

## A COMPARATIVE STUDY OF TOXIC TRACE METALS IN THE ESTUARIES OF THE OOSTER AND WESTERSCHELDT AND OF THE SIERRA LEONE RIVER

P. VALENTA, H. W. NÜRNBERG, P. KLAHRE, H. RÜTZEL, A. G. A. MERKS\*  
AND S. J. REDDY\*\*

*Institute of Applied Physical Chemistry, Nuclear Research Centre (KFA)  
Juelich, Federal Republic of Germany*

### ABSTRACT

Behaviour of the toxic heavy metals Cd, Pb and Cu was studied in the tropical Sierra Leone estuary and the European Ooster - and Westerscheldt estuaries during two seasons with different biological activities. In addition to trace metal levels in the dissolved state and bound to the particulate matter, the salinity and the chlorophyll content were determined.

Investigations in the Oosterscheldt estuary and in the Sierra Leone estuary were performed at several stations on a single day during low tide from the sea into the estuary and the relationship between the metal content and the salinity was determined. In the unpolluted Sierra Leone estuary the metal content is of geological origin and is brought with fresh water into the estuary. Whereas for Cd conservative mixing takes place, Pb is partly deposited in the estuary and Cu is slightly released from the estuary. In the Oosterscheldt estuary polluted fresh water from the Rhine river is the source of the Cd, Pb and Cu in the estuary. While all these metals are partly deposited in the estuary, their removal from the water column is much more efficient in summer than in winter. This is attributed to much more efficient removal of trace metals by the phytoplankton detritus in the season of high biological productivity. The distribution of Cu, Cd and Pb is similar in all studied estuaries. Cu and Cd are preferentially present in the dissolved state whereas Pb is almost exclusively bound to particulate matter.

*Key-Words* : Toxic metals, tropical estuaries, voltammetry.

### INTRODUCTION

Toxic trace metals unlike the major constituents of sea water are not conservative but go through biogeochemical cycles. They are biologically non-degradable and tend to accumulate in marine organisms. Most of these toxic trace metals accumulated at various trophic levels of the marine food webs are cycled back to the terrestrial environment and create potential hazards for man (Venugopal and Luckey, 1978) and many of the organisms of the marine biota (Bernhard and Zattera, 1975). The relatively shallow waters of coastal zones and estuaries are particularly vulnerable to such hazards since they are predominantly subjected to continuous inputs from polluted rivers and coastal waste water outlets. These areas are an important part of the marine environment with usually large biological activity and productivity.

\* Delta Institute for Hydrobiological Research, Yerseke, The Netherlands

\*\* Department of Chemistry, Sri Venkateswara University, Tirupati, India

In estuaries and coastal waters, with respect to ecotoxicological significance, Cd, Pb, Hg, Ni and also Cu, Zn and others are of interest. Reliable data on the levels, behaviour, fate, species and distribution of these toxic metals exist for European and tropical estuaries to only a very limited extent. This is mainly so because of the methodological difficulties encountered in sampling, sample pretreatment and the analytical determination itself, as the toxic metals exist and act in the aquatic systems and organisms at the trace level. Particularly low levels of toxic trace metals are encountered in the dissolved state functioning as the medium for the transfer of the metals from the sediments and particulate matter to the organisms.

In the past, the most serious errors in the analyses of trace metals in aquatic samples have occurred in the sampling step itself and also due to unsuitable sample pretreatment. Therefore, new, efficient methods of sampling and sample pretreatment have been elaborated and applied (Mart 1979, 1982). A prerequisite for a meaningful study of the toxic trace metal levels in estuarine ecosystems is a reliable sampling procedure as well as reliable analytical methods.

Voltammetry provides an excellent approach in sampling and sample pretreatment procedures, with high reliability (Nurnberg, 1982). Differential pulse anodic and cathodic stripping voltammetry at the hanging mercury drop electrode and the rotating mercury film electrode has proved to be a powerful analytical tool for determining the concentrations of many toxic metals like Cd, Cu, Hg, Ni, Pb, Tl, Zn etc. in the sea (Mart, Rutzel, Klahre, Sipos, Platzek, Valenta and Nurnberg, 1982), estuarine, riverine, rain water (Nurnberg, Valenta and Nguyen, 1982) and aquatic organisms. Here a comparative study on the levels of the toxic trace metals Cd, Pb and Cu in two European estuaries and a tropical estuary of West Africa is presented. Two seasons were taken into account with respect to differences in the biological activity: the rainy and dry season for the Sierra Leone estuary and the summer and winter season for the Ooster and Westerscheldt estuaries.

#### MATERIALS AND METHODS

Voltammetric measurements were carried out with a PAR polarographic Analyzer, Model 174A, connected to a Hewlett-Packard X-Y-recorder, Model 7004B. The voltammetric cell, made of Pyrex glass, was equipped with three electrodes. For concentrations above about 100 ng/kg, the working electrode was a conventional hanging mercury drop electrode Metrohm E410. In the lower concentration range the more sensitive rotating mercury film electrode (formed in situ on a glassy carbon substrate) was used (Mart, Nurnberg, Valenta, 1980a). The auxiliary electrode was a Pt-coil, and, as a reference electrode a saturated Ag/AgCl electrode of our own construction was connected to the cell by a salt bridge filled with 1 M KCl, Merck, Suprapur. Before the measurements the solutions were deaerated by bubbling with pure nitrogen

(99.999 %). During measurement, the inert atmosphere over the solution was maintained by flushing with nitrogen.

In the Sierra Leone estuary pH was measured with a portable pH-meter, Horiba, combined with a conductivity and temperature measuring device. In the Ooster and Westerscheldt estuaries, pH was measured with a pH-meter, Orion Model 701, and an Ingold glass electrode, type 401 NS. Conductivity was measured with a conductivity meter, Radio-meter, type CDM 3. Chlorophyll content was determined fluorometrically.

Samples were filtered in a Sartorius device, SM 16511, through a 0.45  $\mu\text{m}$  membrane filter of 47 mm diameter. Ashing of suspended particulate matter of organic origin including organic surface films on inorganic particles and of carbonate particles was performed at low temperature (150°C) by a microwave induced oxygen plasma in either a low temperature asher, LTA-600, or an LTA-device. The blank values of the ashing procedure were (in ng/g): 2.5 Cd, 50 Pb and 60 Cu.

All reagents were Merck, Suprapur. Standard solutions contained 1 g/l of Cu, Cd and Pb respectively and were prepared from Merck, Titrisol, in ultrapure deionised water from a Milli-Q-system. The blank values of the ultrapure water were (in ng/l) 0.1 Cd, 1 Pb and 5 Cu. These low blank values permitted the use of ultrapure water as a reference for evaluating remaining contamination. Polyethylene sampling bottles, membrane filters and polyethylene tips of Eppendorf micropipettes were cleaned by procedures described in detail elsewhere (Mart, 1982).

Only surface water (0.5 m depth) was collected. Samples were collected manually from the front of the bow of the boat by means of a precleaned 250 ml polyethylene sampling bottle attached to a telescopic bar (Mart, 1979). The risks of contamination by the boat were further minimized by moving upstream during the sampling. Within hours of sampling, suspended particulate matter was separated by filtration through 0.45  $\mu\text{m}$  membrane filter. In order to avoid contamination, the filtration was performed under slight nitrogen pressure in a closed device (Mart, 1982). The filtered solution was then acidified to pH 2 with HCl. Subsequently, it was UV-irradiated by photolysis to decompose inert complexes of trace metals with components of dissolved organic matter and surface active substances which tend to block the electrode surface and interfere the voltammetric determination of trace metals. The filters with the suspended matter were subjected to low temperature ashing in an oxygen plasma produced by microwave excitation and the ash was dissolved in HCl. Filters with the particulate matter were stored in a plastic dish protected by a polyethylene bag at - 4°C while the filtered water sample was acidified to pH 2 and stored freeze dried at - 20°C.

The content of Cd, Pb and Cu was determined simultaneously in the filtrate and in the analyte from digested suspended matter by differential pulse anodic stripping voltammetry at the rotating mercury film electrode (Mart,

Nurnberg, Valenta, 1980a). Fig. 1 shows a typical voltammogram. The evaluation of the trace metal concentrations was carried out by standard additions. Total metal load of water is obtained by adding the concentrations of the respective metal in the filtrate and in suspended matter.

## RESULTS AND DISCUSSION

### *Sierra Leone river*

The Sierra Leone river is the estuary of the Rokel river (Fig. 2). The region of tidal influence extends from the Atlantic Ocean into the Rokel river over a total length of about 60 km. The depth in the centre of the river, used for shipping, fluctuates seasonally between 7 and 30 m, the average being 9 m.

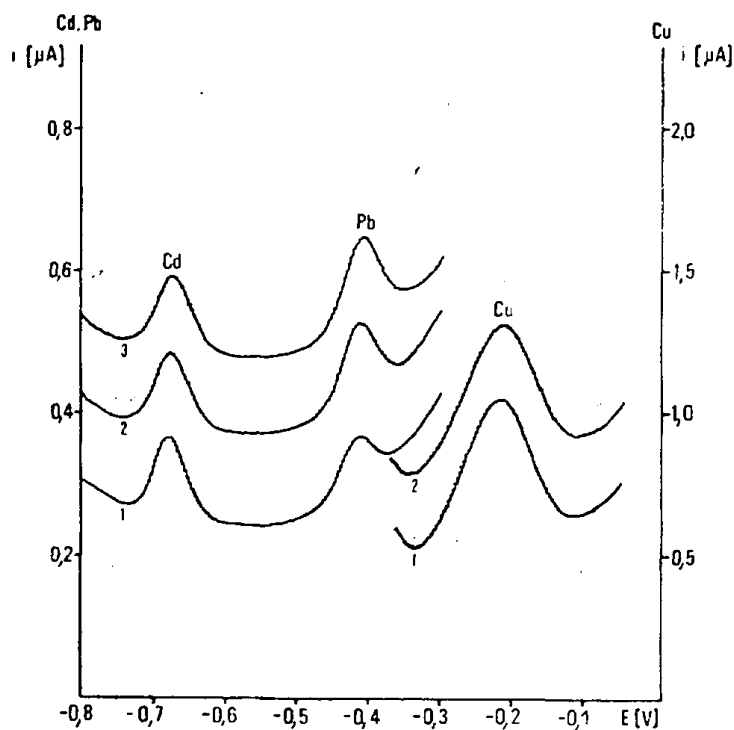


Fig. 1. Voltammogram of the simultaneous determination of Cd, Pb and Cu in the Sierra Leone estuary (sampling station 15). pH 2; rotating mercury film electrode, deposition times  $t_{d1}$  6 min (curves 1),  $t_{d2}$  3 min (curves 2),  $t_{d3}$  2 min (curves 3), deposition potential  $-1.0$  V, stirring during the deposition step at 1500 rpm, 30 s rest period, DPASV parameters: 50 mV pulse height, 29 ms  $t_p$  pulse duration, 240 ms  $t_c$  clock time of pulses (parameters  $t_p$  and  $t_c$  were adjusted internally) 10 mV  $s^{-1}$  scan rate. Determined concentrations (in ng/kg): 20 Cd, 25 Pb, 190 Cu. Curve 1 corresponds to the sample, curves 2 and 3 to the standard additions.

The rainy season usually lasts from May to November with a peak in July–August and monthly rainfall of 75 cm. The dry season lasts from December to April with its peak in February and monthly rainfall of less than 1 cm. Therefore, the salinity changes from very low values in the rainy season to rather high values in the dry season (Koske and Weiler, 1979).

The area around the estuary is rather thinly populated with the exception of Freetown, the capital of Sierra Leone. The possible sources of pollution are the ferry route from Freetown across the Sierra Leone river to the airport and the power station of the Sierra Leone Electricity Corporation. The results for toxic trace metals are summarized in Tables I to IV. Stations A to M were occupied in the rainy season 1978 and 1 to 15 in the dry season 1979 (Fig. 2). Stations 1, 2, H, I and J correspond to fresh water. Stations A, B and C are situated on the sea side and were chosen for obtaining a reference for the toxic metal content in sea water.

*Cadmium*: It can be seen from Table I that in the rainy season the Cd concentration in the dissolved state in the estuary remains generally low approaching values obtained in the open sea (Table IX). Comparatively higher concentrations can be found at stations with lower salinity indicating that Cd

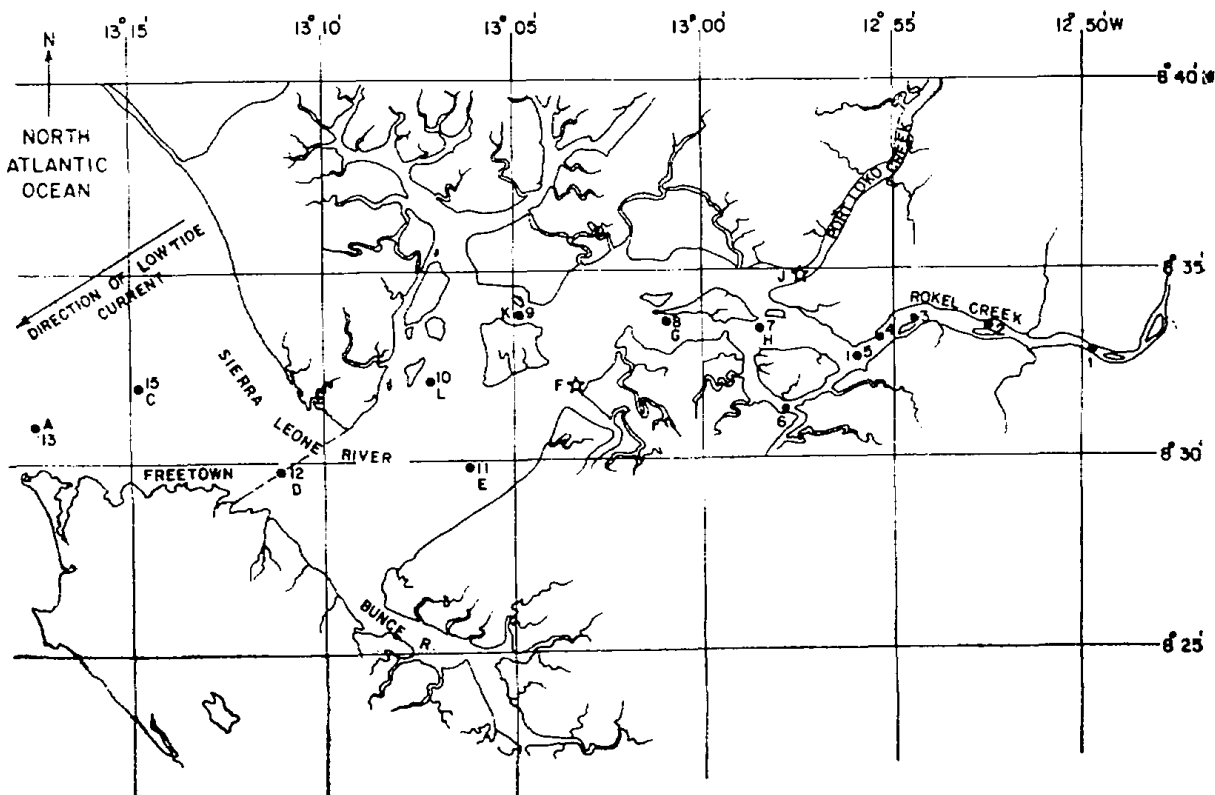


Fig. 2. Sampling stations in the Sierra Leone Estuary.

Table I. Cd levels and other parameters in the Sierra Leone estuary.

Station	Rain season (August 1978)							Dry season (February 1979)							
	S	T	pH	D	P	T	D:P	Station	S	T	pH	D	P	T	D:P
	(‰)	(°C)		(ng/kg)	(ng/kg)	(°C)			(‰)	(°C)		(ng/kg)	(ng/kg)		(ng/kg)
H	0.1	27.1	8.2	5	14	19	0.4	1	0.02	30.1	6.8	6	395	401	0.02
I	0.2	27.4	7.5	18	12	30	0.3	2	0.07	30.0	6.9	8	154	162	0.05
J	0.3	28.0	7.5	5	14	19	0.4	3	6.3	30.0	6.9	44	731	776	0.06
K	10.9	27.9	7.1	9	18	27	0.5	6	9.4	31.0	7.4	12	27	39	0.4
F	11.3	27.7	7.8	7	26	33	0.3	4	10.8	30.0	7.2	11	52	63	0.2
L	14.4	27.6	8.0	5	2	7	2.5	5	11.1	30.3	7.5	16	14	30	1.1
E	19.3	28.1	7.7	6	1	7	6.0	7	17.5	30.6	7.7	12	43	55	0.3
D	20.0	27.5	8.3	4	8	12	0.5	9	27.5	29.6	8.1	18	34	52	0.5
M	20.1	27.7	6.6	5	32	37	0.2	10	29.8	29.5	8.2	10	39	49	0.3
C	23.5	28.1	8.2	3	3	6	1.5	11	31.5	29.1	8.3	15	27	42	0.6
A	24.1	27.5	8.3	4	3	7	1.3	12	31.9	29.4	8.3	6	263	269	0.02
B	26.8	27.7	8.3	3	3	6	1.0	15	35.0	27.6	8.5	20	123	143	0.2
								13	35.8	26.1	8.3	9	49	58	0.2
								14	36.4	28.6	8.5	13	185	198	0.07

S—salinity; T—temperature; D, P, T—concentrations of Cd in the dissolved state, in the particulate matter and total, respectively.

Table II. Pb levels and other parameters in the Sierra Leone estuary.

Station	Rain season (August 1978)							Dry season (February 1979)							
	S	T	pH	D	P	T	D:P	Station	S	T	pH	D	P	T	D:P
	(‰)	(°C)		(ng/kg)	(ng/kg)	(°C)			(‰)	(°C)		(ng/kg)	(ng/kg)		(ng/kg)
J	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
H	0.1	27.1	8.2	50	169	219	0.3	1	0.02	30.1	6.8	14	59	73	0.2
I	0.2	27.4	7.8	56	167	223	0.3	2	0.07	30.0	6.9	35	58	93	0.6
J	0.3	28.0	7.5	71	329	400	0.2	3	6.3	30.0	6.9	19	734	753	0.03
K	10.9	27.9	7.1	48	58	106	0.8	6	9.4	31.0	7.4	18	93	111	0.2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
F	11.3	27.7	7.8	17	50	67	0.3	4	10.8	30.0	7.2	25	170	195	0.1	
L	14.4	27.6	8.0	15	125	140	0.1	5	11.1	30.3	7.5	17	110	117	0.2	
E	19.3	28.1	7.7	45	21	66	2.1	7	17.5	30.6	7.7	13	207	220	0.06	
D	20.0	27.5	8.3	157	23	180	6.8	9	27.9	27.9	8.1	24	863	887	0.03	
M	20.1	27.7	6.6	18	30	48	0.6	10	29.8	29.5	8.2	16	177	193	0.09	
C	23.5	28.1	8.2	25	28	53	0.9	11	31.5	29.1	8.3	8	66	74	0.1	
A	24.1	27.5	8.3	21	20	41	1.1	12	31.9	29.4	8.3	10	146	156	0.07	
B	26.8	27.7	8.3	18	28	46	0.6	15	35.0	27.6	8.5	25	112	137	0.2	
								13	35.8	26.1	8.3	13	29	42	0.4	
								14	36.4	28.6	8.5	48	44	92	1.1	

S—salinity; T—temperature; D, P, T—concentrations of Pb in the dissolved state, in the particulate matter and total, respectively.

Table III. Cu levels and other parameters in the Sierra Leone estuary.

Station	Rain season (August 1978)						Dry season (February 1979)							
	S (%)	T (°C)	pH	D	P	T (ng/kg)	S (%)	T (°C)	pH	D	P	T (ng/kg)		
H	0.1	27.1	8.2	120	70	190	1	0.02	30.1	6.8	160	170	16	
I	0.2	27.4	7.8	130	40	170	2	0.07	30.0	6.9	1130	1350	89	
K	10.9	27.9	7.1	390	20	410	6	9.4	31.0	7.4	150	160	15	
L	14.4	27.6	8.0	230	40	270	4	10.8	30.0	7.2	470	50	520	9.4
E	19.3	28.1	7.7	40	20	60	5	11.1	30.3	7.5	120	80	200	1.5
D	20.0	27.5	8.3	120	30	150	7	17.5	30.6	7.7	140	100	240	1.4
M	20.1	27.7	6.6	50	30	120	9	27.9	29.6	8.1	80	270	350	0.3
C	23.5	28.1	8.2	40	20	60	10	29.8	29.5	8.2	170	60	230	2.8
A	24.1	27.5	8.3	60	40	100	11	31.5	29.1	8.3	220	10	230	22.0
B	26.8	27.7	8.3	40	30	70	12	31.9	29.4	8.3	170	30	200	5.7
							15	35.0	27.6	8.5	190	100	290	1.9
							13	35.8	26.1	8.3	80	30	110	2.7
							14	36.4	28.6	8.5	100	20	130	5.5

S—salinity; T—temperature; D, P, T—concentrations of Cu in the dissolved state, in the particulate matter and total, respectively.

is brought to the estuary with fresh water probably by leaching of rocks. The Cd concentration in the particulate matter is also low, except at station M, where some pollution from the power station can be expected. In the dry season the situation changed considerably as the Cd concentrations in the dissolved state and sorbed at the particulate matter are in general higher than in the rainy season. This can be expected due to a drastic seasonal decrease in the water depth in the estuary. Exceptionally high Cd concentrations in the particulate matter found at stations 1, 2 and 3 in the Rokel river could be caused by the accumulation of Cd in organic particulate matter. The accumulation of Cd in organic particulate matter was observed in the Ooster and Westerscheldt estuaries also. The high Cd concentrations at stations 12 and at 15 are perhaps due to pollution stemming from the ferry route across the Sierra Leone river. An increased Cd content in regions with shipping activity has been observed earlier also, due to the ship paint corrosion (Mart, Nurnberg, Valenta and Stoepler, 1978).

*Lead:* Higher Pb values (Table II) found in fresh waters of Rokel river and Port Loko Creek (stations H, I and J) indicate the presence of sources of geological origin. During the dry season high Pb values have been found at stations 3 and 9 which are due to the high content in particulate matter in the shallow waters. Station D lying at the ferry route is certainly polluted by ship traffic. From the D : P ratios it is seen that Pb is bound overwhelmingly at the particulate matter, a phenomenon which is in accordance with the earlier observations (Mart, Nurnberg and Valenta, 1980b).

*Copper:* The levels of Cu (Table III) are more uniform than those of Cd and Pb. The values found at stations E and C are comparable to the values found in the unpolluted ocean (Table IX). Also, other values are noticeably lower compared to European coastal waters. The elevated values at stations K and 9 indicate some sources of geological origin. Also in the Rokel River exceptionally high values of Cu have been obtained (stations 2 and 4). From the D : P ratio it can be seen that in contrast to Cd and Pb, Cu is almost exclusively present in the dissolved state. The reason for it is the formation of strong inert complexes with organic ligands which are the components of the dissolved organic matter.

*Salinity dependence:* To know the fate of the toxic trace metals in the Sierra Leone estuary the dependence of the metal concentration on salinity has been determined. As the ratio of the sea water and the fresh water in the estuary is changing with the tides and the concentrations of toxic metals depend also on other parameters than salinity alone the sampling at all stations was performed on a day during low tide. From the data obtained during the dry season no meaningful dependence on the salinity could be obtained. The data obtained during the rainy season, however, were consistent enough to get a characteristic salinity dependence of the metal concentration if some exceptionally high concentration values caused by local pollution sources were eliminated. The results for Cd, Cu and Pb are shown in Figs. 3-5 and in Table IV.



It can be seen from these figures that the main sources of the metal in the estuary are in the fresh water region. As there is no industrial activity in this region they must be of the geological origin.

Table IV. Relationship between the salinity  $x$  and the levels  $y$  of toxic trace metals Cd, Pb and Cu in the Sierra Leone estuary in August 1978 (Nonlinear regression  $\hat{y} = a + bx + cx^2$ ).

Coefficient	Metal		
	Cd	Pb	Cu
a	$27.3 \pm 3.6$	$222 \pm 10$	$180 \pm 24$
b	$-0.90 \pm 0.74$	$-15.3 \pm 1.8$	$-2.7 \pm 5.7$
c	$0.002 \pm 0.029$	$0.34 \pm 0.07$	$-0.05 \pm 0.23$
r	0.86	0.99	0.83
Degree Change	++ mixing	+++ deposition	++ slight release

Regression coefficient  $r$  has been determined as

$$r^2 = 1 - (A/Q_y) \text{ with } A = \sum (y - \hat{y})^2 \text{ and } Q_y = \sum (y - \bar{y})^2 \text{ Sachs, 1978.}$$

Degree of significance of  $r$  is denoted as +, ++ and +++ with  $p < 0.05$ ,  $< 0.01$  and  $< 0.001$ , respectively.

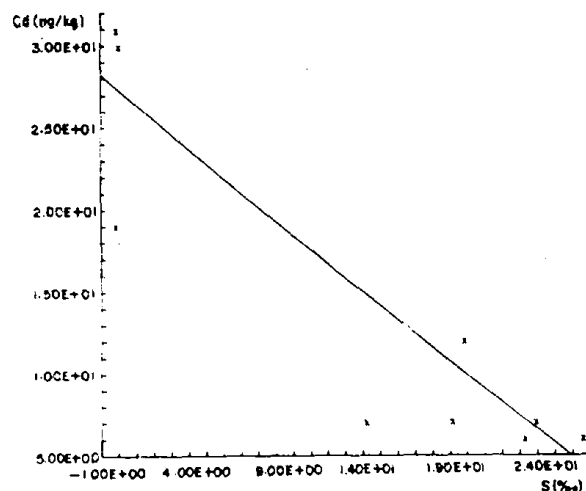


Fig. 3. Relationship between salinity  $S$  and total concentration of Cd in the Sierra Leone estuary in August 1978.

The relationship between salinity and the level of Cd (Fig. 3) indicates pure mixing of the fresh water, containing upto about 30 ng/kg Cd, with sea water. In spite of the difficulties encountered in the determination of such low Cd concentrations a good correlation with the salinity change has been obtained. As can be seen from Fig. 4, the behaviour of Pb is quite different. A substan-

tial part of Pb, brought with fresh water containing about 200 ng/kg, is deposited in the estuary. This is well understandable as increased salinity enhances the flocculation of the colloidal suspensions (Van Holphen, 1966). As it was shown above, Pb tends to be adsorbed on the particulate matter which is more or less efficiently deposited onto the sediments of the estuary. The salinity dependence of the Cu level (Fig. 5) indicates on the other hand a slight release of Cu from the estuary. This is in accordance with the fact that Cu may form complexes with chelating components of the dissolved organic matter and can thus be extracted from the estuarine sediments.

#### *The Ooster and Westerscheldt estuaries*

The geographical location of the Ooster and Westerscheldt estuaries is depicted in Fig. 6. Seawards of the Zeeland bridge the Oosterscheldt estuary is relatively open and wide. It has an irregular input water through the Hollandsch Diep, one of the Rhine delta rivers, and the Dintel. The important pollution sources are the polder drainage water from Zierikzee near station 1 and the Volkerak lock (station 9) through which polluted Rhine water comes into the estuary. Some of the pollution sources of the Hollandsch Diep are chemical factories C and a large coalfired power station. Another important pollution source is heavy commercial shipping in the area.

In the Westerscheldt estuary heavy pollution could be expected from within the estuary itself. Nevertheless, most of the pollutants are brought downstream by the Scheldt river from the heavily industrialized region of Antwerpen. In fact about 80% of the fresh water discharged into the Westerscheldt estuary

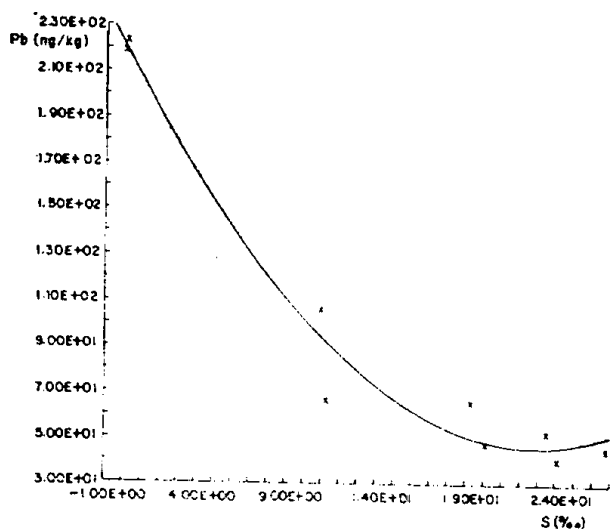


Fig. 4. Relationship between salinity S and total concentration of Pb in the Sierra Leone estuary in August 1978.

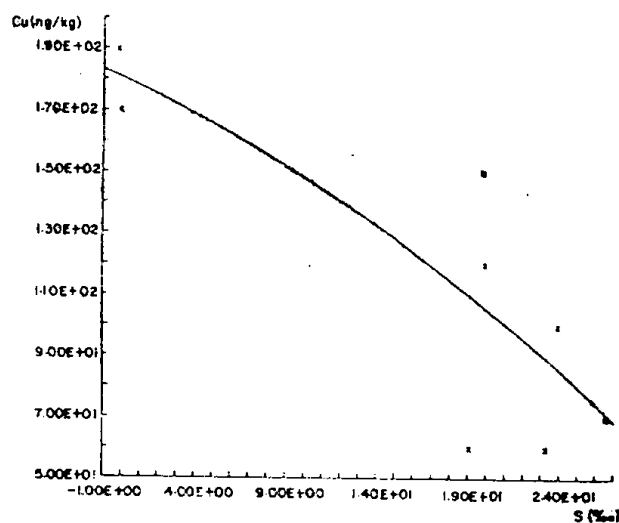


Fig. 5. Relationship between salinity S and total concentration of Cu in the Sierra Leone estuary in August 1978.

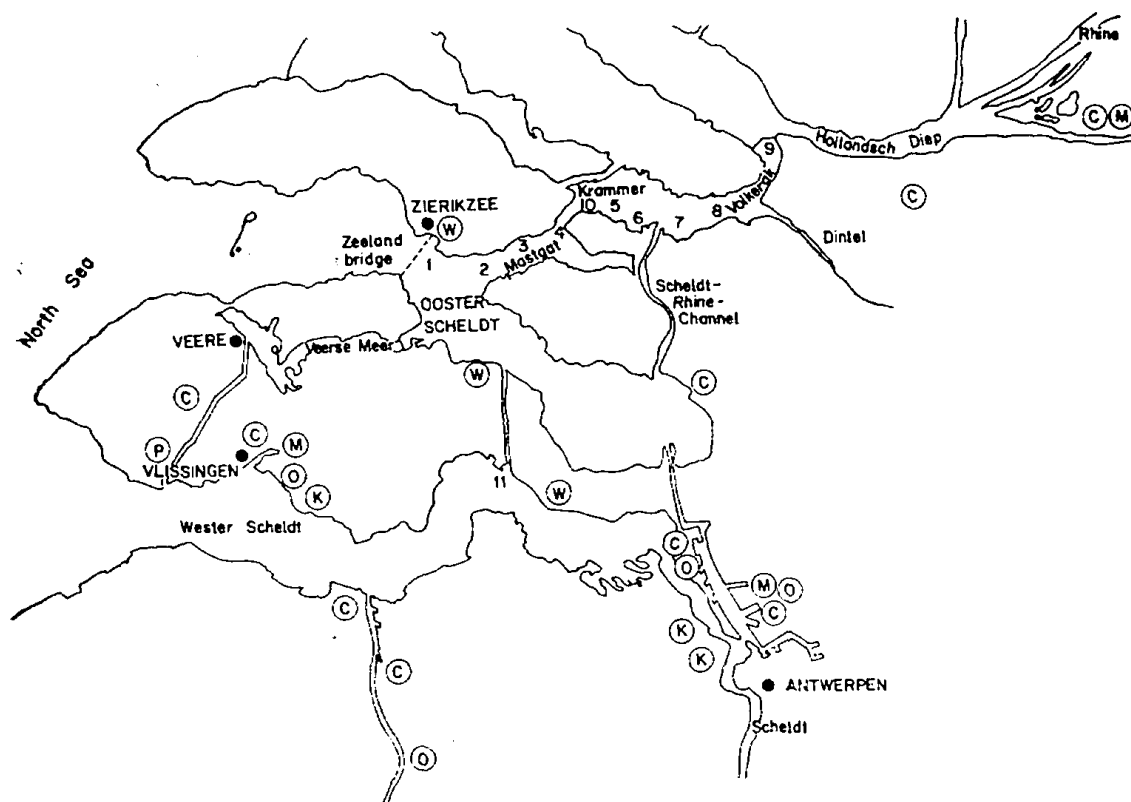


Fig. 6. Sampling area of the Ooster and Westerscheldt estuaries.

arrives from the Scheldt River, and the rest from channels and polder water effluents. Another important source of heavy metal pollution is shipping. The commercial shipping here amounts to 440 millions tons of cargo per year in both directions.

In the Oosterscheldt estuary a longitudinal sampling of surface water was carried out at 9 stations (Fig. 6) along the section from Zeeland bridge to Volkerak lock at low tide in winter (December 1979) when biological activity is low and in summer (August and September 1980) when it is high.

In the Westerscheldt estuary only one station for comparison was chosen into the estuary and close to the shipping route. Water samples were taken at Hansweert (station 11) which is situated near the input of the Scheldt river every hour within a 12 hour period covering one tidal cycle.

The samples were analyzed for dissolved and particulate levels of Cd, Pb and Cu. In addition pH, salinity and chlorophyll content were determined. It can be seen from Tables V-VII that in the Oosterscheldt estuary the salinity decreases upstream due to the high input of river water.

The total concentrations of all three metals increase more or less steeply at stations 8 and 9, obviously due to the input of polluted Rhine water.

Table V. Levels of toxic trace metals Cd, Pb, Cu and other parameters in the Ooster and Westerscheldt estuaries in December 1979:

Station	Ch mg/m <sup>3</sup>	S (‰)	T (°C)	pH	Cd (ng/kg)			Pb (ng/kg)			Cu (ng/kg)				
					D	P	T	D	P	T	D	P	T	D:P	T
1	1.11	27	8.6	7.95	29	21	50	26	1500	1530	0.02	260	1010	1270	0.3
2	0.70	26.3	8.6	7.91	24	17	41	25	1350	1380	0.02	230	520	750	0.4
3	0.70	23.6	8.6	7.91	21	17	38	28	1160	1190	0.02	210	970	1180	0.2
4	0.64	20.9	8.7	7.92	62	20	82	96	1260	1300	0.08	800	520	1320	1.5
5	0.59	18.2	8.7	7.96	49	21	70	2.3	1340	1430	0.06	820	480	1300	1.7
6	0.56	13.8	8.8	7.98	49	21	70	2.3	1050	1130	0.08	460	410	870	1.1
7	0.67	14.1	8.8	8.00	29	48	77	0.6	1800	1830	0.08	380	910	1290	0.4
8	1.09	10.2	8.8	7.78	80	99	179	0.8	3390	3510	0.03	1000	1400	2400	0.7
9	1.61	7.5	9.0	7.99	71	140	211	0.5	4720	4850	0.03	1130	2400	2530	0.5
11	2.2	19.7	8.7	7.69	284	239	523	1.2	2530	3650	0.03	690	2120	2810	0.3

Ch — chlorophyll content; T — temperature; D, P, T — metal concentration in the dissolved state, in the particulate matter and total, respectively.

Table VI. Levels of toxic trace metals Cd, Pb, Cu and other parameters in the Ooster and Westerscheldt estuaries in August 1980.

Station	S (‰)	Ch mg/m <sup>3</sup>	T (°C)	pH	Cd (ng/kg)			Pb (ng/kg)			Cu (ng/kg)					
					D	P	T	D	P	T	D	P	T	D:P	T	D:P
1	28.1	13.7	18.2	8.22	9	11	20	0.8	26	151	177	0.2	380	62	442	6.1
2	26.0	10.9	18.2	8.22	28	6	34	4.7	20	170	190	0.1	680	65	745	10.5
3	24.0	9.0	18.2	8.19	30	2	32	15	41	111	152	0.4	550	62	612	8.9
4	22.6	7.1	18.2	8.17	16	5	21	3.2	21	159	180	0.1	490	66	556	7.4
5	20.2	4.2	18.3	8.16	20	8	28	2.5	63	196	259	0.3	490	56	545	8.7
6	18.4	5.2	18.7	8.13	42	4	46	10.5	121	257	378	0.5	1600	103	1100	9.7
7	17.2	9.7	18.7	8.14	21	8	29	2.6	29	271	300	0.1	410	72	482	5.7
8	15.7	4.8	19.1	8.11	34	4	38	8.5	33	304	337	0.1	630	72	702	8.7
9	10.1	6.7	19.2	8.04	23	72	95	0.3	42	1790	1830	0.02	640	620	1260	1.0
11	4.3	18.1	18.4	7.9	212	108	320	2.0	75	2070	2140	0.04	1130	930	2060	1.2

Ch — chlorophyll content; T — temperature; D, P, T — metal concentration in the dissolved state, in the particulate matter and total, respectively.

Table VII. Levels of toxic trace metals Cd, Pb, Cu and other parameters in the Ooster- and Westerscheldt estuaries in September '80.

Station	Ch mg/m <sup>3</sup>	S (‰)	T (°C)	pH	Cd (ng/kg)			Pb (ng/kg)			Cu (ng/kg)			
					D	P	T	D	P	T	D	P	T	
1	3.2	28.5	17.9	8.16	7	6	13	20	310	330	370	124	494	3.0
2	3.5	27.0	17.4	8.16	7	10	17	32	237	269	330	130	460	2.5
3	3.7	25.2	17.5	8.12	12	11	23	42	220	262	640	122	762	5.2
4	4.1	23.5	17.5	8.10	15	6	21	25	207	232	410	101	511	4.1
5	3.6	21.1	17.4	8.07	40	5	45	8	221	250	550	186	736	3.0
6	4.0	19.7	17.4	8.05	33	6	39	5.5	283	342	460	168	808	3.8
7	4.7	15.9	17.3	8.01	48	5	53	9.6	235	304	---	---	---	---
8	5.4	15.2	17.2	7.98	21	11	32	1.9	388	420	530	152	682	3.5
9	4.9	10.3	17.4	7.90	24	31	55	0.8	802	847	710	388	1100	1.8
11	2.9	20.4	17.6	7.85	376	153	529	2.5	3030	3090	1640	1480	3120	1.1

Ch — chlorophyll content; T — temperature; D, P, T — metal concentration in the particulate matter and total, respectively.

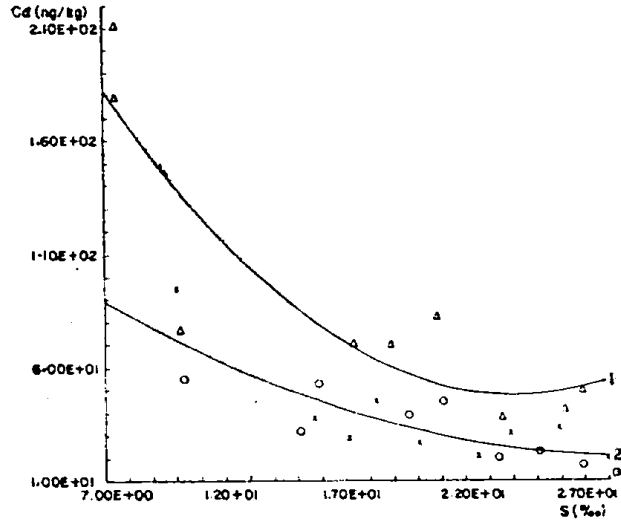


Fig. 7. Relationship between salinity S and total concentration of Cd in the Oosterscheldt Estuary in December 1979 (curve 1) and in August and September 1980 (curve 2).

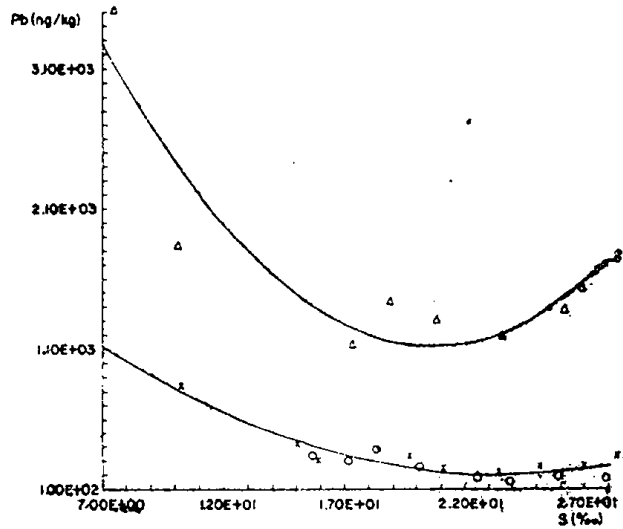


Fig. 8. Relationship between salinity S and total concentration of Pb in the Oosterscheldt Estuary in December 1979 (curve 1) and in August and September 1980 (curve 2).

This increase and the values themselves are larger in winter than in summer probably caused by an increased flushing by wet metal deposition with rain and snow during winter. In the Westerscheldt estuary the total metal concentrations are much larger than in the Oosterscheldt estuary. The difference varies with the season and the metal and is largest for Cd. This is due to the polluted river water of the Scheldt river coming from the region of the harbour of Antwerpen.

In December 1979, the respective ratios, dissolved to particulate, of Cd, Pb and Cu concentrations are about the same in both estuaries, Cu is almost exclusively present in the dissolved state with exception of heavily loaded water in winter, and in the Westerscheldt estuary also in the summer season. Contrary to this Pb is preferentially bound to the particulate matter in both seasons, the ratio D:P being much smaller in winter.

Adsorptive interactions of other metals with the particulate matter in estuaries were observed by other authors (Duinker, 1980). Also, deposition of Cd, Pb and some other trace metals from the particulate matter onto the bottom sediments in the Westerscheldt estuary was deduced based on the relationship between the trace metal to aluminium ratio and the percentage of marine mud in the suspended matter (Salomons, Mook and Eysink, 1981).

The behaviour of Cd is similar to that of Cu, i.e. Cd is preferentially present in the dissolved state but the D:P ratio is generally lower than that of Cu. This trend is similar to that observed in the Sierra Leone estuary taking into account that the content of the particulate matter is different.

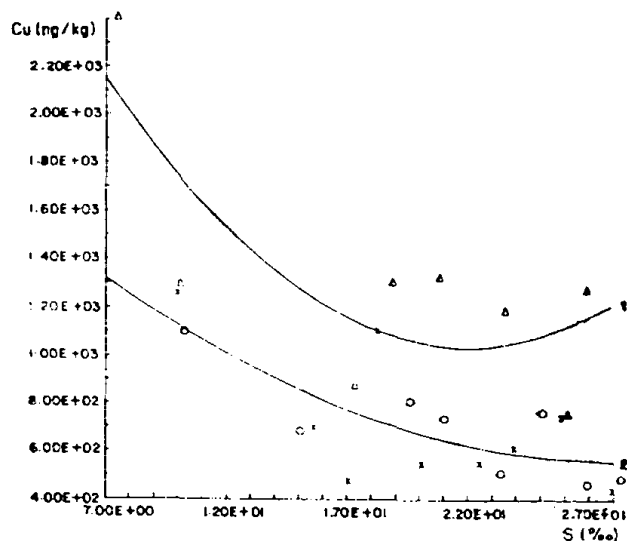


Fig. 9. Relationship between salinity S and total concentration of Cu in the Oosterscheldt Estuary in December 1979 (curve 1) and in August and September 1980 (curve 2).

*Dependence on the salinity*

As in the Sierra Leone estuary the sampling in the Oosterscheldt estuary was performed at 9 stations from the Zeeland bridge to the Volkerak dock during low tide from the sea into the estuary. The data obtained during two sampling periods in August and September 1980 were homogeneous enough to treat them as one event. From these measurements the relationships between the salinity and the levels of Cd, Pb and Cu have been determined (Figs. 7-9 and Table VIII). In winter, due to a limited number of measuring points, the regression coefficient is highly significant only for Pb whereas it is highly significant for all three trace metals in summer. It can be seen from Figs. 7 to 9 that the levels of all three metals in summer are distinctly lower than in winter. On the other hand it is known from our previous measurements in the

Table VIII. Relationship between the salinity X and the levels Y of toxic trace metals Cd, Pb and Cu in the Oosterscheldt estuary (Nonlinear regression  $\hat{y} = a + bx + cx^2$ .)

**(a) December 1979**

Coefficient	Metal		
	Cd	Pb	Cu
a	315 ± 71	6030 ± 910	3430 ± 960
b	-40 ± 17	-850 ± 210	-390 ± 220
c	1.5 ± 0.9	37 ± 11	16 ± 11
r	0.89	0.93	0.78
Degree	++	+++	+
Change	deposition	deposition	deposition

**(b) August and September 1980**

Coefficient	Metal		
	Cu	Pb	Cd
a	140 ± 33	2060 ± 230	1900 ± 500
b	-14.7 ± 6.3	-285 ± 42	-170 ± 96
c	0.45 ± 0.29	10.9 ± 1.8	5.3 ± 4.4
r	0.82	0.93	0.74
Degree	+++	+++	+++
Change	deposition	deposition	deposition

Regression coefficient r has been determined as

$$r^2 = 1 - (A/Qr) \text{ with } A = \sum (y - \hat{y})^2 \text{ and } Qr = \sum (y - y)^2 \text{ (Sachs, 1978)}$$

with  $p < 0.05$ ,  $< 0.10$  and  $< 0.001$ , respectively.

Degree of significance of r is denoted as +, ++ and +++

Table IX. Typical levels of toxic trace metals Cd, Pb and Cu in the open sea, coastal waters and fresh waters (surface water).

(Mart. Rutzel, Klahre, Sipos, Platzek, Valenta and Nurnberg, 1982)

Water type	Cd (ng/kg)	Pb (ng/kg)	Cu (ng/kg)
Pacific Ocean (Cook Islands)	2	5	60
Arctic Ocean	4	45	99
Arctic Ocean (79°N to 83°N)	9	15	95
Belgian and Dutch coast	51	827	1220
Ligurian and Tyrrhenian coast	18	220	740
Lake of Constance (pelagial region)	14	113	600
Rhine River (Rheinheim)	70	150	1700

Oosterscheldt estuary that the amount of seston (particulate matter) is on average larger in winter than in summer (Valenta, Duursma, Merks, Rutzel and Nurnberg, in press). The difference is due to a larger amount of inorganic particulate matter in winter. Thus, it can be concluded that for the concentration regulation of the metals in the water column of the estuary the removal of metals by the phytoplankton detritus is much more efficient than the removal by adsorption of metals on inorganic particles. Therefore, in summer with high biological productivity the metal levels are lower than those in winter.

In the winter season all curves in Figs 7-9 are concave downwards indicating the deposition of Cd, Pb and Cu in the estuary. The main source of these metals is the polluted Rhine water coming through the Volkerak lock. Nevertheless, the curvature of the curves upwards at the stations 1 and 2, especially in winter, indicates that there exists another pollution source seawards in winter. This is probably the polder drainage water from Zierikzee near station 1 running off in increasing amounts due to increased precipitation of rain and snow loaded with heavy metals from the atmosphere. The curvature is much more pronounced for Pb than for Cd and Cu in summer indicating that the deposition with suspended matter on to the estuarine bottom is more pronounced for Pb than Cd and Cu.

In conclusion it can be stated that the behaviour of Cd, Pb and Cu in the Sierra Leone estuary and the Ooster and Westerscheldt estuaries is rather similar. The differences are caused by the different amounts of the particulate matter which remove trace metals, especially Pb, from the estuary. The organic part of the particulate matter (detritus) acts more efficiently than the inorganic particles probably due to the complexation and chelation of the metals by organic ligands.



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