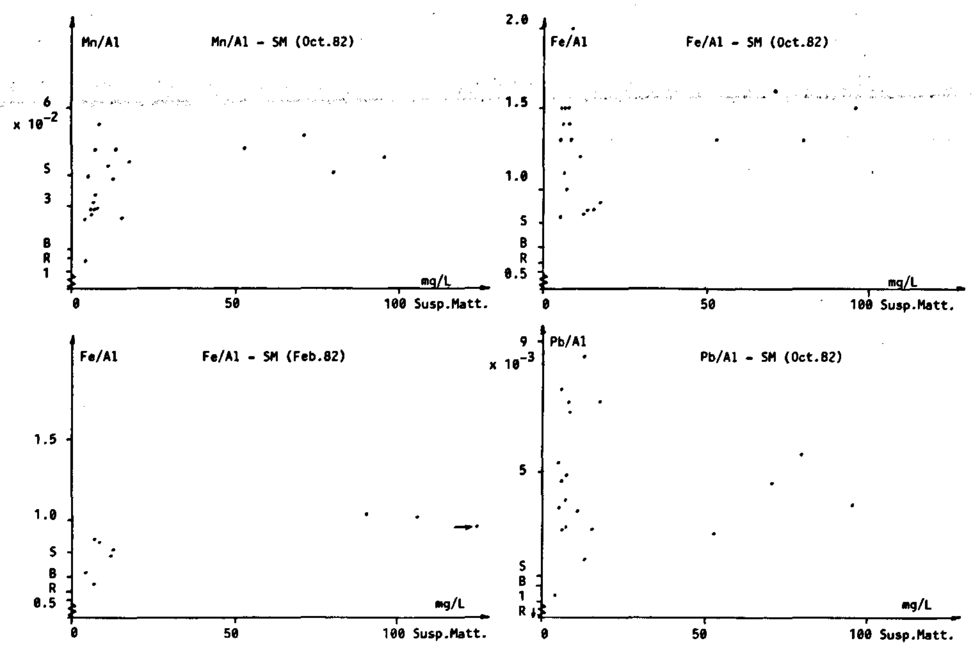

Figure 9

Elemental/Al ratios for Mn, Fe and Pb versus suspended matter concentration, with S = Scheldt value; B = bottom value; R = reference soil value.

At lower suspended matter concentrations, Zn/Al, Cd/Al, Cu/Al and Hg/Al ratios increase, Fe/Al and Mn/Al ratios decrease, while both higher and lower Pb/Al ratios are observed (Fig. 7-9). The increase of X/Al ratios of trace metals at low suspended matter concentrations suggests that the elemental contents in the fine grained fraction are determined primarily by compounds other than Al-silicates. Contents of Cd, for example, co-vary with organic carbon content (Fig. 10) but no correlation with chl *a*, an index of living phytoplankton, is observed (Fig. 10). Most probably detrital particulate organic carbon associated or not with other fine grained mineral compounds is the main carrier of Zn, Cd, Cu and Hg in suspended matter.

Fe/Al and Mn/Al ratios decrease with decreasing concentrations of suspended matter. This is due rather to the very high ratios in the coastal-estuarine suspended matter (high concentrations of suspended matter), than to low ratios in the open sea zone. In addition, Fe seems to be anti-correlated with POC (Fig. 10) in the low suspended matter concentration range. The behaviour of Pb is different from the other metals as a result of its association with iron. In the coastal-estuarine suspended matter, Pb/Al ratios in October 1982 were higher than the average ratios of bottom sediments, of estuarine suspended matter and of the soil reference value (Bowen, 1977).

Particulate to dissolved metal ratios

Dissolved copper, cadmium and zinc proved to account for the major portion of the total in offshore samples (K_D is 0.1 to 0.2 for Cu and Cd, 0.1 to 0.5 for Zn), but in the coastal-estuarine watermass dissolved and particulate fractions are of the same magnitude (K_D between 1 and 2).

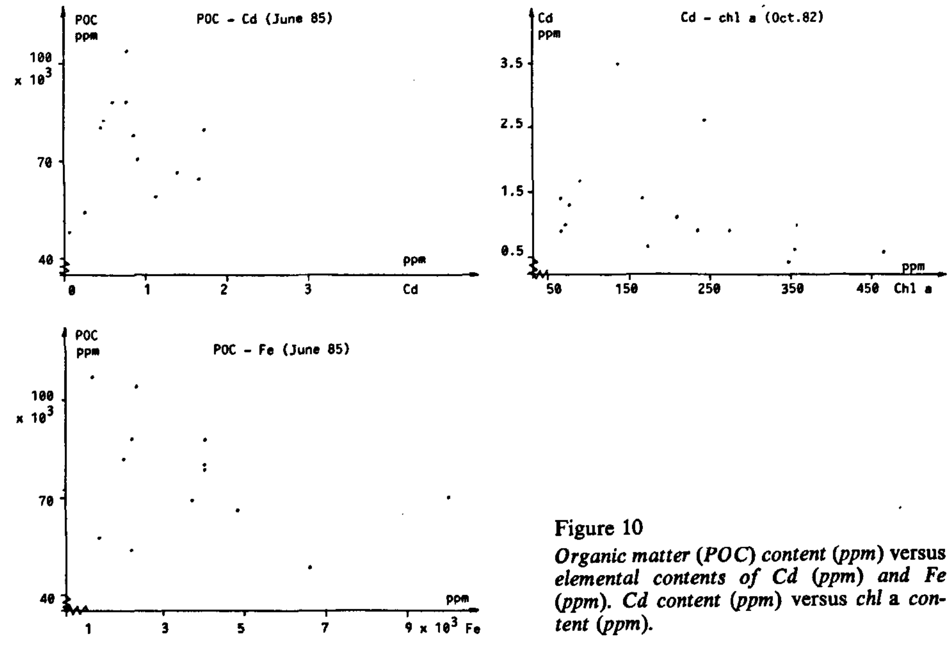

Figure 10

Organic matter (POC) content (ppm) versus elemental contents of Cd (ppm) and Fe (ppm). Cd content (ppm) versus chl a content (ppm).

Lead and mercury are much more strongly associated with particulate matter and show a K_D of about 1 offshore, of ca. 40 (Pb) and 8.7 (Hg) in the coastal-estuarine watermass. Adsorption rate studies demonstrated the great affinity of mercury for suspended matter (*e.g.* Frenet-Robin, Ottmann, 1978; Baeyens *et al.*, 1982).

The ratios (l.g^{-1}) of the concentrations in suspended solids (µg.g.$^{-1}$) to the concentrations in solution (µg.l^{-1}) of Cu, Cd and Zn are respectively ca. 36, 31 and 67 offshore and ca. 22, 12 and 30 in the coastal-estuarine watermass. They are substantially higher for Pb and Hg, respectively ca. 183 and 260 offshore and ca. 382 and 122 in the coastal-estuarine watermass. Pb is thus the only metal showing a decrease of concentration in suspended solids relative to the dissolved form with increasing salinity. The fact is that the iron and manganese hydrous-oxides with which a large fraction of Pb is probably associated do not reach the open sea zone.

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