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TRACE METALS IN WATER AND SUSPENDED MATTER IN THE SOUTHERN BIGHT (COPPER, ZINC, MANGANESE AND IRON)

by

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I. Introduction

From 1971 onwards, trace metals in water, particulate matter and bottom sediments have been determined during a number of cruises, for the river Rhine and its estuarine region, the Southern Bight and the Dutch Wadden Sea in order to establish their input, transport and fate. After a few initial surveys including Cd, Ni, Zn, Cu, Cr, Fe,Mn, copper and zinc have been selected as the elements for a closer investigation on the basis of their concentrations and possible ecological significance. Results for the Dutch Wadden Sea are in press (DUINKER, VAN ECK & NOLTING, 1974); this contribution describes the results of one recent cruise in the Southern Bight, the main characteristics that have been found in the results of the other cruises being similar to the ones described here.

II. Methods

The samples were obtained during a JONSDAP cruise in October 1973; the sampling stations are indicated in Fig. 1. The stations are situated in a number of series off the coast: I off IJmuiden, II off the river Rhine, III off the river Scheldt, IV off Oostende and V in the Straits of Dover; a number of intermediate stations is included in the total number of 81 sampling stations. Surface samples were obtained with a polypropylene bucket, bottom water samples (1-2 meter above the sea bed) with a PVC water sampler. The samples were filtered on board ship in a perspex filtering unit under pressure (3-4 atm) through 0.45 µm pore size millipore filters that had been pretreated with 6 N HCl overnight and dried at 70° C until constant weight.

Particulate matter on the filter was dried at 70° C, the filtered samples, by definition containing the "dissolved" species were frozen and kept at -20° C for analysis in the laboratory.

Dissolved copper and zinc concentrations were determined by atomic absorption spectrometry (Perkin-Elmer 403) after complexation and extraction using the APDC-MIBK procedure of BROOKS, PRESLEY & KAPLAN (1967). The dried filters were weighed and ashed in a low temperature singulet oxygen asher (Tracerlab). The residues were leached with 0.1N HCl during 18 hours (DUINKER ET AL., 1974), the leached concentrations were determined by AAS directly. The fraction of the total amount of metal in the particulate matter is more or less constant for Cu, Zn and Mn being 100, 80 and 90%

respectively; the fraction for iron varies between 50 and 70%.

III. Results

Dissolved species. The concentrations of dissolved zinc and copper are represented in Fig. 2a and 2b. The values for zinc in the series off IJmuiden are considerably higher than those in the other series: the highest values (30 $\mu g.l^{-1}$) have been measured in samples taken near the coast in the series off IJmuiden and the river Rhine. The values for the Straits of Dover are, on an average, 50% higher than in the central part of the Southern Bight in the series II, III and IV, where the values range from 4-8 $\mu g.l^{-1}$. The values upstream (outside the region described here) for the river Rhine are higher than for the river Scheldt. The concentrations of dissolved copper are relatively high in the Straits of Dover compared to the Central part of the Southern Bight, the values increase toward both the Belgian and English coast. The river values for both the Rhine and Scheldt are only slightly higher than for the central part (around 5-6 compared to 3-4 $\mu g.l^{-1}$). Near-bottom values are very much similar to surface values. The data do not show a linear correlation between the concentrations of dissolved copper and zinc and the salinity data although the higher values occur in the samples with lower salinity.

Particulate metals. Fig. 3 shows the contours of the distribution of suspended matter in $\mu g.l^{-1}$; the amounts of leacheable metals (Cu, Zn, Mn, Fe in $\mu g.l^{-1}$) are represented in Fig. 4.

The lowest values for zinc are in the central part (1-2 $\mu g.l^{-1}$). Values in the Straits of Dover and in between these two regions are slightly higher (2-4 $\mu g.l^{-1}$). Values in the eastern part and in the IJmuiden series are considerably higher (up to 13 $\mu g.l^{-1}$). Values in the Rhine decrease toward the sea from 64 to 14 $\mu g.l^{-1}$; Scheldt values are lower (5-12 $\mu g.l^{-1}$).

Copper values in the Straits of Dover are similar to those in the central part (1-2 $\mu g.l^{-1}$), with values toward the English coast slightly higher (2-3 $\mu g.l^{-1}$). Values along the Dutch coast in the series off IJmuiden and the Rhine are higher (2-5 $\mu g.l^{-1}$). Rhine concentrations decrease from 14 (upstream) to 7 $\mu g.l^{-1}$ at the river mouth; Scheldt concentrations are lower (decreasing from 4 to 1 $\mu g.l^{-1}$).

Manganese values in the central part of the Straits of Dover are similar to the ones in the central part of the area studied (0.5-1 $\mu g.l^{-1}$), they increase toward the coast (3-6 $\mu g.l^{-1}$). The values along the eastern coast are very much higher (5-50 $\mu g.l^{-1}$). River values vary from 20-30 $\mu g.l^{-1}$ for the Rhine, and from 20-65 $\mu g.l^{-1}$ for the Scheldt.

Leacheable iron values are more or less constant in the region around the axis of max. salinity (10-20 $\mu g.l^{-1}$) with higher values to the east and west, with extreme values along the Dutch coast, up to 270 $\mu g.l^{-1}$.

The values for the river Rhine within the area studied decrease from 700 to 280 toward the sea, values for the Scheldt vary in the range 170-300 $\mu g.l^{-1}$.

It has been established both for copper and zinc that there is no clear correlation between the amounts of metal in the suspended matter and in the dissolved state per unit volume when comparing these data for all the individual sampling stations. For any individual sample, however, the amount of dissolved copper or zinc is larger than the amount that can be leached from the particulate matter per unit volume of seawater; it is also larger than the total amount of particulate metal. The differences within the samples in the Rhine and IJmuiden series are larger (3-9 $\mu g.l^{-1}$ for Cu and 3-29 $\mu g.l^{-1}$ for Zn) than for the other series (2-4 $\mu g.l^{-1}$ for Cu, 4-7 $\mu g.l^{-1}$ for Zn), the largest differences occurring in the samples close to the coast. The highest values for the sum of these quantities, being a measure of total metal per liter of seawater, including the particulate fraction, are found along the coast:

for zinc in the series I through V: 44, 40, 11, 17 and 10 $\mu g.l^{-1}$, and for copper 15, 10, 5, 10 and 6 $\mu g.l^{-1}$.

Table I summarizes the ranges of dissolved and particulate (leacheable) metal in μg metal per liter of seawater, including the corresponding results of DUTTON, JEFFERIES, FOLKARD & JONES (1973) for comparison.

Additional information on the transport of metals in the particulate fraction may be obtained by considering the concentration of metals in the particulate matter on a weight per weight basis.

In Fig. 5 the ranges for leacheable Mn in μg per g dry particulate matter ($\mu g.g^{-1}$) have been indicated. On this basis it is possible to distinguish four regions: I, representing the central part with more or less constant Mn values of 200-300 $\mu g.g^{-1}$; II, where values (350-1000) are intermediate between the values of the Scheldt, Straits of Dover and the central part, III with higher values than the central part and IV with high values, up to 2000 $\mu g.g^{-1}$, the ones for samples taken close to the coast being much higher than the values in any of the adjacent regions. In the data for all the series a steady increase in manganese concentration toward the coast is observed, to a level of 1300 and 2000 in the Rhine and IJmuiden series respectively. The levels within the Rhine estuary increase toward the sea from a practically constant value of 700 $\mu g.g^{-1}$ upstream to 1100 $\mu g.g^{-1}$ in the area studied. In the Scheldt estuary a steady decrease toward the sea is observed from 1600 to 1000 $\mu g.g^{-1}$. Copper and zinc concentrations show a different pattern. Here, concentrations show a broad (and high) maximum in all the series at around the 3rd to 5th station from the coast, decreasing to lower values on both sides. These lower levels at the stations closest to the coast are highest for the Rhine and IJmuiden series (200-300 $\mu g.g^{-1}$ for copper compared to 100-150 $\mu g.g^{-1}$ for the other series and 600-2000 $\mu g.g^{-1}$ for zinc compared to 200-400 $\mu g.g^{-1}$ for the other series). The maxima that occur offshore in the different series are 350-1100 for copper (the highes value in the Straits of Dover) and 2000 for zinc (Straits of Dover and off IJmuiden), the maxima for Zn in the other series being lower (600-1100 $\mu g.g^{-1}$). The concentration of particulate leacheable copper decreases within the Rhine estuary from a constant 400 to 200 $\mu g.g^{-1}$, Zn concentrations decrease from 2200 to 700-900 $\mu g.g^{-1}$. For the Scheldt a similar decrease is observed, from 90 to 40 $\mu g.g^{-1}$ for copper, and from 260 to 230 $\mu g.g^{-1}$ for Zn. The Scheldt values differ appreciably from the values obtained during other cruises.

Iron shows more or less constant values (0.4-0.7%) except for samples close to the coast in series I, II and III with values of 1-2%. Table II summarizes the levels of leacheable metals in suspended matter that have been determined for the river Rhine (upstream, including data of other cruises), the coastal region and the central part of the Southern Bight, including the changes that occur in the estuarine region of the rivers.

IV. Discussion

The metal concentrations in the central part of the area studied here may be considered as "oceanic" levels. The amounts of copper, zinc, iron and manganese in the suspended matter (per unit volume) and the concentrations of copper and zinc in the dissolved state increase toward the coast.

The result of this contribution may be compared with results of DUTTON, JEFFERIES, FOLKARD & JONES (1973) obtained in the same area for a number of metals among which copper, zinc and manganese. Relatively high dissolved zinc values in the Straits of Dover that they report are also found in the present work; their data for other stations are significantly lower than the present ones (up to 30 $\mu g.l^{-1}$). The present values for dissolved copper contrast even more with the results of DUTTON, JEFFERIES, FOLKARD & JONES (1973), reporting a maximum value of 2 $\mu g.l^{-1}$ for the Southern Bight, observed in the Straits of Dover; present values range from 3-8 $\mu g.l^{-1}$, the highest value for the area studied being 12 $\mu g.l^{-1}$. Our results are however considerably lower than those reported by our Belgian collegues (MODÈLE MATHEMATIQUE, 1972).

The differences that exist in the results of different groups (Brussels, Lowestoft and Texel labs) may be partly due to the different pore size of the Millipore filter being used (0.8, 0.22 and 0.45 µm, respectively).

During 1973 and 1974 samples have been exchanged several times; it is hoped that the reasons for the existing discrepancies will be evaluated during a two-weeks period of close cooperation this autumn.

A clear relationship between the concentrations of either copper or zinc in solution and in the particulate fraction could not be established. DUTTON, JEFFERIES, FOLKARD & JONES (1973) came to the same conclusion. In the present work a relationship between the amount of metal in the particulate fraction and the proximity to the coast is found.

Although an influence of the Rhine/Meuse and Scheldt river systems on the metal levels in the coastal region has been established, a number of details in the particulate matter metal levels are not quite understood yet. The intensive sedimentation of particulate matter (both of fluviatile and marine origin) in the mouth of the river Rhine and consecutive dredging and dumping operations, together with the estuarine circulation processes have to be taken into account. The properties (particle size and metal content) of fluviatile suspended matter changes under influence of the mixing of fresh water and seawater; erosion of particles from the bottom may bring into suspension particles with metal content different from the levels before deposition. Suspended copper and zinc on the one hand and manganese on the other hand show different types of behaviour on their way from the water of the river Rhine to the sea. The relatively low copper and zinc concentrations at the coastal stations in all the series may be due to the contribution of heavy particles with low metal content that have been brought into suspension by wind and current action (DUINKER, VAN ECK & NOLTING, 1974). These authors have also shown that suspended matter may be enriched in metal content from high levels of dissolved metals in the interstitial water of the bottom sediment.

Recently, high manganese concentrations have been found in interstitial water samples in the Rhine estuary. The high manganese concentrations in the suspended matter of the stations along the coast, in particular off the Rhine and IJmuiden, may be due to a contribution from bottom material or through formation of particles from dissolved species.

EISMA et al. (1966) have found a tongue of iron-rich sediment off Scheveningen, the iron being present as coatings on sand grains. A similar process of mobilization and consecutive adherence to particulate matter may also apply to manganese. DE GROOT (1964; 1973) in his studies on metals in sediments has considered manganese as being not mobilized in the estuary.

These aspects will be studied in more detail in the near future.

Values for the amounts of metals transported by the river Rhine and through the Straits of Dover, have been obtained (Table III) under the assumption that the amounts of water entering the North Sea can be approximated by the values 70 and 4000 km^3 per year; the concentrations reported in this work are of the correct order of magnitude over the time period considered.

The present findings of the increased levels of metals in the Dutch coastal water are consistent with the data of Table III.

V. Summary

Metal concentrations (copper, zinc, and for suspended matter also manganese and iron) in Dutch coastal water per unit of volume seawater are found to be increased by the input of the river Rhine.

The amounts of copper and zinc present in the dissolved state are larger than the amounts present as leacheable fraction in the particulate matter per unit volume. The difference between the two quantities for any individual sample increases toward the coast. High concentrations of particulate copper and zinc on a weight per weight basis are found in the offshore samples of the Southern Bight, being much higher than the levels in coastal areas and in the river Rhine.

The amounts of Cu and Zn transported into the Southern Bight through the Straits of Dover are much larger than through the river Rhine. The amounts of both Fe and Mn are roughly of the same order of magnitude.

Maximal values in the Southern Bight for zinc are 44 $\mu g.l^{-1}$ and 15 $\mu g.\ l^{-1}$ for copper, including dissolved and leacheable particulate states.

VI. References

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TABLE I

Range of dissolved and particulate metal concentrations in $\mu g.l^{-1}$; the number of observations are in brackets.

		Surface		Bottom	
		present work	DUTTON et al	present work	DUTTON et al
Zn	particulate	1-13 (66)	3.9-16.3(38)	4-50 (44)	4.1-25.5(13)
	dissolved	3-30 (66)	0.8-12 (42)	5-25 (44)	1.4-8.9 (15)
Cu	particulate	0.5-5.8(66)	0.1-8.9 (39)	1.5-26.5(44)	0.2-2.6 (13)
	dissolved	3-12 (66)	0.3-2.0 (42)	3-13 (44)	0.5-3.0 (14)
Mn	particulate	0.5-50 (66)	0.1-27.0(39)	0.5-110 (44)	0.2-50.2(13)
Fe	particulate	5-260(66)	—	5-750 (44)	—

TABLE II

Metal concentrations in the particulate matter in µg.g^{-1} (ppm). River data: arrows indicate a regular change from the river (upstream) in the direction of the sea. Coastal data: arrows indicate regular change away from the coast.

		Cu µg.g^{-1}	Zn µg.g^{-1}	Mn µg.g^{-1}	Fe %
Rhine (till Rotterdam)		400→200	2200→700-900	700→1100	2.2→1.7
Scheldt		90→40	260→230	1600→1000	1.3→0.8
(till Klooster-zande-Kruiningen)		irregular	increases with other cruises		
Coastal zone					
series	I	200-300	600→2000	2000→300	1.0→0.5
	II	250	700→1100	1300→400	1.5→1.9
	III	100-150	200→250	1000→600	1.0→0.8
	IV	100-200	200→300	800→600	0.6 - 0.7
	V	150	200→500	600	0.4 -- 0.5
Central part (maximal values)	I	900	2000	↕ 200-400	↕ 0.4-0.7
	II	850	600		
	III	350	600		
	IV	850	1100		
	V	1100	1800		

TABLE III

Supply of some selected trace elementsby the river Rhine and the Straits od Dover to the Southern Bight under the assumptions given in the text.

	River Rhine		Straits of Dover		Ratio Rhine:
	$\mu g.l^{-1}$	tons $year^{-1}$	$\mu g.l^{-1}$	tons $year^{-1}$	Str. of Dover
Zn particulate	60	4200	1	4000	1:1
dissolved	45	3100	10	40000	1:13
sum (total)	105	7300	11	44000	1:6
Cu particulate	14	980	1	4000	1:4
dissolved	6	420	6	24000	1:60
sum (total)	20	1400	7	28000	1:20
Mn particulate	20	1400	0.5	2000	1:1.5
Fe particulate	700	49000	20	80000	1:2

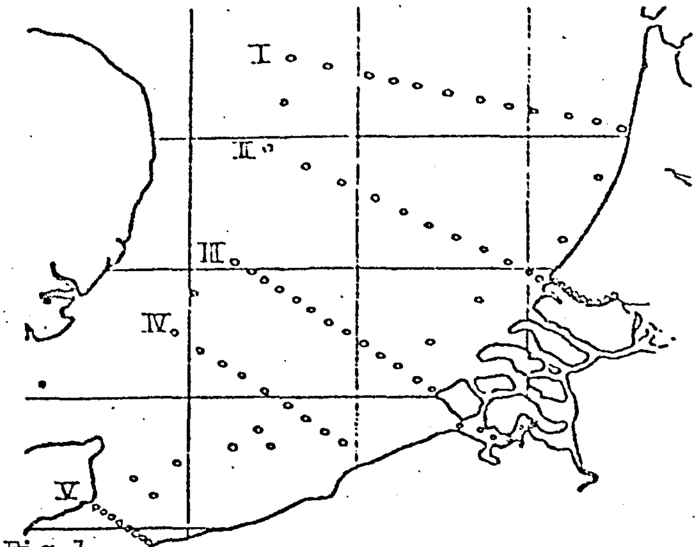

Fig.1.
Net of sampling stations.Series I:off Ymuiden;II:off the river Rhine;III:off the river Scheldt;IV:off Ostend;V:Straits of Dover.

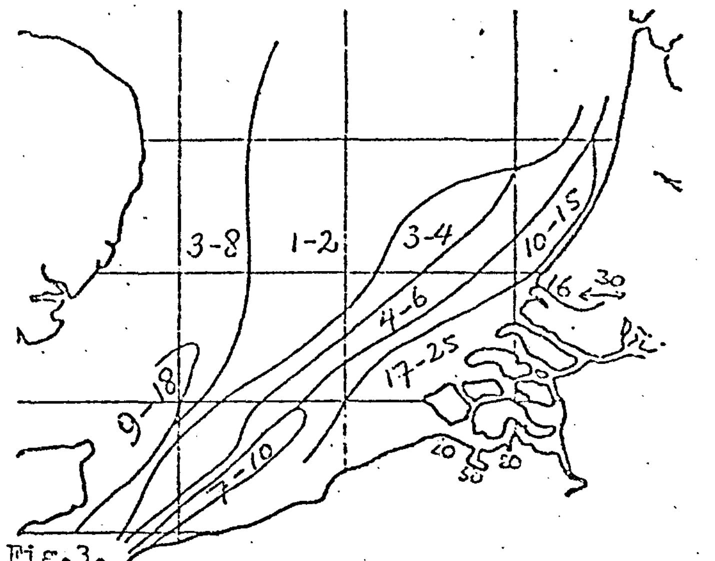

Fig.3.
Weight of suspended matter obtained after filtration through 0.45 μm pore size Millipore filters,in mg per liter.

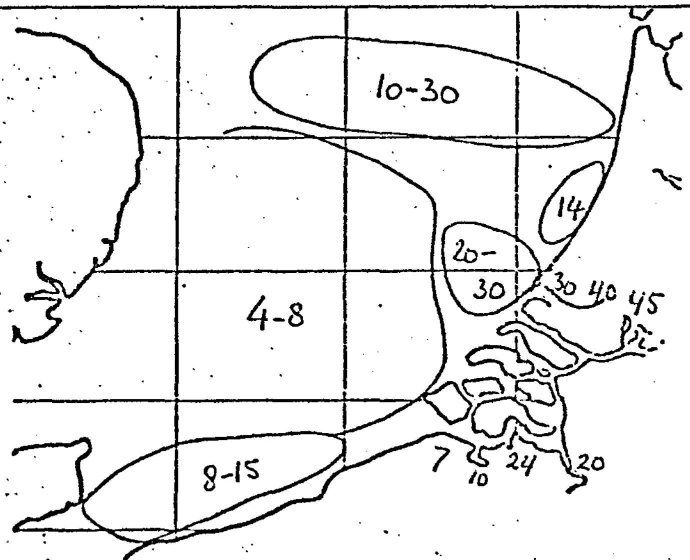

Fig.2a.
Dissolved zinc concentrations in μg per liter.

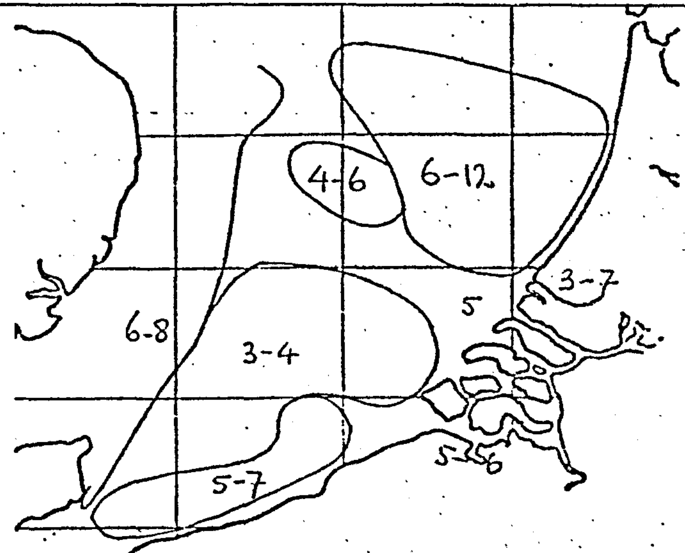

Fig.2b.
Dissolved copper concentrations in μg per liter.

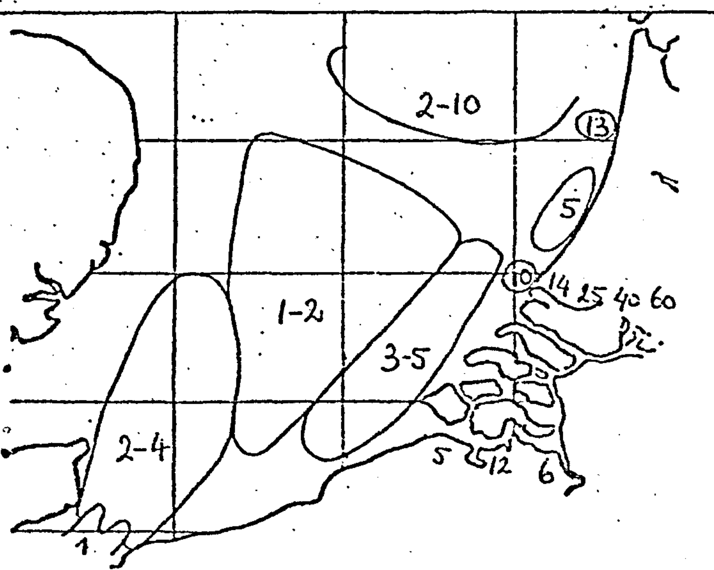

Fig.4a.
Particulate leacheable zinc concentrations in μg per liter.

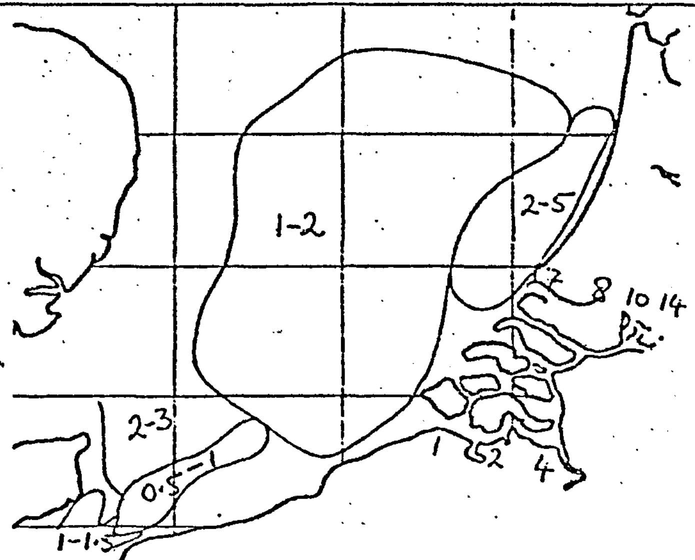

Fig.4b.
Particulate leacheable copper concentrations in μg per liter.

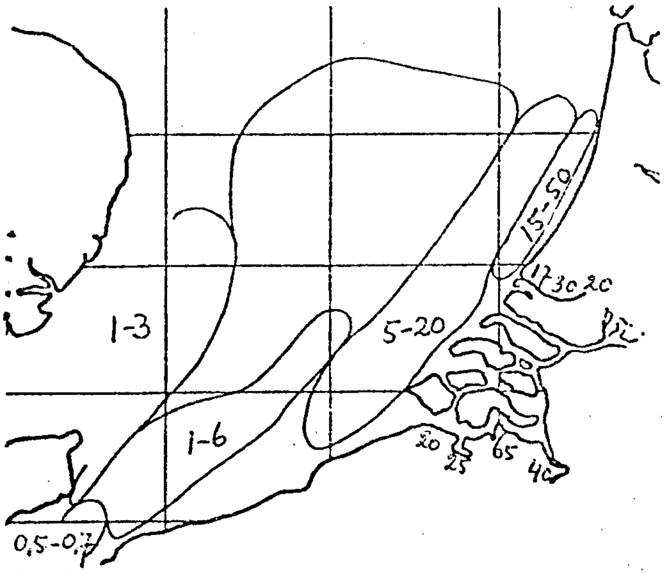

Fig.4c.
Particulate leacheable manganese in µg per liter.

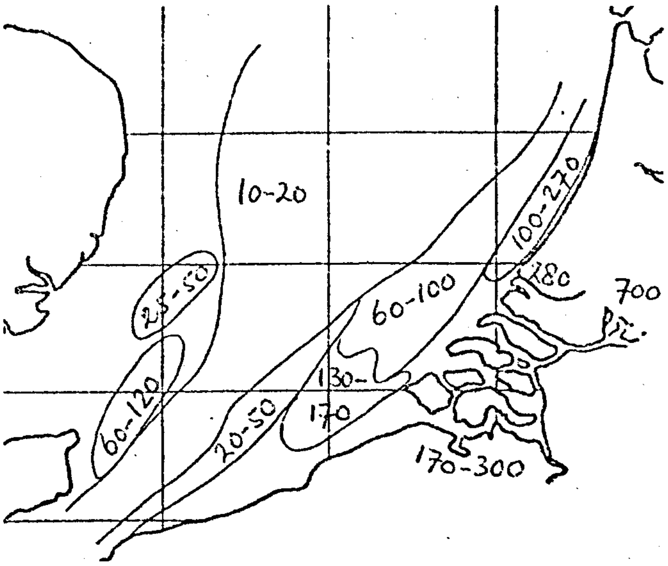

Fig.4d.
Particulate leacheable iron in µg per liter.

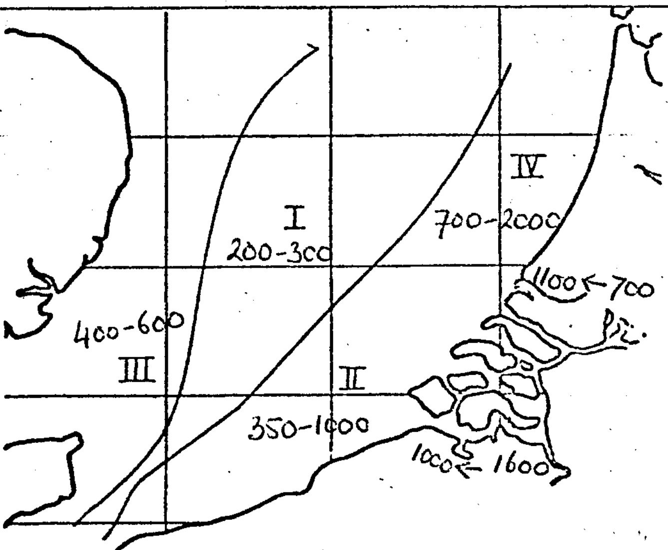

Fig.5.
Different regions with different characteristic particulate leacheable manganese concentrations in µg Mn per g.