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The Weser Estuary: a study on heavy metal behaviour under hydrographic and water quality conditions

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Abstract: In continuation of fixed anchor stations the behaviour of heavy metals was also studied in longitudinal sections in the bottom sediments (Calmano et al. 1982) and in the water (this paper). There are changes in concentrations of dissolved metals in water and changes in contents of metals in seston (suspended matter) in dependence on tides (Duinker et al. 1982 b). These changes can be related to the passing of different water bodies and different seston types, respectively, at the place of observation. In addition, more changes were found at various hydrographically defined „stretches" along the whole length of the estuary. These changes were attributed to dilution of estuarine water by coastal seawater in the lower

estuary; but in the mud reach in the central estuary they were attributed to the interchange with mud (alternating settling and resuspension of loose sediment particles through tides). In the central and the upper estuary they could be attributed to the influence of very low salinity, to the predominance of either organic matter or clay or quartz in seston, to the state of aggregation of seston particles which depends on salinity, the nearness to the mud reach and perhaps the amount of the particles in water; and the changes could further be attributed to emissions from industrial sites, sewage outfalls and the dumping of dredge spoil. Relation to organic water quality criteria were not found. The bioavailability of particulate metals is discussed: it is comparatively high in Cd, Zn and Mn (80 - 95 %) and lower in other elements.

Introduction

In 1976 Duinker et al. (1982 b) observed the behaviour of dissolved and particulate suspended metals in the Weser Estuary during estuarine mixing. Observations were mainly made at a fixed (anchored) position near Brake (Fig. 1 A: D) during summer 1976 when river discharge was extremely low because there was practically no rainfall during the preceding 12 months. Therefore at that time mixing between river water and sea water occurred near Brake and not near Nordenham as would have been normal. Observations were made during spring tide conditions, which means that during flood and ebb all erodable sediments were probably eroded.

Although a one day study at a fixed location would give good information about processes in dependence on tidal dynamics, it would give only little information about spatial distribution patterns of metals in the estuary and about the behaviour of metals during their transport through the various estuarine zones.

This information will be needed for interpretation of data from the newly installed monitoring programme in the North Sea coastal areas. Therefore in 1980 and 1981 we studied concentration and chemical forms of metals in bottom sediments and mud that was dredged during maintenance dredging (Calmano et al. 1982). Sediments were collected along the channel and on both sides beginning in the river water region at Bremen and ending at higher salinities (U-km 90). The sediments with the highest metal contents in the smaller than 63 μm fraction were found in some harbour basins at Bremen and in the mud shoal near Nordenham. These collections were also made at spring tide in order to obtain the permanently sedimented fraction which is not eroded even by the strongest normal currents.

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With the aim to obtain the permanently suspended fraction of the seston which does not settle even during the weakest current conditions, two longitudinal sections were made during neap tide. The results are reported in this paper.

As a hypothesis, we suggest that this permanently suspended fraction, together with dissolved material, is transported to the sea, whereas the temporarily suspended fraction is retained in the estuary and interacts with the bottom and with dredging activities.

It may therefore be expected that along the line from pure river water to pure sea water mixing between both ends is expressed in a linear relationship between metal concentrations in water and salinity (which is used as a measure of mixture with sea water) and where this is not the case, additional processes influence metal concentrations. In order to trace such influences in addition to seston and filtered water samples for metal analyses, the following variables were measured in water: salinity, pH, oxygen concentration (only during the first cruise, 22 Juli 1980), particulate and dissolved organic carbon, light attenuation (for turbidity) and during the second cruise (1 December 1980) dissolved orthophosphate-phosphorus, NH_4-nitrogen and NO_2-nitrogen.

Problems

A great portion of the metals found in the sea are transported by rivers and through estuaries (Förstner & Wittmann 1981, p. 191 ff.). The mode of transport through estuaries is so far not sufficiently well known. When arriving in the estuary, particulate and dissolved matter are subject to special estuarine influences among which increasing salinity, continuous mixing of different water bodies, and the complicated behaviour of suspended matter (seston, sediment) seem to be paramount. Some special problems will be discussed in the following paragraphs.

Chemical forms of metals

A part of the heavy metal influx (Cd, Zn, Pb, Ag, Cu) originates from the Harz Mountain area where heavy metal mining is done for centuries (Baumann et al. 1977). Industrial and urban outflows contribute another part, and especially factories at Bremen and Nordenham obviously lose measurable amounts of their metals into the Weser River either through sewers or by duffusion. Unless the chemical forms of these metal influxes are known, their further rate cannot be predicted.

Environmental conditions

In natural waters generally about 90 % of the metals is bound to particulate material (seston, sediment), whereas less than 10 % occurs in solution. On their way downstream and during alternating tidal transport upstream and downstream, water and seston are influenced by changing environmental conditions: redox conditions, salinity, pH, ion exchange, formation of chloro-complexes, and seasons may alter the chemical forms of metals. This may have a bearing on their bio-availability.

Types of seston particles

Any substance that enters the Weser Estuary encounters a dense concentration of suspended particles (seston) with which it may react. These particles are not only typical clay flocs, but are rather much larger aggregates of various types of particles including organic substances.. These aggregates may be an advanced stage of the evolution from single particles (i. e. clay flocs, fine sand grains, slime flocs, plant and animal debris etc.) to compact mud (Wellershaus 1981 a, 1982). Different particle types may play different roles with respect to metals. It is so far difficult to differentiate between them quantitatively, but in some cases differentiation can be made between permanently suspended seston which contains more organic carbon, and temporarily suspended seston which contains less organic carbon, and between the circumstances under which these types occur (tides, location: Wellershaus 1981 b). Thus seston containing little organic carbon appears mainly in the mud areas and is suspended by tidal erosion. In surface water at neap slack tide the smallest seston concentration is found. This seston consists mainly of the permanently suspended fraction whilst during spring tide currents also a great proportion of temporarily suspended seston (eroded sediment) occurs. The dependance of the fate of metals on different particle types was in part studied by Duinker et al. (1982 a, b), and some more observations will be added in the present study.

Low salinity

A major role in metal behaviour is played by the "very low salinity region" as was described by Morris et al. '(1978). It has to be studied whether such observations could also be made in the Weser Estuary, and under which environmental conditions the main changes in chemical form of metals take place.

Water quality

In general, the term "water quality" describes the degree of pollution with oxidizable organic matter. The Weser Estuary is polluted with organic material mainly from the cities of Bremen and Bremerhaven (A in Fig. 1 A). Together with other inflows the total load amounts to $2.8 \cdot 10^6$ inhabitant equivalents that reached the estuary in 1981 (Weserlastplan 1982). These materials consist mainly of fine organic particles and dissolved organic matter. In addition, heavy metals are disposed into the Weser along the same paths. In general 50-70 % of heavy metals in untreated sewage pass mechanical plants and are transported together with the treated water into rivers. It remains to be seen whether the organic materials and the metals show similarities or mutual reaction during seaward transport.

It should be noted that some of the problems discussed here could not be solved during our study, and that more research is needed, mainly with respect to the variation of metal concentration and transport in course of one year or longer periods, and with respect to the real effect that the metals have on biota.

Methods

To obtain seston that consisted as much as possible of permanently suspended particles, a weak tidal current situation was chosen in the following way: during the sampling trips along the estuarine "thalweg" the mud zone was reached with the boat al slacks, and the whole surveys were made during neap tide. Since in July 1980 preceding stormy weather was suspected to have disturbed the hydrographic structure of the estuary, a second trip was made at 1 December 1980, but it was found that the storm did not alter the structure considerably.

All samples were taken and all in-situ measurements were made from on board a 40 m research boat.

Hydrographic data were obtained by means of the estuarine probe, "Heupferd", which had been built in the institute. The system allows measuring pressure, temperature, electric conductivity and light attenuation at 1 cm and 10 cm light path (for light attenuation see Ohm 1979). Depth, salinity and al light extinction coefficient were calculated from these data.
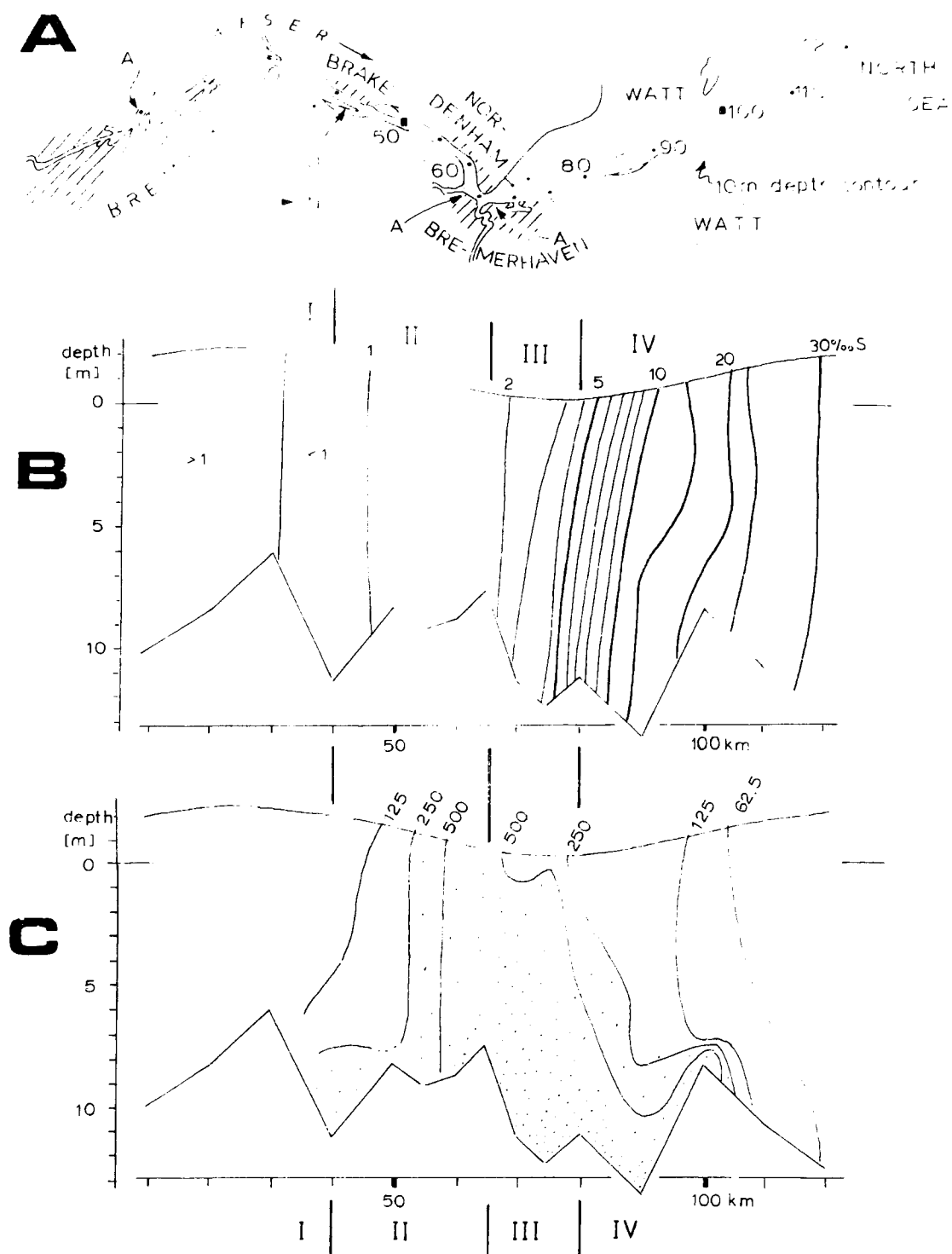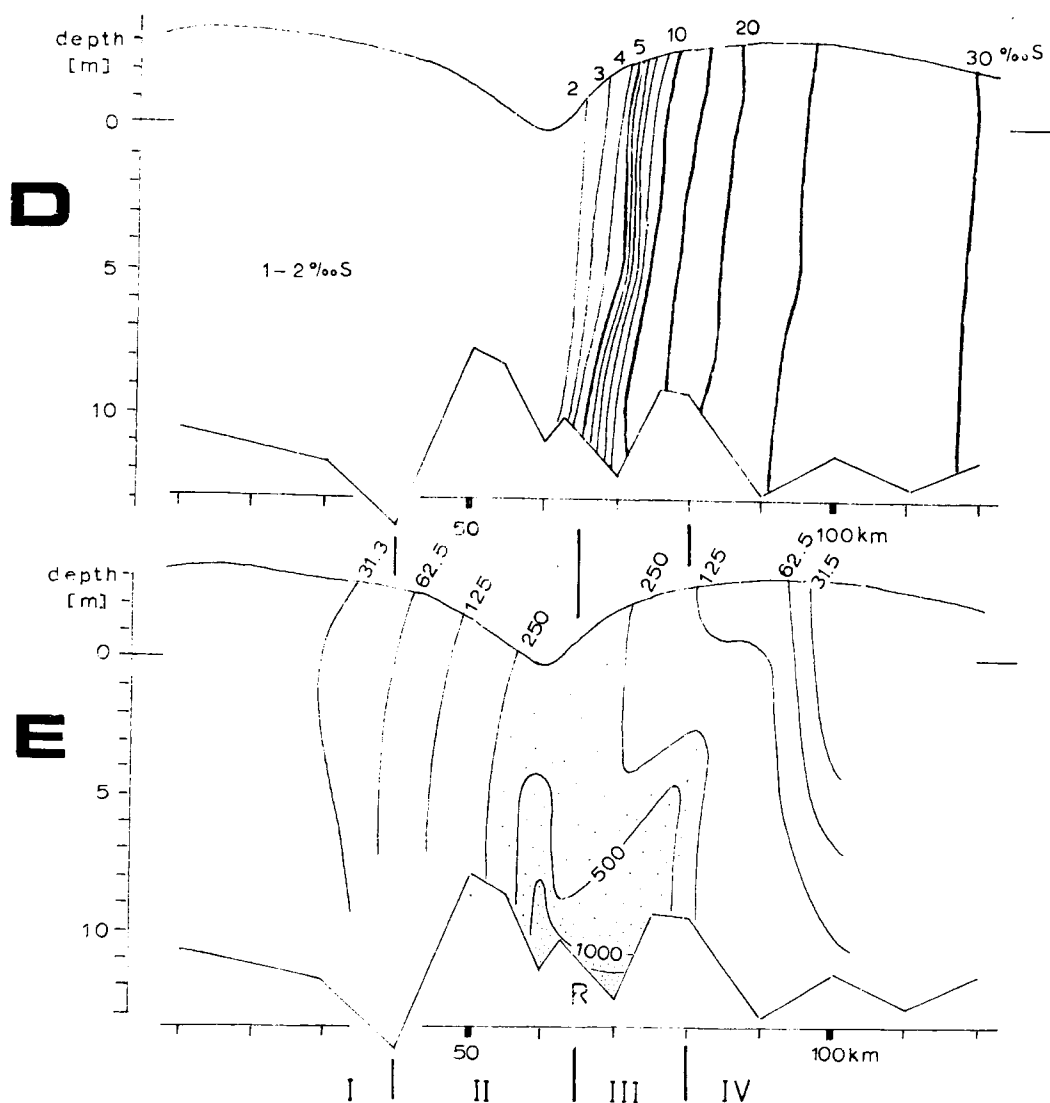
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Fig. 1: Map of the Weser Estuary (A) and basic hydrographic description during collections at 22 July 1980 (B-C) and 1 December 1980 (D-E).

Salinity: B and D, turbidity: C and E. Numbers 10 to 120 in Fig. 1 A indicate the distance (km) downstream from the Große Weserbrücke at Bremen

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(UW-km in the following). UW-km 65 has the position 53°32'N, 8°34'E. I -
IV: stretches in the hydrographic structure of the estuary.

In the isopleth-graphs (B - E) the water level is drawn according to the tide
at the moment of in-situ measurements and collections. Depth contours re-
present the actual position of the boat with respect to the middle of the
channel and irregularities in channel depth. In the very low salinity region,
salinity data are not absolute (calculated from electrical conductivity); for
more details see Fig. 3.

Turbidity (C and E) is given as 1000 · extinction coefficient · (light path in
cm) $^{-1}$. Highest values were found in the mud area around UW-km 65.
Erosion of mud at the very beginning of flood was only observed at 1 De-
cember 1980 (R in Fig. 1 E). For this day no turbidity data were obtained at
UW-km 110 and 120.

(Continuation overleaf)

Water samples were taken with a tube pump at 3 m distance from the boat and about 1 m below the surface.

For particulate metal analyses the water was pumped into a 50 l plastic bottle, then through a continuous flow centrifuge (Heraeus Christ Junior 15,000 at 10,000 rpm). Depending on seston concentration 30 - 100 l water were centrifuged. These seston samples were freeze dried and homogenized in the laboratory, then digested with concentrated HNO_3 for two hours at 120° C. By this method all heavy metals with the exception of Fe und Ni were almost completely solubilized. For dissolved metal analysis the water was sucked through a 0.45 μm membrane filter, the filtrate adjusted to pH 0 – 1 with HNO_3 Suprapur [R] and then frozen.

As already mentioned (Calmano et al. 1982; Förstner & Calmano 1982) we introduced an extraction method for the assessment of the chemical forms of particle-associated heavy metals. We applied the following five step-scheme as simply as possible:

1st step: "exchangeable cations" – 1 M ammonium acetate, ph 7, solid: solution ratio 1:20, 2 hours shaking;

2nd step: "easily reducible phases" (Mn-oxides, partly amorphous Fe-oxyhydrates and carbonates) – 0.1 M $NH_2OH \cdot HCl$, pH 2, dilution 1:100, 12 hours shaking;

3rd step: "moderately reducible phases" (e.g. amorphous and poorly crystallized Fe-oxyhydrates) – 0.2 M ammonium oxalate + 0.2 M oxalic acid, pH 3 dilution 1:100, 24 hours shaking;

4th step: "organic fraction including sulfides" – 30% H_2O_2, 85° C, extraction with 1 M ammonium acetate, dilution 1:100, 12 hours shaking;

5th step: "residual fraction" – concentrated HNO_3, 120° C, dilution 1:100.

Legend to Fig. 1, continued

Temperature is not presented. In July values between 15.1° C and 16.1° C and in December between 4.2° C and 7.6° C were found. At both days highest temperatures occurred around low tide and in December lowest values at UW-km 90.

For comparison see figure 7 in Wellershaus' (1981) description of the turbidity maximum where a similar situation was demonstrated for UW-km 62 on a neap tide fixed station over a period of two tides.

Analyses were made using flame- and carbon furnace atomic absorption spectroscopy for the metals Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The accuracy of analysis was tested with a sediment standard. As an example for dissolved metals only Cd was measured. This analysis was made without enrichment according to the standard addition method.

For determination of particulate and dissolved carbon contents in seston samples were filtrated through Whatman GF/C glass fibre filters. For chloride titration and water quality parameters unfiltered samples were stored in bottles (see below).

Analysis of seston dry weight and particulate and dissolved carbon was made according to the methods described previously (Wellershaus & Walter 1980).

For water quality analyses the water was pumped into polyethylene bottles, preserved with chloroform (1 ml/250 ml) and deep frozen. In the laboratory the water was filtrated through 0.2 μm Nuclepore[R] membrane filters. Analysis was done in a Perkin-Elmer Auto-Analyzer C4B

Calibration of the C4B was made at 4 calibration points. The calibration curves were adapted and concentrations calculated with the aid of a 3rd order polynome regression. Three parallel analyses were made of each sample of which the arithmetic means are used in this paper. The mean standard-deviation of each set of three parallels was ca. 1 %.

The following reactions were used: for ammonium Berthelot, for nitrite Griess-Ilosvays, for orthophosphate molybdenumblue, and for chloride rhodanite.

Results

Hydrography

Stretches

An estuary can be divided either into reaches or into stretches. The term "reach" is often used to characterize a geographically fixed section of the estuary, whilst "stretch" is used here to characterize a hydrographically fixed section. The latter explanation means that certain properties like salinity and turbidity move up and downstream in dependence on outer influences like tides, river discharge, erosion and sedimentation of sedi-
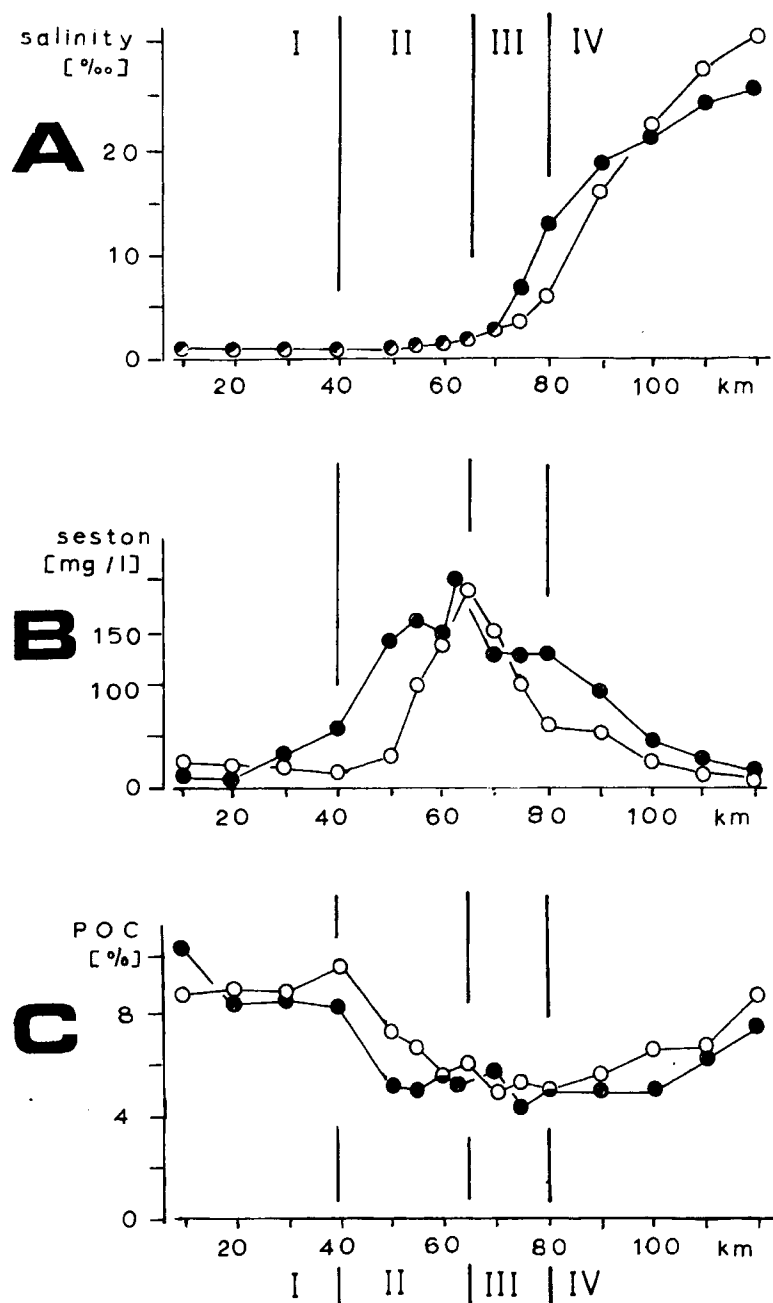
Fig. 2: Salinity (A, titrated in the lower ranges), seston concentration in water (B) and organic carbon content (C) in surface samples between Bremen and North Sea. Open circles: 22 July, dots: 1 December 1980.

Decrease and increase of salinity in the very low salinity region are more clearly shown in Figure 3 A. At both days neap tide caused low seston con-centration in water; this seston consisted of relatively little mineral matter which can be seen from the POC data.

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ments, and mixture (Wellershaus, 1981 a: Figs. 11 and 12). So a certain water property may occur always at the same hydrographic place but at different geographic locations.

Following this concept, four stretches could be characterized in the Weser estuary. They move, however, up and downstream together with tides (Figs. 1, 2). During one cruise they seem to be fixed, but it should be kept in mind that during the cruise, tides went on and an accurate synchronous picturre could not be given by using only one boat. So, fixations to UW-km-points (km-counting downstream of the Große Weserbrücke at Bremen) are only relative.

The four stretches in the Weser Estuary were (Fig. 2):

I. Tidal weir at Hemelingen (UW-km – 4.7) to UW-km 40, river water: due to brine disposal into one tributary the Weser River does not contain freshwater. Due to mixture with other tributaries, salinity decreases; but along the next stretch,

II. UW-km 40 to 65, salinity increases as a consequence of mixing with estuarine brackish water. Stretch II contains the riverward slope of the turbidity maximum. It is roughly identical with the "very low salinity region" as descriped by Morris et al. (1978).

III. UW-km 65 to 80: here salinity increases more intensively than in the former reach, but turbidity decreases again depicting the seaward slope of its maximum.

VI. Seaward from UW-km 80 salinity changes demonstrate more mixture of estuarine water with sea water.

The system described here should not be taken strictly. There are no abrupt borders between these stretches, but rather there is a flowing transition between them which is expressed as a crowding of isolines or the steepness of longitudinal gradients (Fig. 1 B and 1 D).

Tides

In an estuary the water flows upstream during flood and downstream during ebb. If there were no tides in the Weser Estuary, the river water mass would flow a path of 6.6 to 12 km per 12.5 hours at the foot of the tidal weir, and this distance would be reduced to 0.1 to 3 km at UW-km 50 due to the widening of the bed volume (Wärmelastplan Weser 1974; Stückrath 1970: Fig. 15). The actual path length, however, has to be corrected by the tidal paths. Of these, the ebb (i. e. downstream flow) path
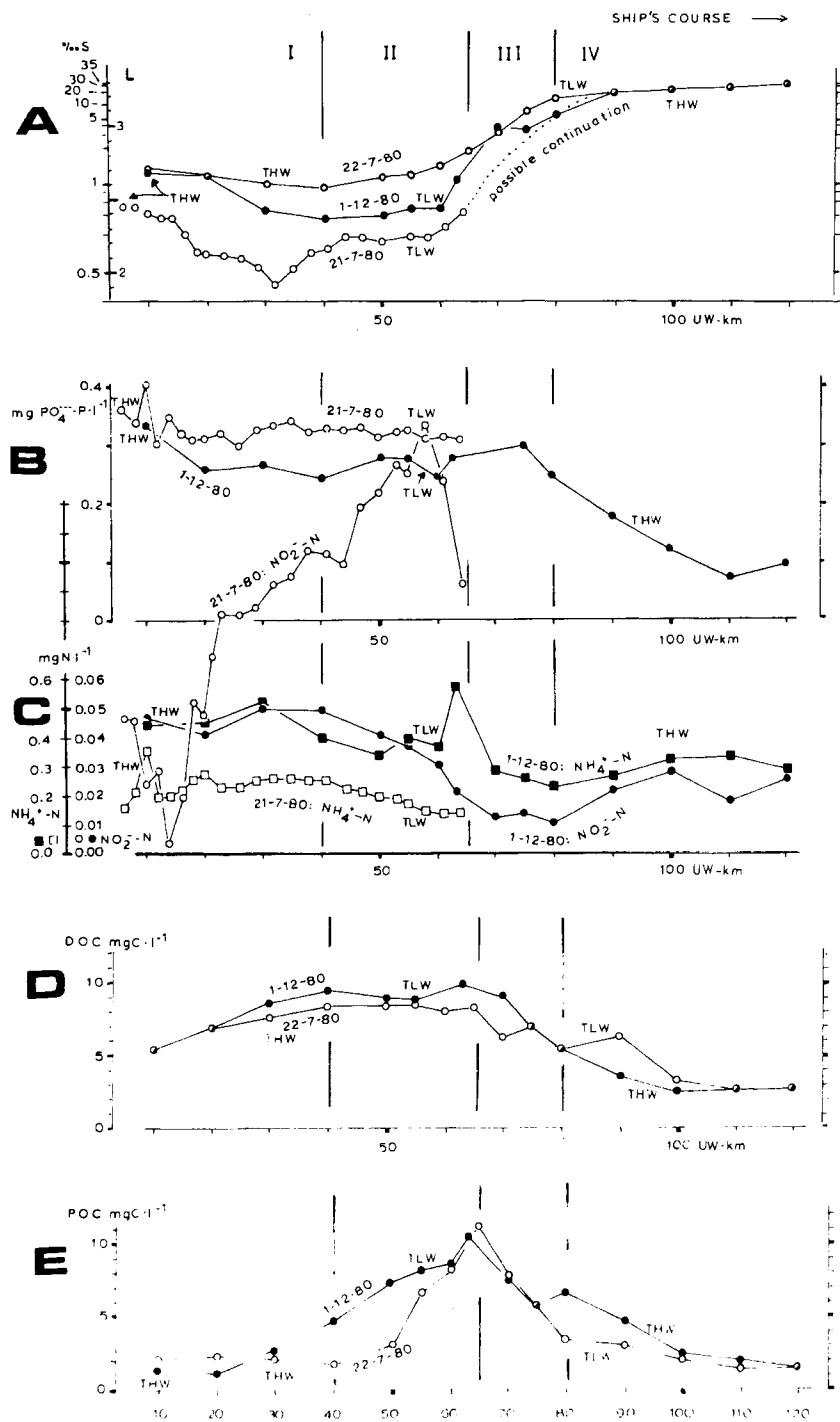
Fig. 3: Surface samples between Bremen and North Sea: salinity and water qual-
ity criteria. All data refer to 1 l water. 21 and 22 July 1980 and 1 December
1980.

A: Salinity (titrated in the lower ranges) on a log (logS)-scale (L). B: Dis-
solved PO_4^{---}-phosphorus. C: Dissolved nitrogen-ions. D: Dissolved or-
ganic carbon (DOC). E: Particulate organic carbon (POC).

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length is 12 km at the foot of the weir increasing to 14.1 to 16 km at UW-km 50, and the flood path length is zero at the weir increasing to 14 km at UW-km 50. There are possibly minor changes farther downstream. These data undergo, however, great changes due to river discharge, different tidal forms (spring/ neap) and wind.

During these flows, mixing occurs so that a certain water body, observed at a distinct place and moment, changes its properties during the tidal flow (see Wellershaus 1981a: Figs. 11 and 12).

Salinity, seston, organic carbon and water quality

The area of lowest salinity was found near UW-km 40-65 (Figs. 2A, 3A). The second stretch represents the "very low salinity region". Where the estuarine salinity changes from a weak into a steep gradient, turbidity in water is highest (indicating the turbidity maximum).

For our observations neap tide was chosen to obtain the permanently suspended fraction of sestion and to avoid as far as possible the fraction that is only temporarily suspended (Duinker et al. 1982a). To improve this scheme sampling was planned in a way that we arrived at the mud shoal of the estuary during slack low tide when as much particles as possible were expected to have settled down to the bottom (Wellershaus 1981a, 1982).

In the turbid zone seston in water (Fig. 2B) is mainly derived from the mud shoal at UW-km 65, where tidal currents at the beginning of flood and at the end of ebb usually re-suspend sediments that are then distributed in the water column and form the turbid zone. This turbid water mixes with seston poorer water at both ends of the turbidity maximum.

In the turbid zone the re-suspended sediments contained less organic carbon (POC in Fig. 2C) than the seston does that was found more up and downstream, or in other words: the tides erode mainly minerals (clay and fine sand size particles) that then occur in the water together with permanently suspended organic and clayey particles. During slacks, POC-content in surface seston increases slightly but still remains low. This shows that a part of, but not all suspended sediment settles during slacks. These observations are important because they show that sediment and seston are not fully identical (for more details see Wellershaus 1981b) and further, that in the turbid zone permanently suspended seston never occurs

without a certain proportion of suspended sediment, i. e. the temporarily suspended seston.

From Figure 2C it seems that seston in the outer estuary (UW-km 80-110) also contained more minerals than in coastal water. This seston either originated from the neighboured wadden flats ("Watt" in Fig. 1A) or it represented a seaward flux of suspended sediments out of the turbidity maximum.

In the fourth stretch (beginning at UW-km 80) linear correlation of POC with salinity shows that pure mixture with coastal water caused the data observed.

In the usual water quality criteria in the Federal Republic of Germany metals are not included. Instead, organic load is used and expressed in various terms. One day before our summer metal survey, on 21 July 1980 and in addition on 1 December 1980, PO_4^{---}-phosphorus, NH_4^+-nitrogen, NO_2^--nitrogen, dissolved and particulate organic carbon in surface water were analysed and all results are depicted in Figures 3B-E to characterize the water quality. In addition, salinity is plotted in a way that minor changes near 0 ‰ are exaggerated (Fig. 3A).

With regard to load with particulate organic matter (POC), the turbid zone has the least water quality. This is an effect of the amassment of seston in this zone by hydrographic processes.

The load with dissolved organic matter (DOC) is highest in the second stretch. The DOC-distribution pattern seems to be independent of any greater sewage outlet known to us (A in Fig. 1A), and the causes for the low DOC-values in the first stretch are not clear. At UW-km 60 a DOC-peak and at UW-km 62 a NH_4^+-peak are conspicuous. They can be easily explained by the influx of untreated sewage from the city of Bremerhaven (A in Fig. 1A).

Though the effects of the Bremen waste water downstream of the outlet of the sewage treatment plant (UW-km 10) are not clearly seen, in connection with other data obtained during various cruises (Schirmer et al. 1983) the following picture can be given: In contrast to the hydrographic stretches I...IV, described above, these data suggest the following division into zones that correlate with similar compartments in a sewage treatment plant:

A from UW-km 5 to 15: zone of intensive carbon oxidation, extreme consumption of dissolved oxygen up to 6 mgO_2/l.

B from UW-km 15 to 30: recreation zone, hardly any oxygen consumption, in summer formation of organic flocs from activated sludge.

C from UW-km 30 to 50: intensive nitrogen oxidation, place of the lowest oxygen concentration of the whole estuary, which is almost identical with the place of maximum nitrite concentration.

During the summer cruise typical summer conditions did not exist (actual water temperatures 15-16° C, normally 20° C; actual river discharge at the tidal weir at UW-km – 4.7 was 520 m³/sec, normally 120 m³/sec; actual oxygen content in the minimum 6.5 mg O_2/l, normally 1-2 mg O_2/ l). That means that during the summer cruise water quality was relatively good, compartments with poor or no oxygen content could not be detected.

Phosphate shows special dynamics between UW-km 10 and 70. The same was found by Liebsch et al. (1983). Seaward of UW-km 70 dilution with seawater determines the phosphate concentration in water.

Principally a similar zonation, A - C, is valid for the reaches downstream of Bremerhaven, whereby zone A is found between UW-km 60-90, and B possibly seaward of this reach.

This classification is, however, disturbed by the re-eroded mud (which also contains organic matter) in the mud reach between UW-km 50-70 which is partly transported downstream. It is further disturbed by extreme longitudinal dispersion along the tidal paths.

This classification stands for the period from May to middle of November: When water temperature decreases below 10° C, the nitrite oxidizer, *Nitrobacter*, and the ammonia oxidizer, *Nitrosomonas*, become inactive and consequently nitrification slowly fades away.

During the December 1980 cruise the Weser was still in a period of seasonal transition: One week earlier water temperatures were above 10° C and very slight nitrification was observed.

Metal contents in seston and sediments

Highest contents were found in the first stretch, and they decreased towards the sea (Figs. 4 to 8).
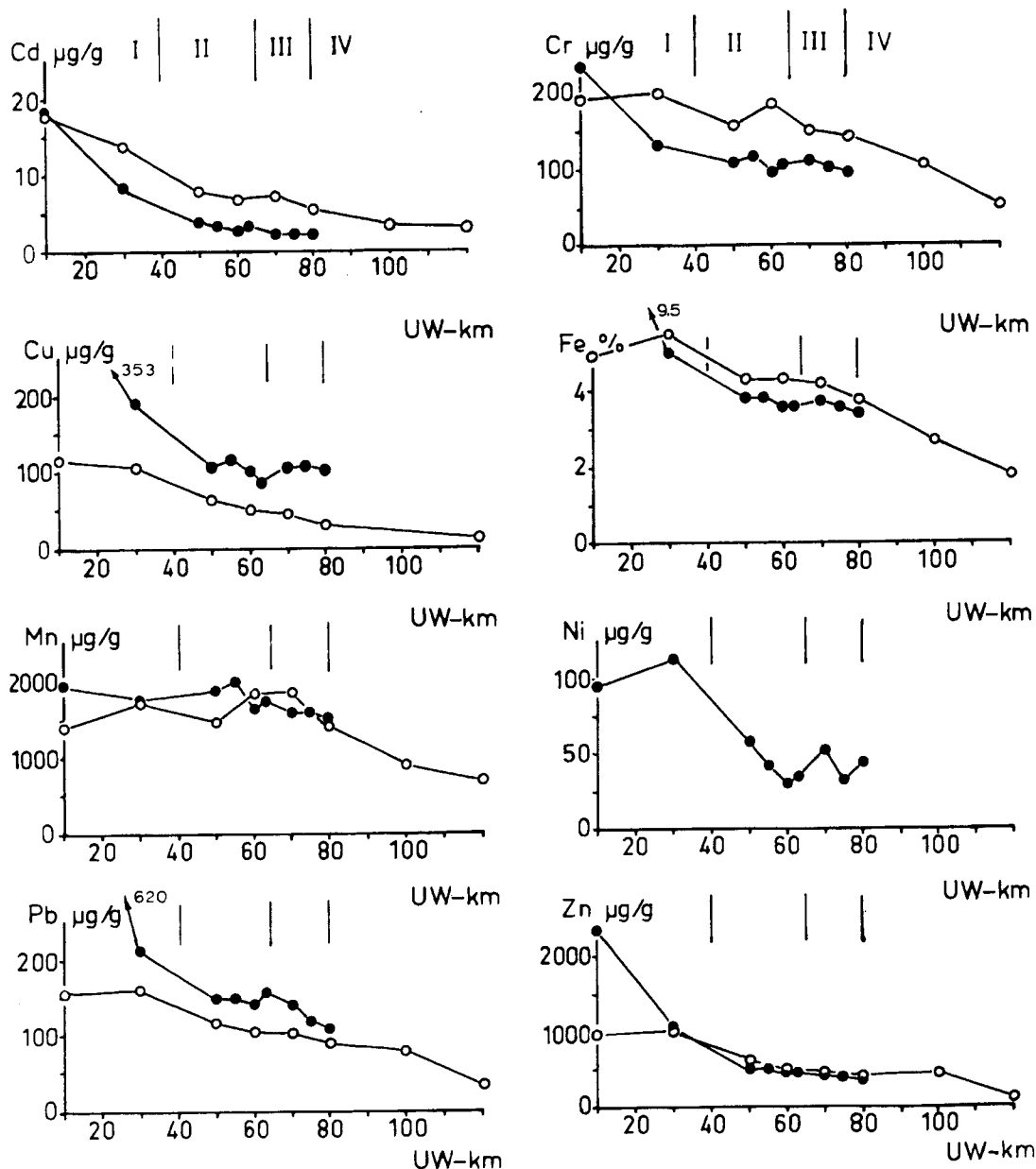
Fig. 4: Metal contents in seston (dry weight) of surface samples between Bremen and North Sea. Open circles: 22 July 1980, dots: 1 December 1980.

Stretch III - IV, the outer estuary

Downstream of UW-km 70 in the third stretch salinity increased as usual with a steep gradient from 3 to more than 20 ‰ (fig. 2) and metal contents in seston were in good negative correlation with it – except for Cu and Ni – (fig. 6). This shows that in this area mixture between estuarine and coastal seston was mainly responsible for the distribution of particulate Cd, Cr, Fe, Mn, Pb, and Zn.
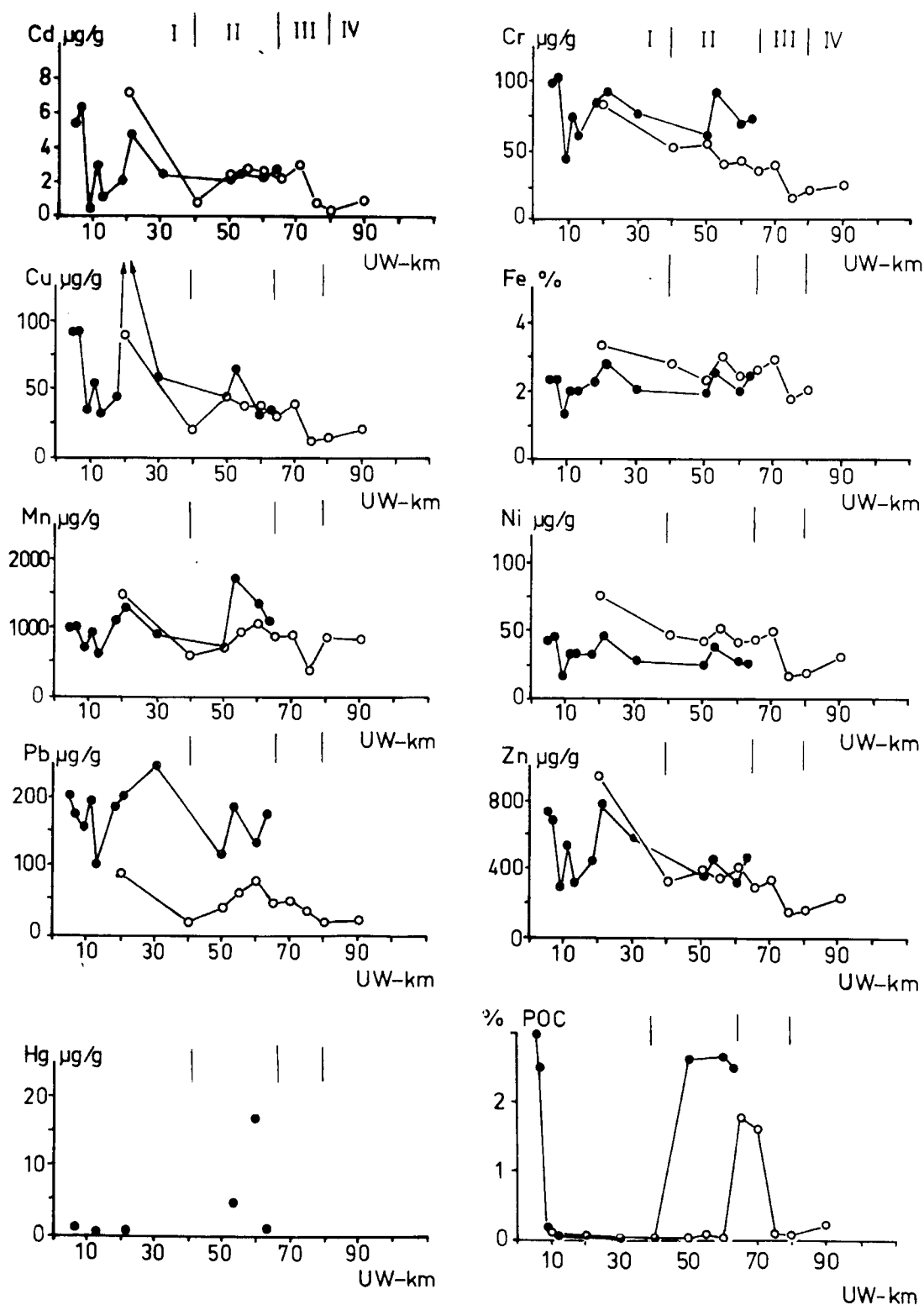
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Fig. 5: Metal and organic carbon (POC) contents in sediments (smaller than 63 µm fraction), middle of thé channel. Open circles: 16 May 1980, dots: 17 March 1981.

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Stretch I - II, the central and upper estuary

Upstream of UW-km 70 the changes cannot simply be explained by dilution with marine seston. Especially in the first and second stretch, some phenomena were observed by us that more or less clearly influence the metals:

1. Sediments (fig. 5): These curves are less smooth than the seston curves. They reflect even minor inflows of metals because the sediments are less affected by the tidal currents than seston. Seston is more evenly mixed along the estuary than sediments. An exception is found in the mud reach where re-suspended sediment (occuring as seston that was eroded by tidal currents) and the smaller than 63 μm fraction of the sediment proper are roughly identical.

2. Upwhirling of sediments: Upwhirling occurs in the mud reach mainly at the beginning of flood and at the end of ebb. During slack tide the up-whirled sediments settle again (more details have been described earlier: Wellershaus 1981 a) and we studied mainly the permanently suspended seston (see chapter "Methods").

The whole tidal cycle was observed in 1976 by Duinker et al. (1982 b) at an anchor station in the 3 - 10 %o area during spring tide. They observed both, permanently suspended seston and temporarily suspended seston in the same samples. The latter derived from the loose fraction of the sediment which was upwhirled and occurred in the water during full tidal currents and disappeared during slacks. In their samples seston contained less POC (2.0 - 4.5 %) than in our samples (4 - 9 %) which shows that more minerals occurred in the samples. The reason may be seen in the strength of the spring tide currents.

3. Low salinity region: Greatest differences were observed in the "very low salinity region" (Figs. 3, 6). It is not clear whether these effects were caused by the particular phenomena of this region or by the inflows from industries, harbours, or incompletely treated sewage of Bremen. From UW-km 30 to 70 (the first and the second stretch) metal content in seston decreased in seaward direction although there was no marked salinity increase. This can be interpreted as follows: coastal seston – poor in metals – incrudes farther upstream than salt water because different transport mechanisms are responsible. This coastal seston mixes with riverine seston, and the proportions between both yield the observed metal contents.
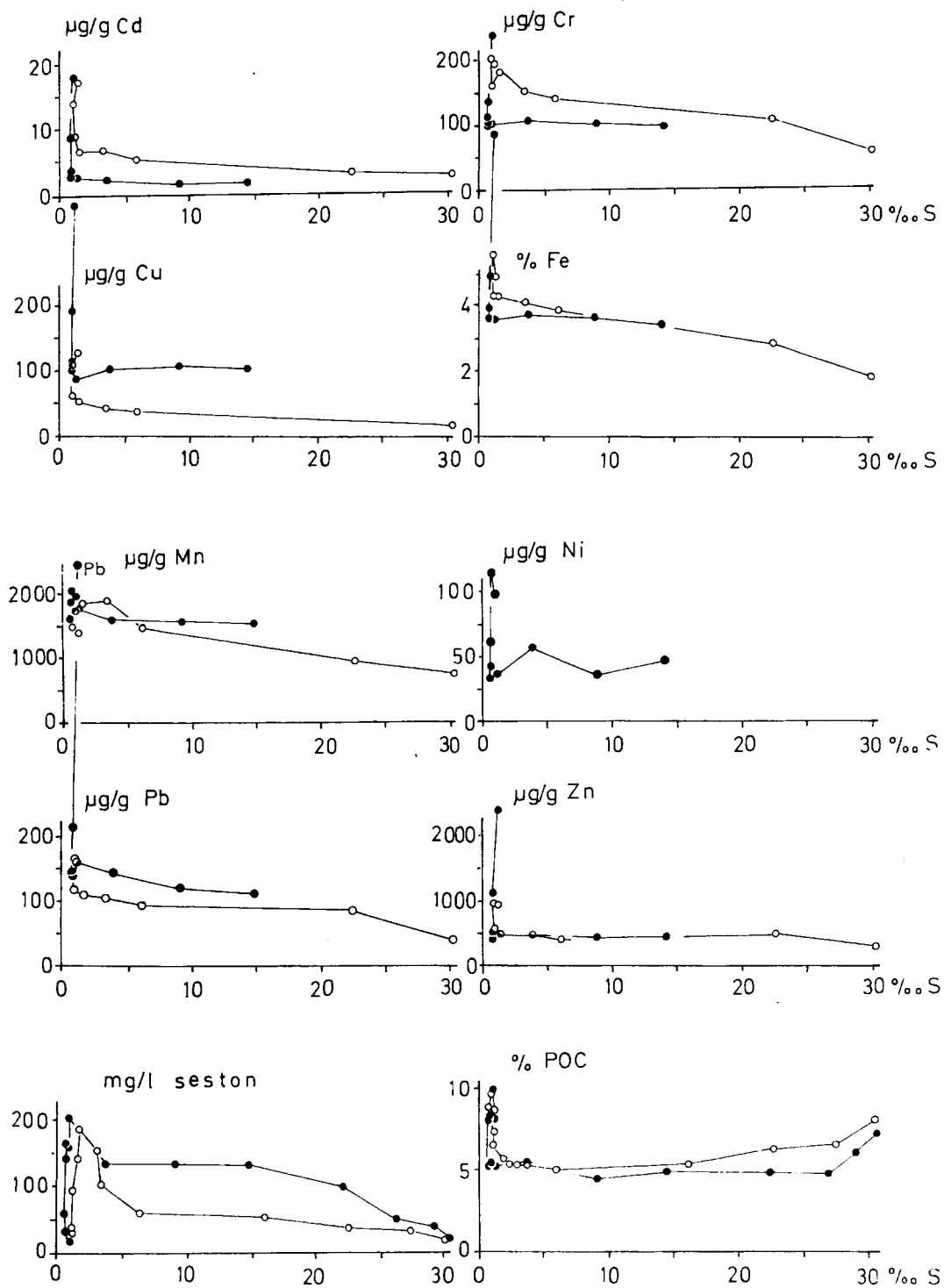
Fig. 6: Metal and organic carbon (POC) contents in seston and seston concentration in water versus salinity. Open circles: 22 July 1980, dots: 1 December 1980.
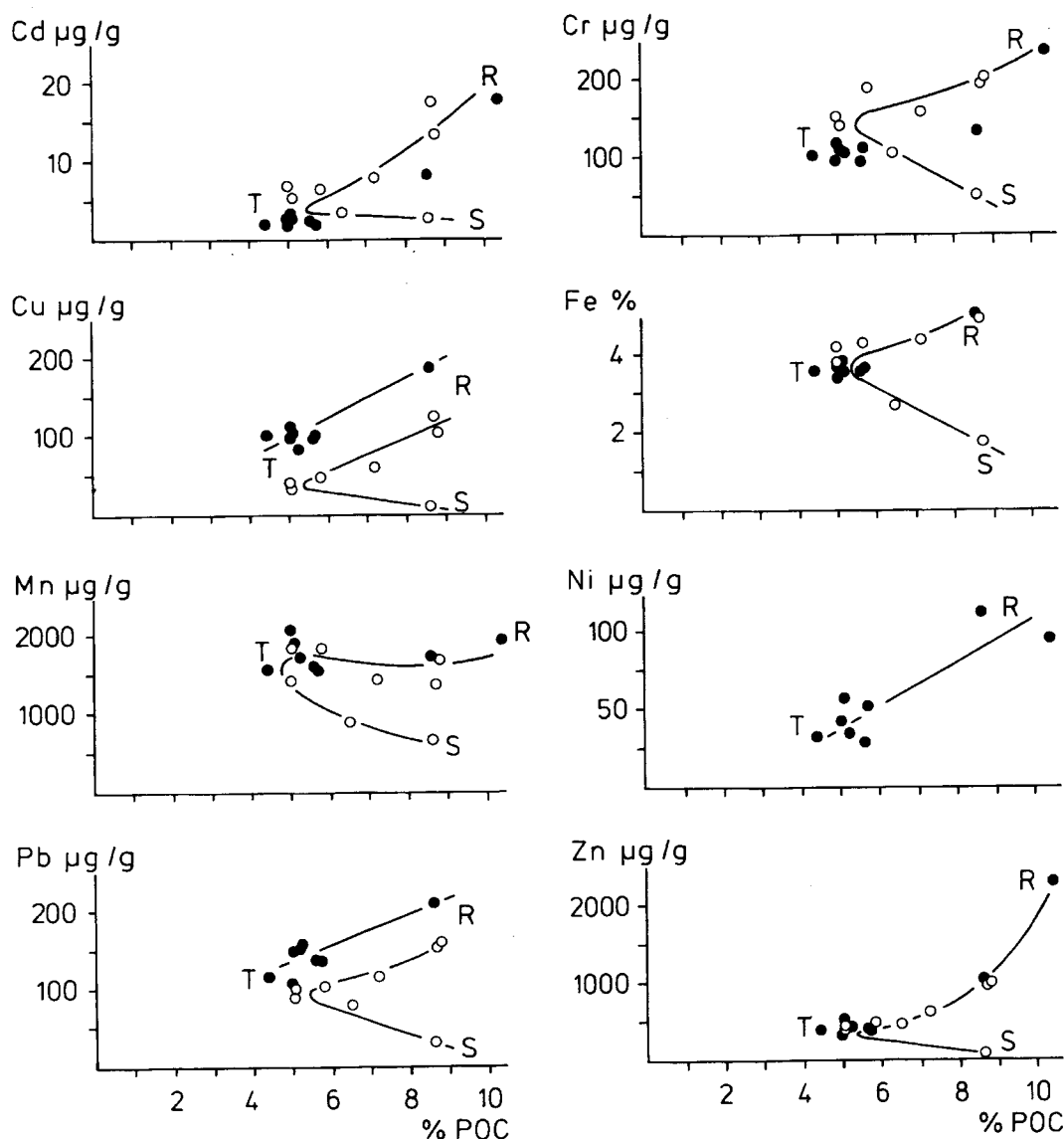
Fig. 7: Metal content in seston versus content of organic carbon (POC) in seston. Open circles: 22 July 1980, dots: December 1980. R = river end, T = turbidity maximum, S = sea end of the estuary.

4. Location in the estuary: This of course represents various influences of which some are discussed above and below. At the 1976 anchor station (Duinker et al. 1982 b) above a seston concentration of 200 mg · l^{-1} some metal contents decreased and some increased with increasing seston concentration. If Al and Si are taken as representatives for mineral material and organic C and N for organic material, the following affinities and behavioural patterns can be deducted: Mn, Fe and in some samples Ca, Ti and Mg were bound to the mineral fraction that occurres in water predo-
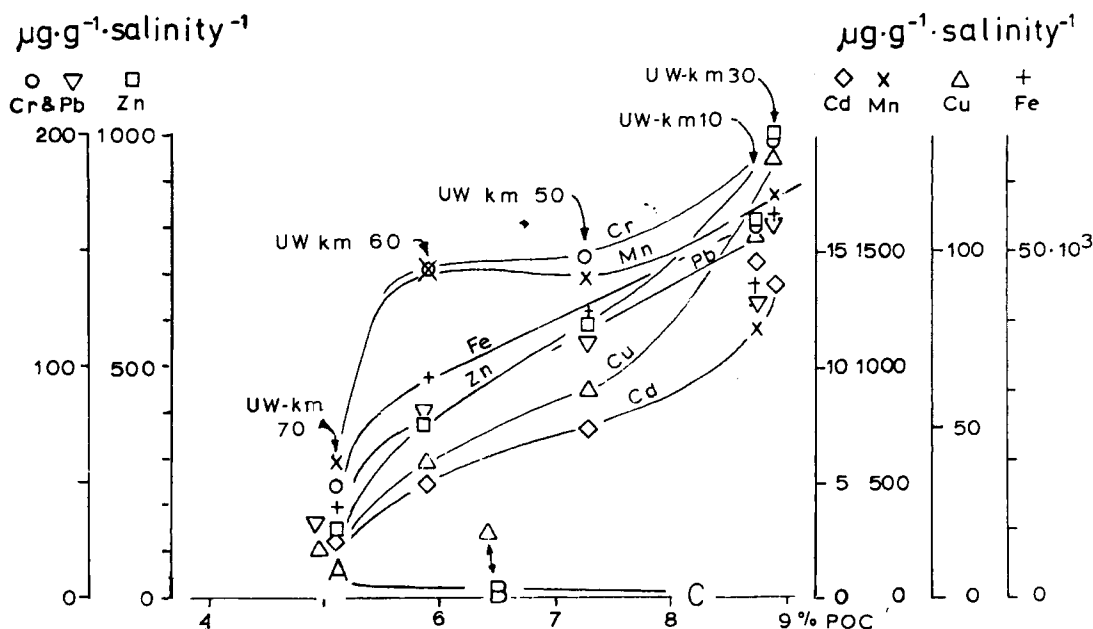
Fig. 8: Particulate metals standardized salinity versus POC, 22 July 1980. The signs A, B, and C represent the metal values for all metals analysed at UW-km 80, 100, and 120, respectively (except Cu at UW-km 100).

Between UW-km 30 and 70 metals (except Cr and Mn) in seston correlate with organic matter in seston (represented by POC). Up and downstream of this area other factors than POC are more relevant (Influx from land, mixture with marine detritus and plankton).

minantly during upwhirling. On the other hand Cd, Zn, Cu, Pb were bound to the organic fraction – not to clay minerals, see the Al-curve in figure 10 in Duinker et al. (1982 b) – that remained permanently suspended. So the changes in metal contents we have observed in seston along the estuary might depend on different types of seston derived from different places in the estuary: predominance of organics near Bremen, of clays near the mud reach (UW-km 65), of quartz minerals farther downstream, and of organics again in the coastal waters.

5. Organic particles: In Fig. 7 the relationships of particulate metals versus POC are plotted. But any dependence on POC cannot be seen – it is veiled behind the greater influence of mixture between estuarine and marine seston. The influence of POC on particulate metals can, however, be made visible in the following manner:

Mixture between river and sea water yields mixed water, and the ratio between both waters is roughly expressed by salinity. If one wants to eliminate mathematically the effect of mixing on metal distribution, the me-

tal data have to be divided by salinity (standardization). So in Fig. 8 the dependence of particulate metals and POC becomes visible:

a.) Between UW-km 10 and 30 there must have been a source, for example industries or poorly treated urban sewage.

b.) From UW-km 30 to 70 there is a positive relationship between particulate metals (except Mn and Cr) and POC.

c.) From UW-km 80 to 120 mixing between estuarine and marine seston determines its metal content almost alone.

6. Types of seston particles: Along the estuary the composition of seston changed much more than it would do at any anchor station. This can be seen from the POC graphs in Figs. 2, 3 and 7, but also from preliminary microscopic studies of the suspended particles. These organic aggregates contain clay flocs but little quartz grains. They have a great surface to which metals preferably get sorbed. The greatest surface is to be found in such particles that contain much water. Such particles have little dry weight, therefore comparison of particulate elements or compounds with dry weight of seston is often misleading. The small dry weight of organic substances is counteracted by great surface and consequently by an over-proportionally great physico-chemical reactivity.

Summing up this chapter it can be stated: There was a general decrease of metals in the sediment fraction smaller than 63 μm from river to sea except for Fe and Mn. In seston this tendency is much clearer and correlates to salinity changes; a reason may be seen in the permanent mixture during the tides. Sediments proved to be more conservative in that they preserve and reflect typical local influence like inputs from land or sedimentation of certain particle types like organics or clays that contain much, or sand that contains little, metals. Also the content of organic carbon in seston reflects its ability to sorb metals, and next to immissions and dilution with metal poor seston, organic carbon (together with clayey material) determines the metal content in seston.

Cadmium

The distribution of dissolved Cd is given for July 1980 (Figs. 9-11).

In comparison to the estuaries of the Elbe (Duinker et al. 1982a), the Varde (Duinker et al. 1980), the Schelde, Meuse and Ems (Duinker 1981), the Cd concentrations were high in the Weser Estuary. Only in the Rhine Estuary (Duinker 1981) values were higher, reaching the 2 μg Cd $\cdot$ l^{-1} level.
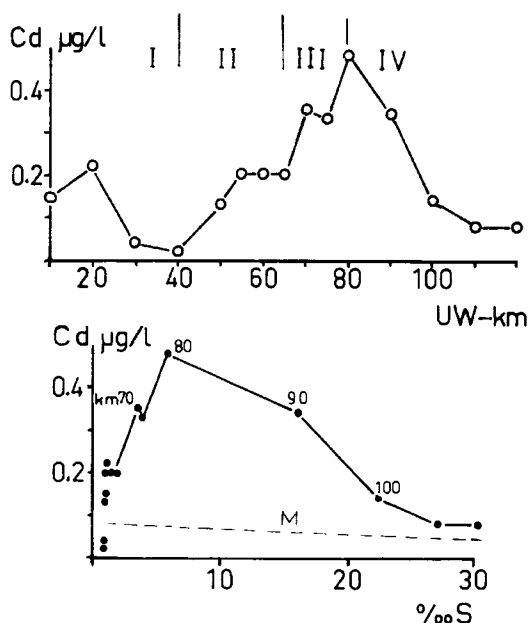
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Fig. 9:
Concentration of dissolved cadmium versus distance from Bremen and versus salinity. M refers to natural conditions (Duinker et al. 1980).

As was shown by Duinker et al. (1980, 1982a, b), a 0,05 μg Cd $\cdot$ l^{-1} level seems to characterize the natural conditions at the seaward end of estuarine water and a 0.05 to 0.1 μg $\cdot$ l^{-1} at the riverward end. A straight line (M in Fig. 9) would show conservative mixing between both ends. Elevations above this line may be supposed to mark emissions or remobilisations from sources at various locations: in the very low salinity water upstream of Brake (UW-km 40), around UW-km 50-75, and mainly around UW-km 80.

The Cd sources can be suspected to have been from the Bremen area, the Nordenham area, and the place at UW-km 80 were dredge spoil is regularly dumped. This spoil is taken by a hopper dredge to maintain the channel depth – mainly in the mud reach around the area of Nordenham. This material contains up to 30 % clay size minerals (dry weight) which contain 2 to 3 and in one sample 18 μg Cd $\cdot$ g^{-1} (Wellershaus 1981 a; Calmano et al., 1982). It is the area where all light weight particles being washed down the river accumulate before they get dredged and dumped at UW-km 80, and together with these particles metals undergo the same fate.

Another possible interpretation for the increase in concentration of dissolved Cd can be drawn from a plot versus salinity in Fig. 9 (lower graph): along the section UW-km 60-80, Cd was remobilized from upwhirled sediments by reaction with Cl^{-}-iones and formation of chloro-complexes. These Cd-Chloro-complexes where then transported downstream. Simi-
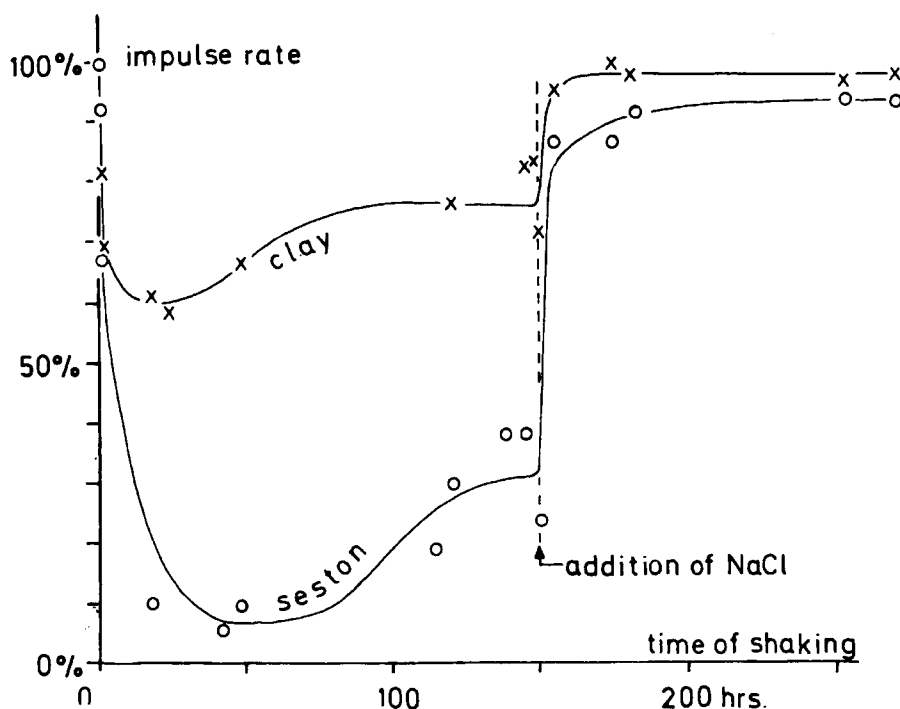
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Fig. 10: Experimental sorption of Cd by seston in fresh water and remobilisation after addition of NaCl so that a 30 ‰ NaCl solution was obtained: Cd in solution in % of initial concentration versus experimental time. The upper curve shows the behaviour in clay suspension, the lower in a natural river water suspension (after Calmano & Lieser 1981).

lar observations were made by Duinker et al. (1981, 1982a, b), and it was shown in experiments by Calmano & Lieser (1981): To study exchange processes, 109 Cd (a radio tracer) was added in solution to a suspension of clay in Main River water and to a similar sample containing natural seston. During shaking sorption and remobilization was observed by measuring dissolved Cd in water. The experiment is depicted in Fig. 10. In both samples Cd was sorbed, but more effectively by natural seston than by clay alone. The experiment was continued after addition of 30 g NaCl to 1 l water. Immediately after addition of the salt, almost all of the Cd was re-dissolved so that after some time about 95 % Cd were found in solution again.

To demonstrate the relations between particulate and dissolved Cd, the distribution coefficient K_d of Cd content in seston ($\mu g \cdot g^{-1}$) upon dissolved Cd concentration in water ($\mu g \cdot ml^{-1}$) is plotted in Fig. 11 versus salinity. K_d demonstrates transfer of this element between both phases: low K_d shows the preceding transfer into the dissolved condition – or influx of dissolved Cd – and vice versa. This figure eliminates changes in
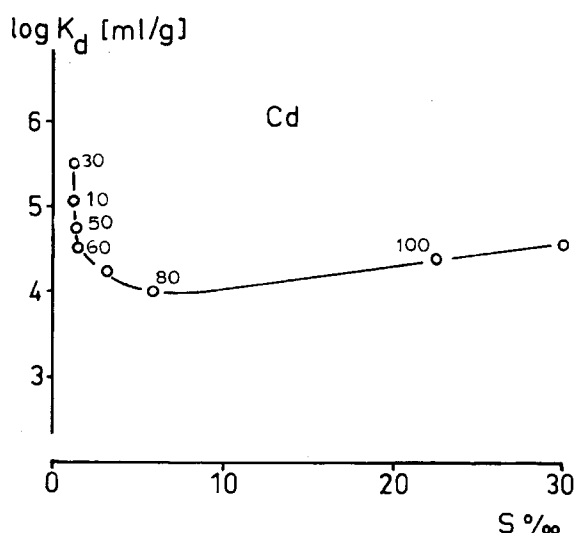
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log K_d [ml/g]

Cd

Fig. 11:
Distribution coefficient K_d [K_d is a dimensionless relation between content of metal in seston ($\mu g \cdot g^{-1}$) and concentration of metal in water ($\mu g \cdot ml^{-1}$)], July 1980.

seston concentrations. During our study K_d decreased markedly along stretches I to III with a minimum at 6 ‰ salinity which suggests that mobilization of Cd has occurred downstream of Bremen. But in the outer estuary, i. e. seaward of UW-km 80, sorption, re-precipitation, or dilution (see above) seem to be more effective. This is, however, only valid for the dissolved Cd that was released during dumping or preceding remobilization, not for the background concentration.

Chemical forms of metals in seston (Fig. 12)

To estimate the biotic effect of trace metals in the environment, their chemical form has to be known. A rough measure for the bio-availability of a certain trace metal can be obtained by a sequential extraction procedure (Calmano 1981). This was done on four seston samples in the estuarine mud reach between UW-km 50 and 80. It seems that the first and second treatment steps in this procedure are well suited for the estimation of the potential availability of metals for biochemical processes. Problems which arise with the selectivity of the extraction scheme are discussed elsewhere (Förstner et al. 1982).

In our samples two categories of metals can be distinguished:

– metals such as Cd, Zn, Mn, and Ni that have a relatively large potentially mobilizable portion, which are possibly available to organisms, and

– metals such as Cr, Cu, Pb and Fe that are more stably bound to particles so that the available portion is much smaller than in the first category.

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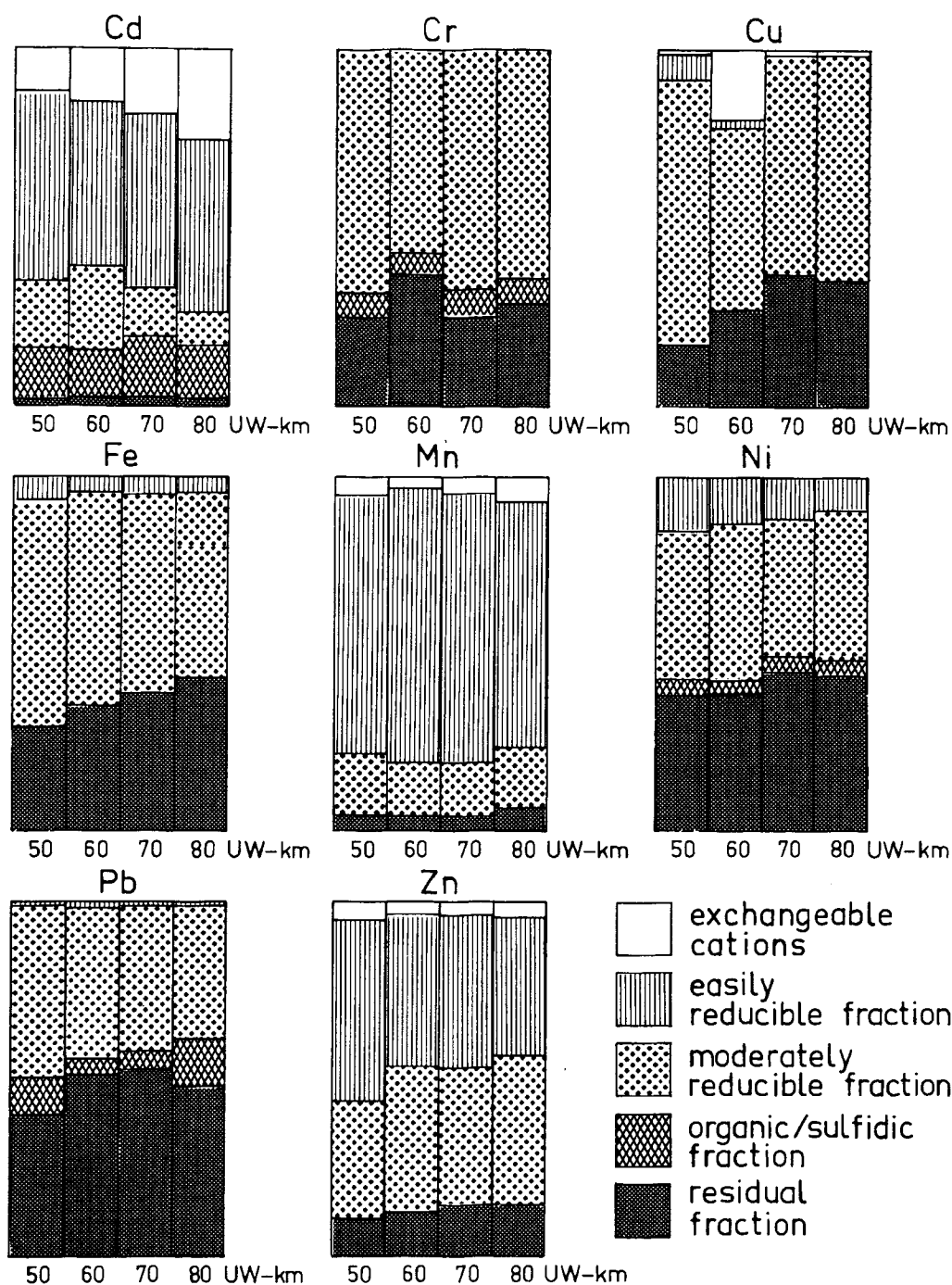
Fig. 12: Speciation of metals in seston (i. e. the particulate phase) at some stations, 22 July 1980. In each column the amount of a metal belonging to any of the fractions in percentage of the total metal amount is given. The bio-availability decreases from the upper to the lower fraction. Mn, Cd and Zn mainly occur in the highly bio-available compounds whereas the remaining metals have their predominance in the unavailable fraction.

Similar results had been found in the sediments of the Weser Estuary by Calmano et al. (1982) suggesting that chemical forms in seston and mud are roughly identical.

Cd and Zn show very similar association behaviours. They were found mostly in the easily reducible and exchangeable phases from which they, like Mn, can be released into the water under anaerobic conditions. Such conditions were regularly observed since 1973 in the mud sediment and at times also in the bottom-close water above the mud, and they can further be expected in secluded areas like small bays or channels.

It is apparent that the exchangeable portion of total Cd increased downstream (see preceding chapter) which means that the possibility of mobilization was easier at UW-km 80 than 50. At UW-km 80 the maximum of dissolved Cd may be understood by this phenomenon in addition to the basic precondition that Cd rich dredge spoil was dumped here.

Metals and water quality

The term, water quality, is used here in the sense of an organic and nutrient salt pollution criterion. The present data do not suggest definite relationships between water quality and heavy metals – neither in summer nor in winter.

When during summer oxygen concentrations in water are between 1 and 2 mg/l, suspended organic flocs may be deficient of oxygen in the enclosed water. In this case remobilization of metals – mainly Cd, Zn and Mn – can be expected. Such flocs are generated from activated sludge in the B-zone downstream of the Bremen sewage treatment plant. Flocs may be as big as 2 cm.

Conclusions

Monitoring

Above a certain concentration, heavy metals have negative effects for aquatic biota. These effects are in addition to other factors determined by their chemical form. Metals may occur sorbed to suspended particles (seston) and are, thus, transported until being deposited as muddy sediments. Therefore fluvial mud sediments are good indicators for the degree of pollution as was stated by Förstner & Müller (1974). The same is true in estuaries as was concluded from our studies.

In the Weser Estuary the transition zone between river and sea water acts as a trap for suspended matter (sand and finer particles) which then becomes mud, and, consequently, it acts as a trap for metals that are bound to these, mainly the finer particles. This can be seen from the decrease of metals in the 63 μm fraction of mud along the estuarine length: high values closer to the source, smaller values closer to the sea. As accumulation of heavy metals in mud is probable (in addition to accumulation of mud in the estuary), more metals should enter the estuary than leave it towards the sea, otherwise the curves in figure 5 would not have a decreasing gradient in seaward direction. A part of the mud in the transition zone is temporarily upwhirled, transported and precipitated again by the tidal currents. The upwhirled sediment renders the water turbid and creates the typical turbid zone (turbidity maximum) in many estuaries (Wellershaus 1981 a, 1982) and it may contribute to dissolvedmetal-compounds in water (Duinker et al. 1980, 1982 a, b; our results).

Excess amounts of the trapped mud are dredged out to keep the channel clear for ship traffic. It is difficult to find suitable places to deposit the dredge spoil because it contains heavy metals and possibly other persistent toxicants in greater than natural concentrations. In some estuaries the spoil is disposed on land (where permanent control is easy) or in the sea. The Weser spoil is normally dumped near UW-km 80. The sudden encounter of some compounds with new milieu conditions seems to set cadmium free and to render it available for organisms.

It remains difficult to estimate how much metals are transported to the sea. To obtain reasonable data a series of further research will be needed: behaviour of seston and adhered metals during tidal processes (erosion, sedimentation, mixing etc.); variation of metal concentration in course of at least one year; sources of metals; sinks; loss to the Wadden Sea etc.

From experimental studies on differentiation of chemical forms it can be concluded that only a certain portion of the total amount of a metal is bio-available, another portion seems not to be dangerous. Therefore one has no real possibility to say anything about the biotic effects of an element by measuring only its total concentration in water – particulate plus disolved. To give the opportunity to compare both methods of monitoring, Fig. 13 shows concentrations of both phases of Cd in water.

In a monitoring programme the following should be examined with respect to metals:

separately the dissolved and the particulate phase;

water and sediments;

chemical forms and their bio-availability under
environmental conditions such as pH, EH, chlorinity,
sedimentation – erosion, electrical charge of seston
particles, seston composition etc.

During our study Cd and Zn in seston seemed to be relatively available by
almost their total amount whilst Cr, Cu, Ni and Pb by only a minor por-
tion were reactive. It seems, therefore, important for any assay of the tox-
ic effects of heavy metals in suspension to measure separately a bio-che-
mically reactive and an inert fraction of metallic compounds.

In the estuarine mixing and turbidity zone – and perhaps also in guts of
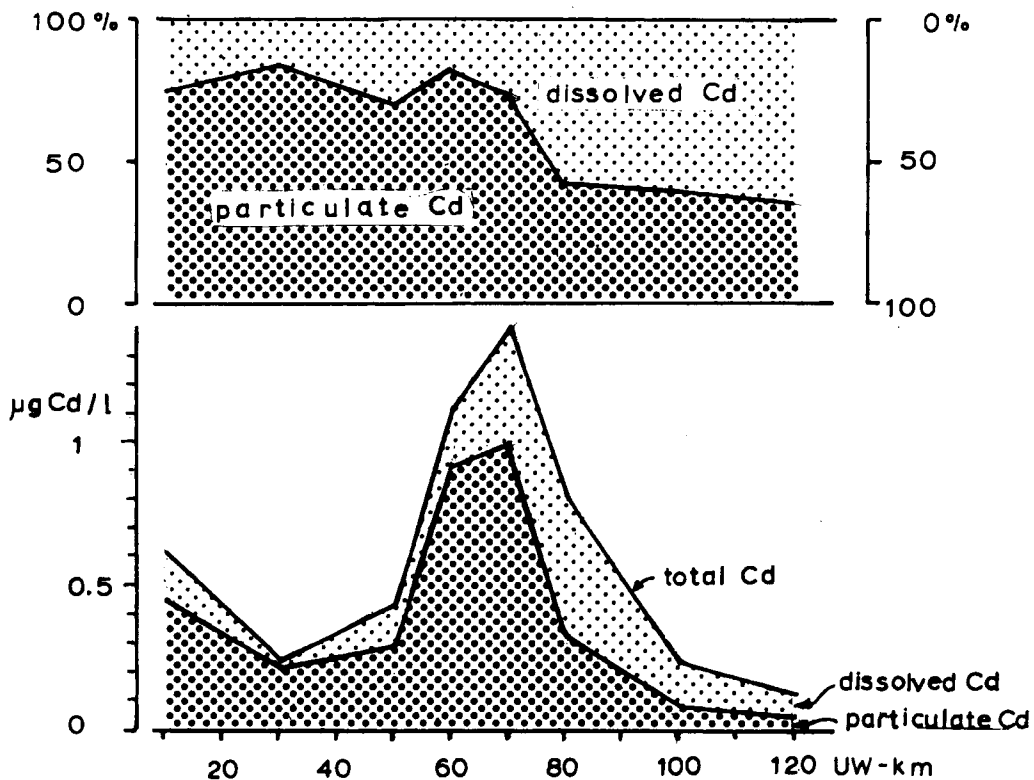animals – under certain conditions changes between the dissolved and

Fig. 13: Longitudinal section in the Weser Estuary, 22 July 1980: dissolved and
particulate Cd in water. Measuring total Cd alone gives little information,
because relations between the dissolved and the particulate phase change
according to milieu changes. The peak around UW-km 65 is caused by
maximum seston concentration (turbidity maximum, Wellershaus
1981a, 1982) rather than by chemical changes.

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the particulate phase take place so that measuring one phase does not necessarily give information about the other. Both phases behave differently during their passage through an estuary. For monitoring transport of heavy metals in estuaries and their effects on living systems, it is essential for both reasons mentioned above that the dissolved phase and the particulate phase be measured separately. This should at best be done at the upstream end of the fourth stretch since in this stretch no essential changes seem to take place – if no additional disturbances like artificial sources occur – and since at its upstream end concentrations of river borne metals are highest. Parallel measurements of salinity supplys an indicator for mixture so that the riverine concentration plus or minus changes in the estuary can be estimated. In the Weser, however, this method is difficult to apply because of an important drawback: the unknown transport to and from the neighbouring Wadden Sea ("Watt" in Fig. 1).

Cadmium is especially important because very low concentrations are toxic, and it is easily remobilizable. As was already shown by Millward (1980), the smallest increase of salinity in water will hinder sorption of dissolved Cd by iron (III) precipitates. This may be different in relatively clean estuaries like the Varde Aa, where Duinker et al. (1980: p. 250) observed sorption of Cd, Zn and Fe by upwhirled clayey sediments. But the Weser is not clean and therefore the conditions seem to be more complicated than under natural conditions.

Synthetic complexing agents – possible effect

As long as metals are bound to particulate matter – seston or sediment – their bio-availability is low (Fig. 12, and Calmano et al., 1982). However, remobilization, i.e. transfer into dissolved compounds, renders them available. Re-mobilization may among other factors be caused by complexing agents like nitrilotriacetic acid (NTA). The latter is planned to substitute phosphate in detergents. The U.S. Environmental Protection Agency no longer objects the use of NTA. But it still remains unclear how far NTA or its decomposition-products will involve re-mobilization of heavy metals from muds in rivers, estuaries or coastal areas where they were accumulated, or will hinder sorption of dissolved metals on particles. There are, for instance, indications that a relatively stable Cd-NTA-complex is formed in sewage-sludge under increased NTA-concentrations (Förstner 1981).

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The effects of NTA-concentrations in rivers will have to be examined under various environmental conditions (pH, redox conditions, hardness of the water...) and for relevant chemical forms of the metals.

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