

STABLE POLLUTANTS IN THE SCHELDT-ESTUARY.

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ABSTRACT:

Samples were taken at several dumping and dredging sites, situated in the Scheldt-estuary, between Antwerp (80 km from the mouth) and Vlissingen (at the mouth).

Besides analysis of different metals (Al, Pb, Cd, Cr) other parameters such as organic carbon content (POC), Ash-weight (AW), granulometric distribution, metal content in the fraction smaller than 63μ , were determined.

METHODOLOGY:*Sampling procedure:*

All samples were taken on board of the Belgica, ship for oceanological research.

i) sampling procedures for metals in solution and particulate matter, based on a continuously pumping system are discussed in detail in Baeyens et al. (1987).

ii) sampling of bottom sediment occurred with a Spade-Usnell box-corer (0.5×0.5 m).

A polyethylene bottle was completely filled with a subsample taken out of the middle of the box-corer and stored in the refrigerator until analyses. In the laboratory part of the sample is lyophilized and homogenized, whereafter analyse is performed.

Another part of the sample together with overlying water was immediately placed in an ultrasonic device to separate the fraction smaller than 63μ .

*Analytical procedures:**i) Metals*

Analyse for metals in solution is performed by use of a differential pulse anodic stripping voltammetric technique (DPASV), as described in Gillain et al. (1979)

To perform analysis of the metals in the bottom sediment, it is necessary to carry out a so called "acid-digestion":

approximately 0.25g of sediment is brought in a PTFE container, together with 2ml of HF and 8 ml of aqua regia. The closed container is heated overnight at 60°C . The residual solution is evaporated and the residue is resuspended in 4% nitric acid.

Al is determined by use of a Varian 10QAB flame atomic absorption spectrometer.

Pb, Cd and Cr are determined with the use of a Perkin-Elmer AAS (3030) with oven and Zeeman correction.

.A slightly modified technique is applied for the digestion of the suspended material: instead of a HF/aqua regia solution a HF/HNO₃ solution is used.

Measurements are carried out as described above.

ii) Organic Carbon (POC) and ash-weight (AW) analysis:

AW is determined by heating the sample, which is previously dried at 105°C, for 4 h. at 1100°C. The loss in weight is set equal to the AW.

Organic carbon content is determined by use of a Ströhlein Coulomat. Principle of detection is a coulometric titration of the, in carbondioxide converted, carbon.

iii) The granulometric distribution is measured with the aid of the classic sedimentation technique, which is based on Stokes law:

$$v = \frac{2gr^2(d_2 - d_1)}{9\eta}$$

where: v =settling velocity

g = gravity constant

d_2, d_1 = particle- and liquid density

r = particle radius

η = liquid viscosity

From the obtained granulometric distribution, the fraction of material smaller than 63 μ is easily obtained.

RESULTS AND DISCUSSION:

First of all we like to point out the fact that the values, shown in the following tables and figures, are mean values calculated out of the results

of several campaigns. The use of these mean values diminishes the variability in the results which is caused by 2 major reasons:

1. the hydrodynamic- and morphological characteristics of the Scheldt-estuary cause a varying salinity profile as well on a short term (tidal influence) as on a long term basis (small and varying river flow rate).

2. The highly industrialized zone, situated between Antwerp and the Dutch border, is a source of irregular metal input. This input influences the metal versus salinity profile. Even in the case the metal behaviour would be conservative as that of the salinity, lateral input would disturb it.

a) *distribution constants:*

Using the obtained values for metals in solution and particulates, one can calculate distribution constants (K_d -values).

We distinguish two possibilities:

1. the ratio between the particulate metal concentration in the water column (moles/liter) and the dissolved metal concentration (moles/liter). The obtained K_d is nondimensional.

2. the ratio between the particulate metal concentration in suspension (moles/gram) and the dissolved metal concentration (moles/liter). So the K_d is expressed in liter/gram.

In case of the Scheldt estuary the second approach is the most interesting one because it eliminates the influence of the turbidity variations on the K_d -value.

From these K_d -values we can deduce the behaviour of the metal during transport through the estuary: a decreasing K_d indicates that the metal becomes mobilised, an increasing K_d that it is adsorbed.

In this approach both adsorption and mobilisation are used in a general way which includes for instance: sedimentation of enriched particles (decreasing K_d) or mixing with "metal poor" particles (increasing K_d).

Fig. 1 shows the calculated K_d -values for both cadmium and lead as a function of salinity.

In the case of cadmium a sharp decrease in the K_d value towards the river mouth can be distinguished. This phenomenon is due to two reasons: at one hand a slight mobilisation towards the dissolved phase (which is seen in the longitudinal profile of the dissolved cadmium) and at the other hand the mixing of the existing particle population with a new one, originating from the sea, which is far less contaminated.

The K_d values of lead, compared to those of cadmium, remain almost constant. There is, however, a minor decrease towards the mouth with a local minimum in the so called high-turbidity zone of the estuary, located between Antwerp and the Dutch border. Possibly this zone offers certain conditions favouring remobilisation of lead which do not occur in other parts of the estuary.

b) longitudinal profiles:

Fig. 2 shows the longitudinal profiles of particular cadmium and lead for both the bottom sediments and the suspended matter.

Both elements are behaving in the same way, with a local maximum which is again situated in the high turbidity zone.

Another perception is the fact that although the metal concentration is locally far higher in the suspended matter, than in the bottom sediments, the concentration in the sediments of the high turbidity-zone exceeds the one in the suspended matter at the rivermouth. As a consequence dumping dredged material from this zone in the Western Scheldt could have implications for the water quality. This may be due to

mobilisation (according to the solid-liquid distribution constant K_d) of particulate metals in the dredged material of which the metal load is higher than the metal load in the suspended matter at the mouth.

A problem in comparing results obtained from different sampling points is caused by the heterogeneity of the material. sedimentary characteristics vary between very sandy, nearly 100% of coarse material, and real fluid mud, almost entirely fine material. Due to the fact that trace metals tend to associate with the finer fraction in the sediment, this heterogeneity in composition strongly influences the obtained analysis results. To avoid this kind of problems it is necessary to develop an appropriate normalisation method.

For this purpose four parameters, representative for the finer fraction, were determined (AW, POC, Al, Fraction $\leq 63\mu$). Cross correlations between these parameters showed always a positive relation, however with varying correlation coefficients (Fig.3). This indicates that in the case of a rough estimation all studied parameters are useful but in the case of a more profound research one should be aware that the correlation is not always very good.

Regarding to the trace metals the POC-parameter shows a very good positive correlation for both metals.

c) Metal associations with the finer fraction:

Comparison of results obtained both from bulk analysis and analyses of the smaller fraction reveals a very homogeneous metal content, with few exceptions for all studied metals, in the fraction below 63μ . (table 1)

TABLE 1

Metal concentrations in the material $\leq 63\mu$.

Wet sieved, 2/88					
Plaats	Cr, mg/g	Al, mg/g	Cd, μ g/g	Pb, μ g/g	Hg, ng/g
A	0.156	43.166	9.383	163.864	1.62
C	0.150	62.224	10.079	182.296	1.32
D	0.156	49.420	8.615	135.175	1.36
G	0.223	47.337	3.390	151.332	/

In the context of normalisation it is very interesting to look how accurate one can calculate the metal content in a sediment sample, existing for 100% of finer material, starting from grain size distribution and metal content in the bulk sediment.

We have carried out this kind of calculation for 3 sampling points and compared the obtained results with data derived from analysis on the finer material of the appropriate stations. (table 2)

TABLE 2

Metal concentrations in the in the material smaller than 63 μ . Comparisson between measured values and those values calculated by use of the grainsize distribution.

% smaller than Bulk 63 μ	Bulk			100% smaller than 63 μ					
	Cd.	Pb	Hg	Calculated			Measured		
	Cd.	Pb	Hg	Cd	Pb	Hg	Cd	Pb	Hg
77.5	6.92	113	1.05	8.93	146	1.35	8.62	135	1.36
24.8	6.26	95.6	0.68	25	385	2.74	10.1	182	1.32
1.2	0.06	8.84	0.015	5	737	1.25	3.4	151	/

The calculations show clearly that the used extrapolations are only useful in case of muddy sediments (50% > 63 μ).

In case of more heterogeneous samples, calculated results differ to much (up to 403 %for lead) from measurements to be acceptable.

CONCLUSIONS:

One of the most important regio's in the Scheldt-estuary, is situated between Antwerp and the Dutch border. This regio is called the high turbidity zone due to the high turbidity values which are measured .

This is due to several phenomena:

- high tidal velocities and finer bottom material cause an increased erosion.
- flocculation does occur due to the increasing salinity
- High waste input from industrial plants and the city of Antwerp.
- Suspended matter which is transported downstream, arrives in a low-turbidity regio where it can settle down and is moved upstream again by the bottom current.
- Particle residence time is increased due to the converging flows.

Metal content is here rather high, compared to other parts of the estuary, in al compartments of the aquatic system. This is mainly due to to the high concentration of suspended matter and the influence of the industrial plants situated near Antwerp.

We want to stress the fact that particulate metal concentrations are far higher than dissolved concentrations, does not necessarily implicate that the particulate phase is the most important for the metal transport through the estuary. Residence times of dissolved compounds are very small compared to those of the particulate matter.

To compare results obtained at different stations it is essential to obtain an uniform normalisation method. Studying the relations between the various parameters show positive correlations between them in all cases. The relations between these parameters and the metal content are again positive, however with strongly varying correlation coefficients. The best correlation is obtained between the metal content and the AW(1100°C). But on the other hand measurements of the finer fraction eliminate most of the occurring fluctuations and indicate a more or less constant metal content throughout the estuary. The problem here is a methodological one. Enough material smaller than 63 μ should be separated from the bulk material.

Finally we want to point out the risk of recalculating the metal contents in the sediment fraction smaller than 63 μ , obtained from analyses of so called "bulk-material" to results obtained in the case of direct analysis of the material smaller than 63 μ . The recalculating technique yields only reliable results in case of muddy sediments.

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Fig. 1a: Kd-cadmium in function of salinity

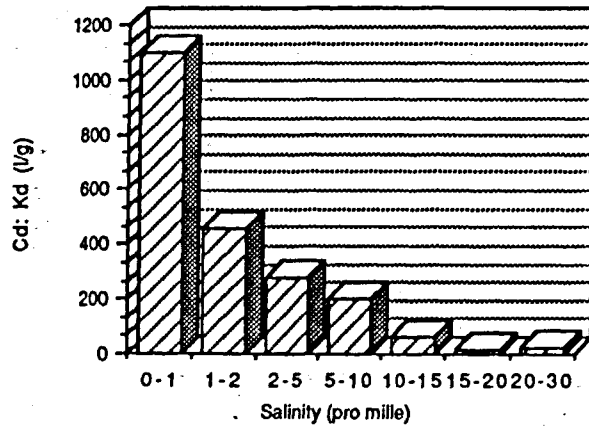


Fig. 1b: Kd-lead in function of salinity.

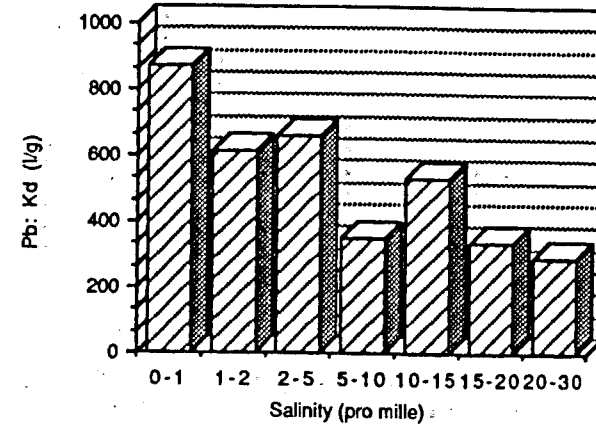


Fig. 2a: longitudinal particular concentration profile of lead in the sediment and in suspension

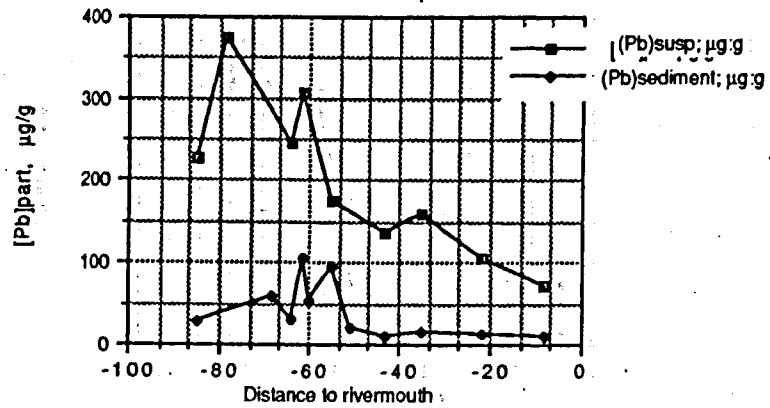


Fig. 2b: longitudinal particular concentration profile of cadmium in the sediment and in suspension

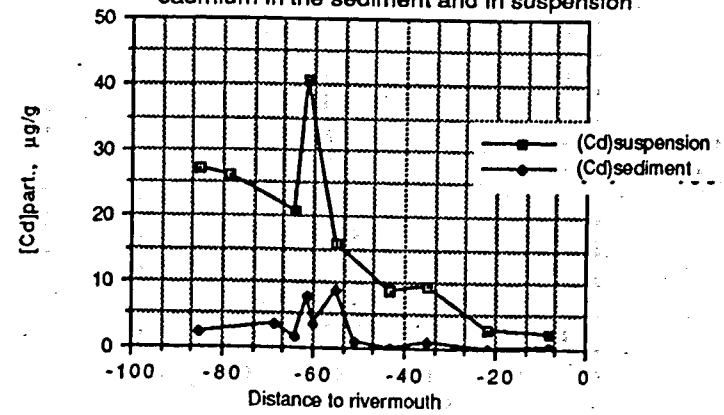


Fig. 3a: aluminium concentration in the sediment in function of the Ash-weight

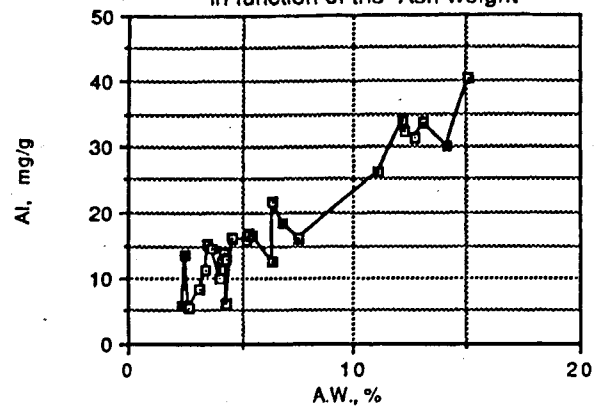


Fig. 3b: aluminium concentration in the sediment in function of organic carbon content

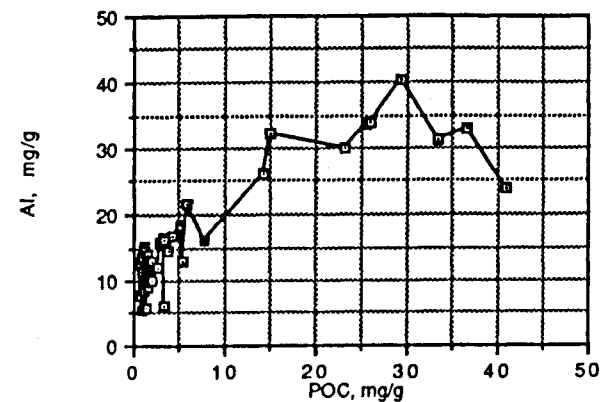


Fig. 3c: organic carbon in function fraction smaller than 63µ.

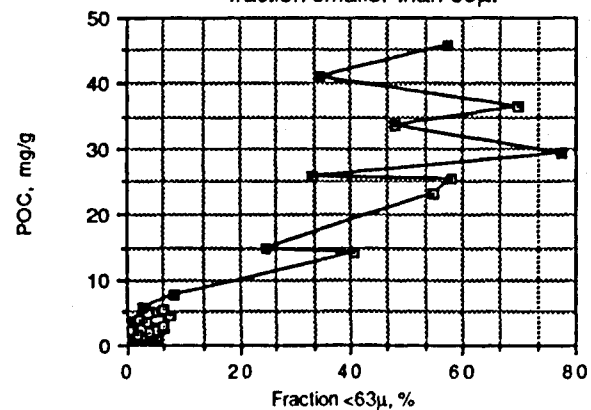
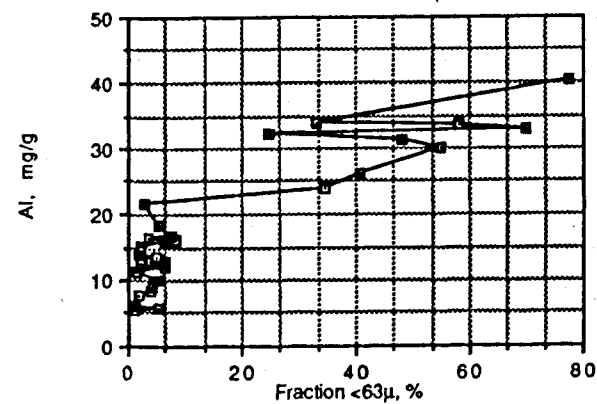


Fig. 3d: aluminium concentration in the sediment in function of fraction smaller than 63µ.



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