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Part 4

THE RIVER SCHELDT AS A TRANSPORT ROUTE FOR HEAVY METALS IN THE SEA

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ABSTRACT : Cd, Cu, Fe, Hg, Mn, Pb and Zn have been analyzed in sediment cores, suspended matter and water samples from the Scheldt estuary with high performance analytical techniques.

During early stages of mixing, most dissolved heavy metals concentrations show a maximum. Owing to real time analyses of dissolved mercury in function of a number of physicochemical parameters, we found evidence that, at least for Hg, the concentration maximum was correlated with the upstream decrease of the pH (from 7.83 on) to its estuarine minimum (7.50). Dissolution of upstream transported iron and manganese oxides and hydroxides rich in trace metals, due to a pH decrease, can be a possible explanation of the heavy metals increase.

Particulate trace metals concentrations decrease strongly in the central estuarine area, due to mixing with large amounts of resuspended bottom

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deposits. The particles which escape the area of turbidity maximum are in the downstream estuary diluted with sea-borne suspended matter in a more or less conservative manner.

The overall longitudinal decrease of heavy metals concentrations corrected for grain size differences in a seaward direction, in the top layer as well as deeper sediment layers, is tightly related to the decrease in heavy metals of the suspended material. At the bottom, the finer sediments are abundantly mixed with a coarse, recent sand fraction. An important fraction of this recent sand population seems to consist of reworked subbottom deposits.

INTRODUCTION

To understand the transport of heavy metals in an estuary, it is essential to understand the physical behaviour of the estuary, and the way in which the individual parts of the system react with each other and how each affects, or is affected by, the others.

Estuaries are governed by tidal action at the sea face and by river flow. In the mixing zone of salt and fresh water, strong longitudinal gradients in physico-chemical parameters such as salinity, pH, temperature, ... are created. They have an influence on internal processes such as precipitation of solutes (Spencer and Brewer, 1971; Gibbs, 1973; Duinker et al., 1979), coprecipitation of solutes (Sridharan and Lee, 1972; Gibbs, 1973; Inoue and Munemori, 1979), flocculation and net sedimentation of fine suspended matter, associated metals included (Wartel, 1971; Sholkovitz, 1976; Baeyens et al., 1981), removal of trace elements from the dissolved phase by adsorption (Reimers and Krenkel, 1974; Gadde and Laitinen, 1974; Frenet-Robin and Ottmann, 1978; Baeyens et al., 1982), desorption and solubilization of particulate metals (Kharkar et al., 1968; De Groot et al., 1971; De Groot, 1973; Martin and Salvadori, 1974; Hanor and Chan, 1977; Etcheber, 1979), suspension of sediments and subsequent release of their metals (Windom, 1975; Lindberg and Harriss, 1977; Gambrell et al., 1980), and transformation and migration of trace metals species in interfaces of seawater and sediments (Spangler et al., 1973; Olsen and Cooper, 1974; Kudo et al., 1975; Bartlett et al., 1977; Lu and Chen, 1977; Bothner et al., 1980).

These processes as well as external effects mainly anthropogenic activities such as discharging of pollutants or cooling water, dredging of the channels and in some cases subsequent disposal of the spoil on the shoals or on the river bank, may modify the conservative mixing of river-borne and sea-borne solutes and

particulates (Muller and Förstner, 1975; Duinker and Nolting, 1978; Salomons and Eysink, 1979; Etcheber, 1979).

The overall effect of the internal and external processes is an often unexpected and complex distribution pattern, which differs from element to element and from estuary to estuary.

In this study heavy metals were analyzed in solution, suspended matter and sediment cores sampled in the Scheldt (Scheldt) estuary. Concomitantly related variables such as physico-chemical parameters, grain-size distribution, organic matter content were measured in order (1) to understand better the role played by external and internal processes, (2) to distinguish between the effects of physical mixing and physico-chemical processes and (3) to obtain an estimate of the heavy metals input to the North Sea via the river Scheldt.

Sampling, Methods and Materials

At seven estuarine stations (2, 7, 12, 15, 22, 25, 29 see Figure 1) and two stations a few kilometer off the mouth, samples have been taken at slack water of the ebb in 1981 between March 16 and 20. During one hour water samples were collected with a peristaltic pump and conducted to a closed pressure filtration system (G. Gillain et al., 1982), a teflon coated centrifuge and physico-chemical measuring devices (turbidity, temperature, salinity).

Sediment cores were sampled by divers of the Belgian Navy in 6 cm plexiglass tubes. The coring locations were selected by examining in situ recorded high resolution subbottom profiles made with a system (Wartel, 1980), capable of resolving sedimentary layers about 30 cm thick.

The cores were segmented according to textural variations with depth shown by X-radiographs, using an X-ray tube (W-anticathode and Be-window) at an excitation potential of 90 KeV; see for example Figure 7. Analyses of heavy metals in solution, suspended matter and bottom sediments were carried out as described by Gillain et al. (1982). On several liquid and solid samples, cross determinations of heavy metals with two independent analytical methods (DPASV and AAS) were performed to ensure that analytical results were exact. Particulate organic matter was determined with a Perkin-Elmer C, H, N-analyzer, Model 240. The amount of carbonate was determined using a Scheibler-Dietrich calcimeter. On a few samples inorganic and organic particulate carbon were also measured by coulometry and particulate nitrogen by Kjeldahlisation and colorimetry. Grain size analyses were performed on dry samples. Salts, organic compounds and carbonates were previously eliminated with a H_2O_2 (1:2) solution and HCL (1:10).

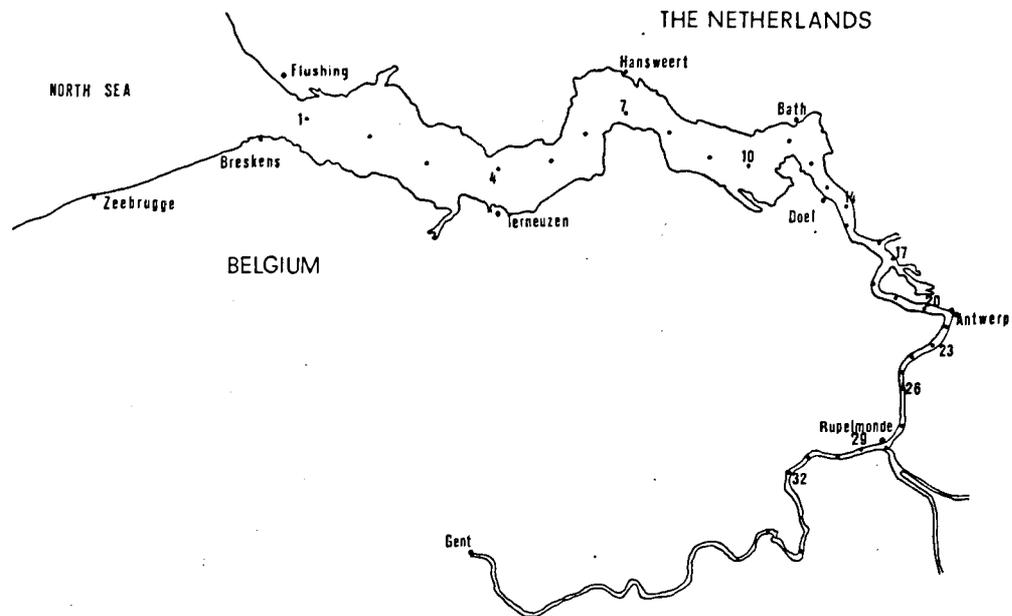


Fig.1 : Sampling stations in the Scheldt estuary.

The sample was suspended by adding 500 ml of distilled water and 50 ml of a solution of 8.93 g Na-oxalate and 1.33 g Na-carbonate per liter solution. The suspended sample was then poured on a 5 ϕ sieve. The finer particles (< 5 ϕ) were analyzed using a sedimentation procedure and the coarser particles by dry sieving using A.S.T.M. sieves with a 1/4 ϕ interval.

Hydrographical and physicochemical characteristics

The Scheldt estuary extends from Ghent (Gent) to Flushing (Vlissingen). The average tidal differences are 3.8 m at Flushing, 5 m at Antwerp (Antwerpen) and 2 m at Ghent where the tide is stopped by a sluice. The average total fresh water supply at Schelle (89.5 km from the mouth) is about 80 m³.s⁻¹ (Valcke, 1966). Daily values vary from a few m³.s⁻¹ to 600 m³.s⁻¹. These values are small compared to the flood discharge of 2.590 m³.s⁻¹ at the same place. As a result large tidal velocities (up to 1.4m.s⁻¹) occur in the Scheldt estuary but the residual transport is very small. The residual current is of the order of one cm.s⁻¹ in the upstream area, and decreases to 0.1 cm.s⁻¹ at the mouth.

The salinity distribution in the estuary mainly depends on the fresh water supply and can easily be calculated in function of the latter variable with a one-dimensional stationary model (Figure 2). Vertical stratification is limited (it never exceeds 0.25 gCl⁻¹. ℓ^{-1} .m⁻¹) and only occurs over short periods of the tide.

Downstream from km 55 to the mouth, the redox potential has the normal value of an aerated water. Upstream, an anaerobic zone exists, except under high fresh water supply conditions.

In the central area Antwerp to Doel the finest bottom sediments, fine sands to clayey silts, occur (Wartel, 1977). Most of these sediments are transported either as a uniform or as a graded suspension. Flocculation and local hydrodynamic conditions govern the settling down of this material in the central area (Baeyens et al., 1982). A large part of these sediments are resuspended after deposition when the bottom shear stress exceeds the critical erosion shear stress and contribute to the observed high suspended sediment concentration indicating the turbidity maximum of the estuary. From this central area towards both the up- and downstream area, a marked increase in grain size of bottom sediments (gravels and medium to coarse sands) occurs. About 10 to 30 % of the sediment here is transported by rolling and the rest as a graded suspension, and to a lesser extent as a uniform suspension.

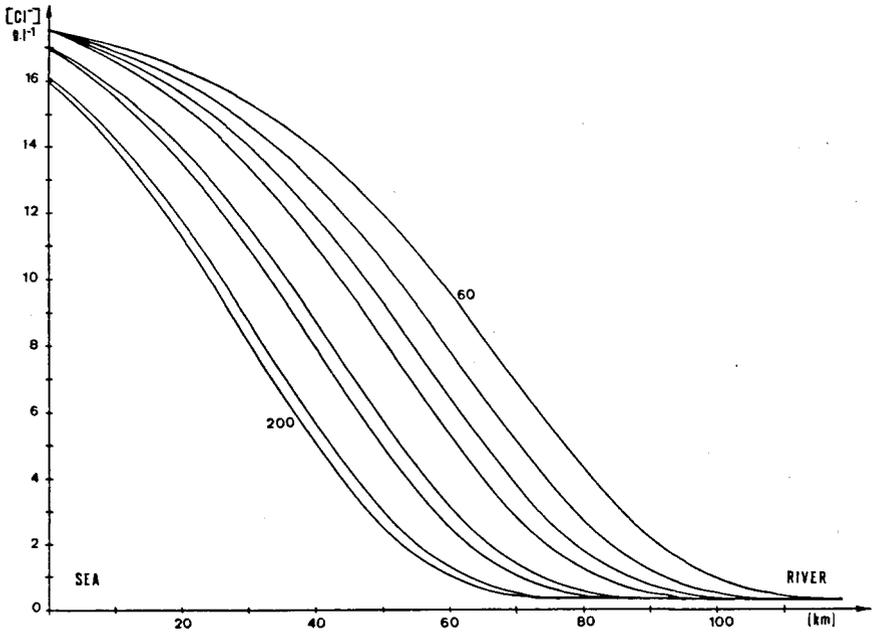


Fig.2 : Longitudinal chlorinity profiles in the Scheldt estuary as a function of the river flow (60 to 200 $m^3.s^{-1}$).

Results and Discussion

None of the heavy metals considered in this study appear to behave in a conservative way. The dissolved concentration profiles of mercury, copper, zinc and cadmium observed in March 1981 are very similar: a rather constant concentration level in the fresh water area, an almost symmetrically sharp increase and decrease during early stages of mixing and again a rather constant concentration towards the mouth (Figure 3). The lead, manganese and iron profiles differ however (Figure 4): lead and manganese show an irregular but definite overall decrease, suggesting removal processes are predominant in the estuary, while iron shows a sudden increase at the mouth. The plots of these heavy metals against salinity all show deviations from the ideal dilution line. Provided the fresh and salt water end member concentrations observed, reflect correct boundary conditions, mercury, zinc, copper and cadmium are produced and removed from solution in a rather narrow (1-5 ‰) salinity range, lead and manganese are removed in a broader salinity range, except, a small production during early stages of mixing, and iron is besides a small production during early stages of mixing too, strongly produced at the mouth (24 ‰ S) taking into account that dissolved iron concentrations in our coastal zone never exceed 100 ppb. Etcheber (1979) also observed maxima for Cu, Zn and Pb in the Gironde estuary especially in periods of low fresh water supply and in the middle area of the estuary. In the Rhine estuary, dissolved metal-salinity plots show that Cu, Zn, Fe and Mn are removed from solution during estuarine mixing (Duinker and Nolting, 1978).

Unless a very important and simultaneous discharge of Hg, Cu, Zn and Cd took place at station 12, four mechanisms may be responsible for their sudden increase in concentration: (1) desorption from suspended sediments, (2) dissolution of iron and manganese oxides and hydroxides as well as their associated metals, (3) diffusion and migration of interstitially dissolved metals to the overlying water (4) degradation of organic matter and mobilisation of the associated metals.

In a very recent cruise up and down the estuary, dissolved mercury concentrations (filtered and centrifuged) were measured in real time on board the ship. Samples were taken in function of conductivity, pH, dissolved oxygen and temperature values which were recorded continuously. The most striking correlation observed (twice since we went up and down the estuary), was the upstream increase of dissolved mercury when the pH fell below 7.83, and the subsequent mercury decrease once the pH estuarine minimum (7.50) was passed. Changes of other physicochemical parameters such as (in the upstream direction) a 25 % dissolved oxygen drop, the decrease of the conductivity down to 7.6 mS or the temperature raise, appeared in a first approximation, not to be linked to a substantial change in the dissolved mercury concentration.

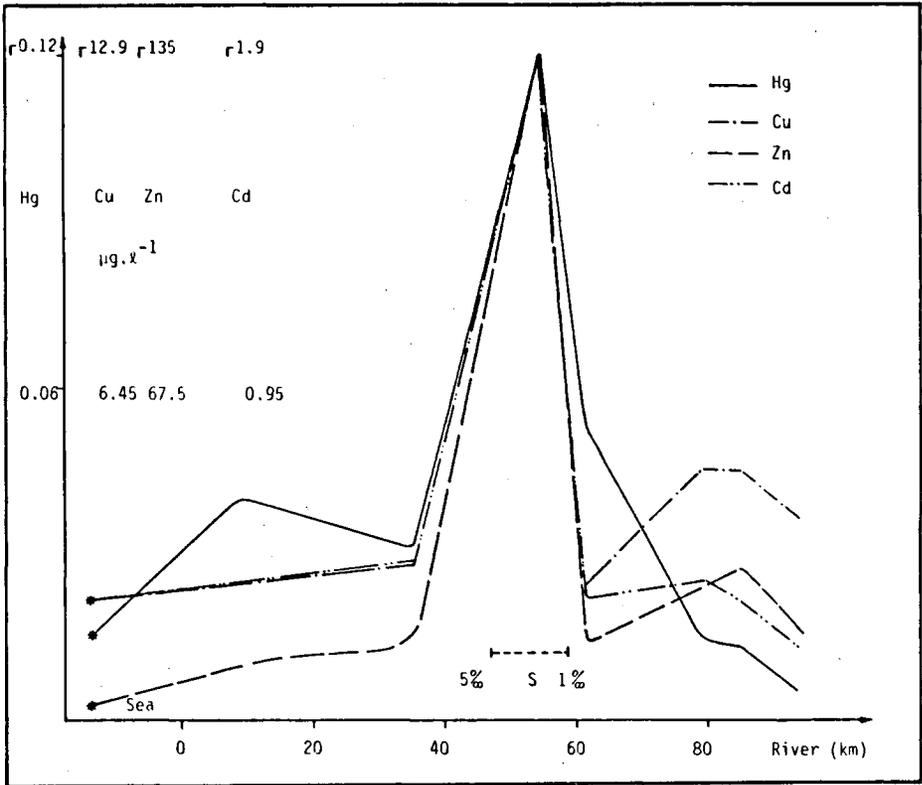


Fig.3 : Longitudinal profiles of dissolved Hg, Cu, Zn and Cd concentrations in the Scheldt estuary.

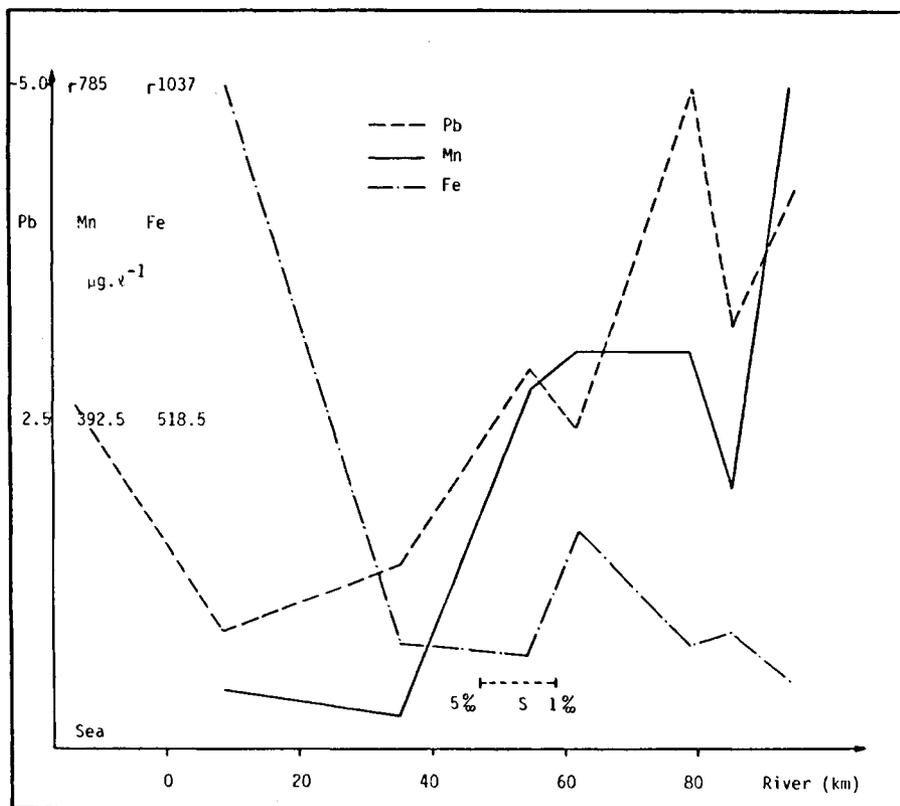


Fig.4 : Longitudinal profiles of dissolved Pb, Mn and Fe concentrations in the Scheldt estuary.

Assuming the observations made during this cruise do not reflect a particular situation -the pH minimum is in any way according to Mook and Koene (1975) a normal phenomenon when the pH of the river water is lower than that of seawater- and assuming adsorption-desorption characteristics of river-borne and sea-borne particulates are similar, desorption from suspended sediments seems not to be a major cause for the dissolved metals increase. Indeed, river-borne particles contain much more heavy metals than sea-borne particles, but when the river pH decreases to the estuarine minimum, no dissolved mercury increase is observed.

Dissolution of upstream transported iron and manganese oxides and hydroxides, due to a pH decrease, can however explain the heavy metals increase. For a better understanding of this phenomenon, it is worthwhile to discuss the general estuarine behaviour of manganese and iron.

In the early stages of mixing, a production of about 130 and 40 $\mu\text{g}\cdot\text{l}^{-1}$ of dissolved Fe and Mn respectively has been observed compared to their ideal dilution curves, but when the pH and dissolved oxygen concentration increases in the downstream area, both metals and also several other trace metals are removed from solution by (co) precipitation. This corresponds to the trace metals decrease once entering the middle part of the estuary and has also been observed by Duinker and Nolting (1978) in the Rhine estuary. These freshly precipitated particles, enriched in most trace metals, progressively settle down in the downstream estuary; part of them are, however, reintroduced into the upper estuarine zone by the upstream current. Arriving in the upstream area, they meet suddenly a much lower pH which favours their dissolution and a concomitant release of the associated metals. Continental derived manganese and iron particles probably are more reluctant to pH changes or contain less heavy metals.

In an area where the bottom shear stress is large, one may expect a contribution from interstitially dissolved compounds to the overlying water. Since a turbidity maximum was observed at station 12, great evidence exists that this condition was fulfilled there (Wartel, 1977; Baeyens et al., 1981). In one core, at point 22, interstitial metal concentration were determined. Zn, Pb and Cu were approximately 10 times, Cd 25 times larger than in the bulk water at the same station. Assuming the same interstitial to bulk water ratios at point 12, one can calculate that only a slight increase of the bulk water concentrations may be expected.

The degradation of organic matter may be accompanied by a release of heavy metals to the solution. But despite that the heterotrophic activity observed in the upper estuary is indeed very high, it drops rapidly when the salinity reaches a value of 2 to 4 $\text{gCl}^{-}\cdot\text{l}^{-1}$ (Billen et al., 1976) and can thus not explain the sudden dissolved metals increase.

An additional remark concerning the very high dissolved iron concentration at the mouth has to be made. This excessive concentration is probably due to regular dumping of TiO_2 -waste, containing large quantities of dissolved iron. Evidence was found by examining the particulate material at the same station; the Fe:Ti ratio corresponded to that in the waste material itself.

Almost all particulate heavy metals concentrations drop abruptly (Figures 5 and 6) between km 60 (station 15) and km 40 (station 7). In this area dissolved trace metals are also produced and removed from the solution. Besides conservative mixing of highly polluted upstream suspension with suspended matter of marine origin which is far less contaminated, two other mechanisms are involved. On the one hand dissolution of upstream transported manganese and iron oxides and hydroxides as explained above, on the other hand in the area of the turbidity maximum, a strong dilution of the suspended material by mixing with locally eroded, less contaminated bottom sediments. Due to flocculation and a decrease of the turbulence at the bottom, a subsequent sedimentation of the suspended material occurs. The remaining particles are in the downstream area in a more or less conservative manner diluted with marine suspension. As mentioned before, manganese and iron oxides and hydroxides will precipitate when the pH and oxygen concentration increase.

The longitudinal profiles of heavy metals, total and organic carbon, percentage of grain size smaller than $16 \mu m$, etc. in the upper, superficial sediments, acting as an interface between the water flow and underlying sediments, are very erratic. Two distinct areas, however, can be distinguished: an upstream area (stations 12 to 25) showing, organic carbon:nitrogen ratios in the range 10.2 to 12.8 and higher trace metals concentrations corrected for grain size differences (similar results were obtained if not the grain size but organic carbon or total carbon was used as the correcting parameter) and a downstream area (stations 2 to 7) showing organic carbon:nitrogen ratios in the range 6.2 to 7.4 and lower trace metals concentrations corrected for grain size or carbon (organic or total) differences.

The overall longitudinal decrease in a seaward direction of heavy metals concentrations corrected for grain size differences, in the sediments, is tightly related to the decrease of heavy metals in the suspended material. The metal-fine sediments ($<16 \mu m$) correlation, found in the suspended matter is, however, modified in the sediments due to the fact that (1) an ultrafine, metal rich fraction will probably not settle down, and (2) in the sediments mobilisation and precipitation processes can occur.

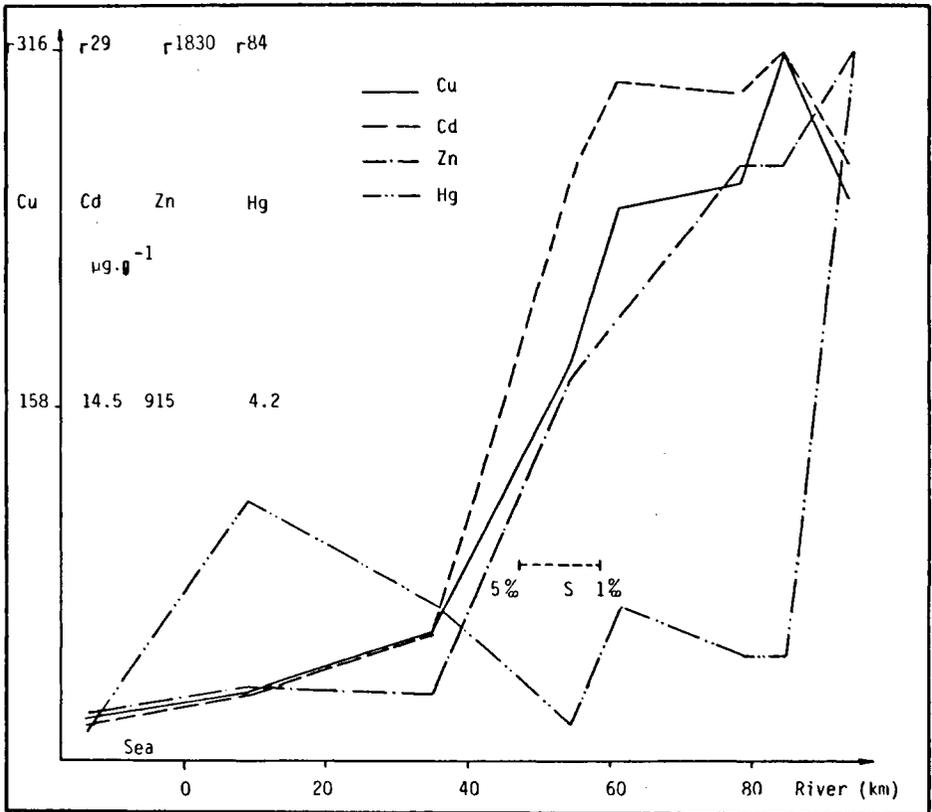


Fig.5 : Longitudinal profiles of particulate Cu, Cd, Zn and Hg concentrations in the Scheldt estuary.

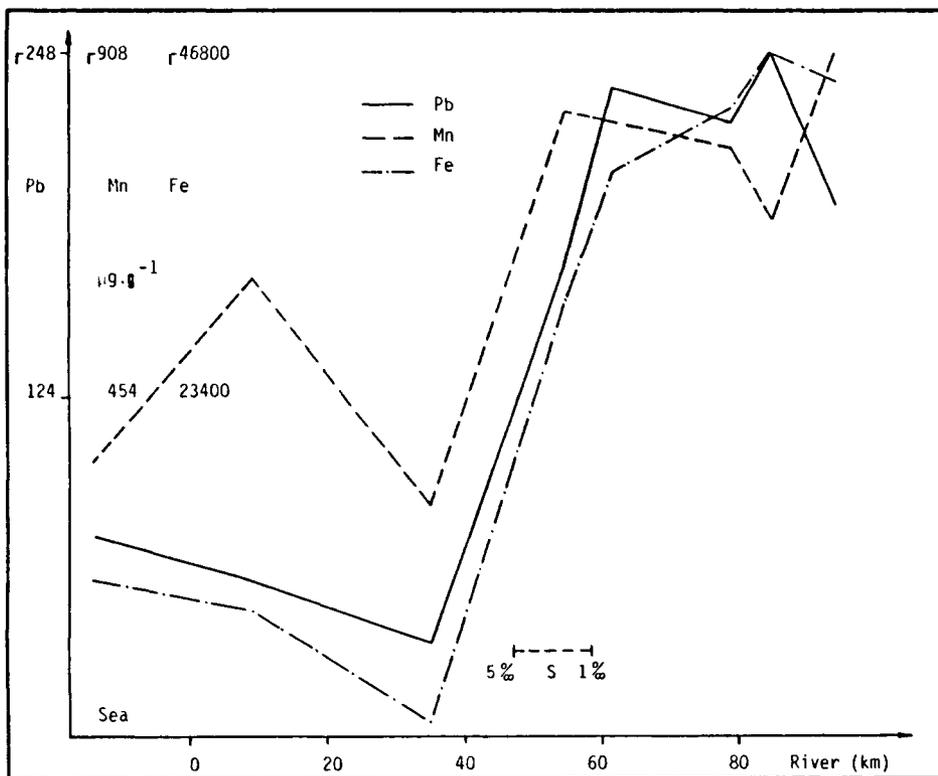


Fig.6 : Longitudinal profiles of particulate Pb, Mn and Fe concentrations in the Scheldt estuary.

During a tidal cycle, an important fraction of the suspended particles obeys an almost cyclic movement; sedimentation when the tidal energy in the watercolumn falls beneath a critical sedimentation threshold, resuspension when it exceeds a second critical erosion value. To increase the probability to find on top of the cores freshly deposited suspended matter, coring was carried out at slack low water. However, only the top layer of cores 12 (Ballastplaat) and to a lesser extent 15 (Doel) showed concentrations of the same order as the suspended particles. This is not surprising, since these stations were in the area of turbidity maximum, where the magnitude of sedimentation and resuspension phenomena is strongly enhanced due to local hydrodynamic conditions and flocculation processes.

The cyclic sedimentation-erosion pattern is, however, definitively disturbed when the freshly sedimentated, fine particles are mixed with or covered by a much coarser sand fraction. According to Wartel et al., (1979), it can be assumed that at least an important part of the recent sand population, abundantly present in all our sediment cores, consists of reworked subbottom deposits. Horizontal transport of the sand fraction as far as it could be deduced from the foraminifera analyses, is limited and has a prevailing downstream component between the river Rupel and Kallo and a downstream as well as upstream component in the Western Scheldt (downstream area). The mixing of the finer sediments ($<16 \mu\text{m}$), rich in metals, with a much less contaminated sand fraction diminishes the absolute metal content of the sediments. The vertical texture of the sediment cores varied from almost homogeneous to very heterogeneous. Therefore two coring sites - Hansweert (station 7) and Ballastplaat (station 12) - are described in more detail.

Subbottom profilings:

Hansweert. Down to a depth of 2 to 5 m below the actual bottom surface and concordant with it, several (maximum 5) reflecting horizons exist. They show regular layering consisting of beds 0.4 to 1 m thick and composed of subrecent Scheldt sediments.

Ballastplaat. Near the sampling station an old gully, crossing the actual valley and filled with layered sediments exists. The deepest point of it occurs at approximately 5 m below the actual surface.

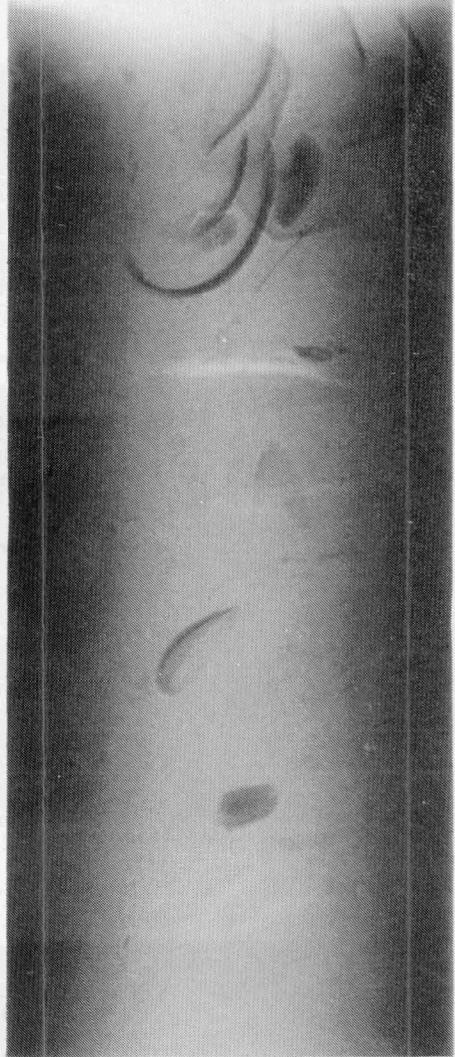
X-ray photography:

Hansweert. The X-ray photographs of both cores (Figure 7) show over their whole length a rather homogeneous structure. In core 7A a gravel and shells, in core 7B a few gravels and shells occur. Apart from that, no substantial differences between both cores were observed.

Ballastplaat. Both cores 12A and 12B are structurally identical (Figure 8). Irregular beds, 1 to 4 cm thick and composed of alternating silt and sand laminae 1 to 2 cm thick,

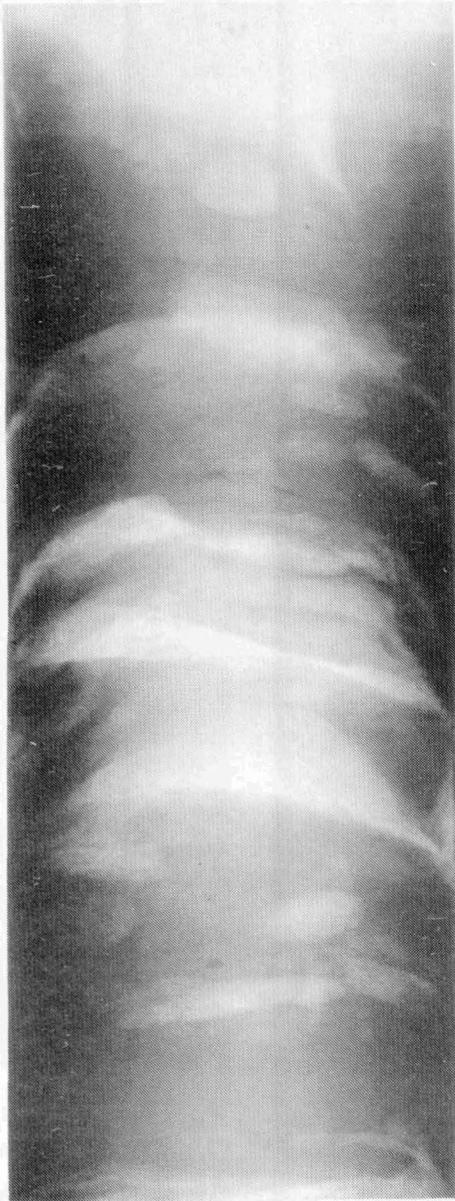


7A

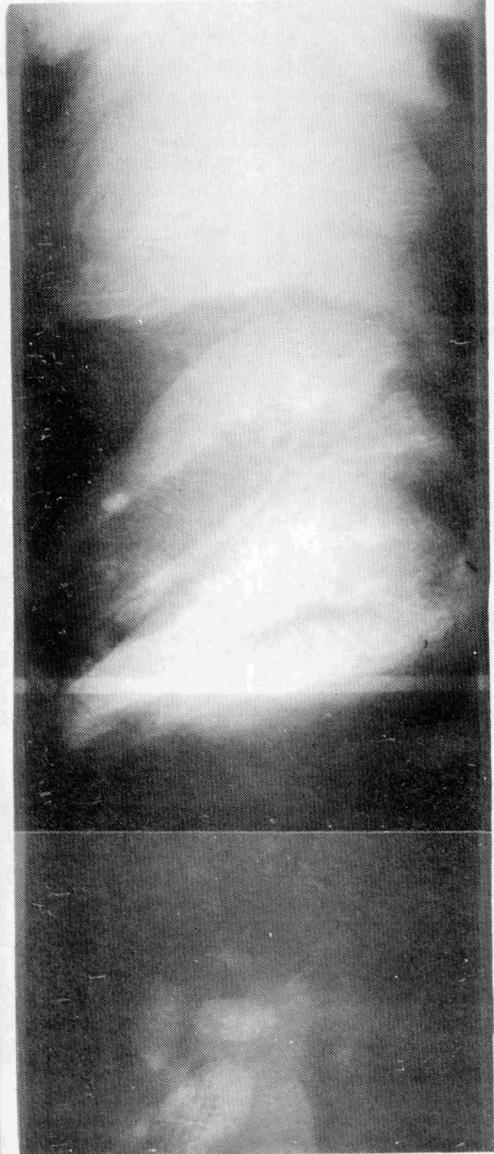


7B

Fig. 7: X-ray photographs of the top of cores 7A and 7B collected at Hansweert.



12 A



12 B

Fig. 8: X-ray photographs of the top of cores 12 A and 12 B collected at Ballastplaat.

Table 1: grain size distribution of bottom sediments at Hansweert
(station 7) and Ballastplaat (station 12)

| Sample | Depth | Sand | Silt | Clay | Md | Sorting |
|--------|-----------|------|------|------|---------------|---------|
| | cm | % | % | % | μm | |
| 7A-1 | 0-2 | 97 | 1 | 2 | 191 | WS |
| 7A-2 | 5-8 | 97 | 1 | 2 | 212 | WS |
| 7B-1 | 0-2 | 97 | 1 | 2 | 235 | WS |
| 7B-2 | 2-4 | 99 | 0.5 | 0.5 | 224 | WS |
| 12A-3 | 0-2 | 62 | 23 | 15 | 21 | VPS |
| 12A-1 | 2-6 | 93 | 4 | 3 | 150 | MWS |
| 12A-2 | 6-7 | 93 | 4 | 3 | 150 | MWS |
| 12A-4 | 15-16.5 | 96 | 1 | 3 | 179 | MWS |
| 12A-5 | 17-20 | 92 | 6 | 2 | 180 | MWS |
| 12A-7 | 28.5-29.5 | 83 | 13 | 4 | 100 | PS |
| 12B-1 | 0-3 | 43 | 36 | 21 | 12 | VPS |
| 12B-2 | 20-22 | 95 | 2 | 3 | 160 | WS |
| 12B-4 | 38.5-40.5 | 94 | 3 | 3 | 153 | MWS |
| 12B-5 | 44.5-46.5 | 76 | 16 | 8 | 68 | PS |

Sand : 2 mm - 0.063 mm

Clay : < 0.002 mm

VPS : very poorly sorted

MWS : moderately well sorted

Silt : 0.063 mm - 0.002 mm

Md : median grain-size

PS : poorly sorted

WS : well sorted

Table 2: heavy metals concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) in bottom cores 7A (Hansweert) and 12B (Ballastplaat)

| Depth (cm) | CORE - 7A | | | | | | | |
|---------------|-----------|--------|--------|--------|--------|--------|--------|--|
| | [Cu] | [Pb] | [Cd] | [Hg] | [Fe] | [Mn] | [Zn] | [TPC] ($\text{mg}\cdot\text{g}^{-1}$) |
| 0-1 | 2.82 | 10.0 | 1.075 | 0.10 | 6,828 | 61.1 | 23.0 | 5.4 |
| 14-16 | 2.125 | 8.25 | 0.70 | 0.08 | 6,693 | 62.9 | 17.0 | 3.2 |
| 26-28 | 1.80 | 7.75 | 0.575 | 0.02 | 6,020 | 54.3 | 15.0 | 2.9 |
| CORE - 12B | | | | | | | | |
| 0-3 | 111.75 | 174.0 | 18.75 | 2.60 | 30,462 | 1017.9 | 788.8 | 67.3 |
| 20-22 | 9.25 | 21.5 | 2.15 | 0.20 | 11,875 | 123.6 | 70.3 | 8.5 |
| 25-26 | 45.00 | 65.50 | 8.50 | 1.09 | 19,028 | 511.0 | 348.2 | 27.4 |
| 38.5-40 | 7.57 | 16.75 | 1.46 | 0.11 | 11,042 | 99.3 | 60.4 | 7.1 |
| 44.5-46.5 | 35.25 | 46.0 | 6.0 | 0.69 | 18,394 | 372.2 | 188.2 | 21.4 |

alternate with sand beds of similar size. In the sand beds mud pebbles occur.

Grain size:

Hansweert. According to the very homogeneous structure shown by the X-ray photography, only two samples of the top of the core were analyzed. In both cases the sediment appeared to be composed of a well sorted fine sand (Table 1).

Ballastplaat. Both cores yield similar results. The sand fraction is high (76 to 96 %), except for the 2 to 3 cm thick top layer (43 to 62 %). In all subsamples the silt fraction is higher than the clay fraction. Sorting varies from very poorly for the finer sediments (median between 12 and 21 μm) to moderately well for the coarser ones (median between 150 and 180 μm). The coarsest sand fraction is approximately 300 μm .

Heavy metals and total carbon:

Hansweert. The absolute amounts in this sandy sediment are very low (Table 2).

Ballastplaat. The silt laminae contain much higher metal and carbon levels than the sand laminae (Table 2).

From these results, as well as those from the other stations it appears that in two layers belonging to one core, and with comparable grain size and total carbon content, the highest metal concentration can be found either in the upper or lower layer. Varying contamination levels of the sedimentating material in former years can be one of the main reasons. Similar to the top layers, higher metals concentrations corrected for grain size (or for total carbon) occur in the upper estuary.

Finally, zinc and copper levels observed in the Scheldt are compared to those prevailing in other estuaries and to a global mean value.

| | Global mean | | Gironde | | Ems | | Rhine | | Scheldt | |
|------------------|-------------|----|---------|----|------|----|-------|-----|---------|-----|
| | Zn | Cu | Zn | Cu | Zn | Cu | Zn | Cu | Zn | Cu |
| Water (ppb) | 10 | 5 | 50 | 5 | | | 150 | 10 | 38 | 5 |
| Suspension (ppm) | 300 | 50 | 600 | 30 | 1000 | 70 | 3000 | 400 | 1060 | 190 |
| Sediments (ppm) | 100 | 50 | 300 | 25 | 600 | 50 | 900 | 200 | 218 | 28 |

Table 3: Comparison of heavy metals levels in the Scheldt estuary with these of other estuaries (from Etcheber, 1979)

The pollution level in the Scheldt estuary seems to be comparable to that in the Gironde. Only the particulate metals concentrations in the Scheldt are somewhat higher, owing to its lower load of suspended matter, which is about 100 mg. l^{-1} compared to the 1200 mg. l^{-1} in the Gironde (Etcheber, 1979).

The input of heavy metals to the sea via the river Scheldt has been estimated. Annual amounts of dissolved and particulate Cd, Cu, Fe, Hg, Mn, Pb and Zn supplied to the North Sea by the Scheldt are .98 and .48, 6.6 and 5.3, 420 and 1500, 0.10 and 0.50, 180 and 100, 2.3 and 9.9, 28 and 32 tons.year⁻¹ respectively.

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