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Part 2

SPATIAL, TEMPORAL AND COMPARTMENTAL DISTRIBUTION
IN THE WATER COLUMN

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ABSTRACT : The concentrations of dissolved and particulate Bi,
Cd, Cu, Hg, Pb, Sb and Zn have been measured during
surveying cruises along the Belgian coast (1979-1981)
to determine the distribution of these heavy metals
and to determine how this distribution is effected by
coastal discharges, dumping and river discharges (main-
ly the Scheldt estuary).

Dissolved Cd, Cu, Hg, Pb and Zn concentrations average
respectively 0.11 µg/l, 2.2 µg/l, 12 ng/l, 3.9 µg/l
and 6.6 µg/l.

The large scattering of the results do not allow to
observe a clear spatial distribution pattern. On the
other hand, dissolved mercury concentrations clearly
decrease with distance from the coast.

Mean particulate Cd, Cu, Hg, Pb and Zn concentrations
are respectively 20 ng/l, 0.24 µg/l, 35 ng/l, 0.36
µg/l and 1.3 µg/l. Particulate metal concentrations
are highest in the zone near the Scheldt estuary and
diminish progressively with distance from both the
coast and the mouth of the Scheldt estuary.

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INTRODUCTION

Increasing awareness of the potential hazards of large scale contamination of the ecosystem by heavy metals from urban and industrial sources, has led to the need of regularly monitoring the levels of these substances (Dutton et al, 1973 ; Duinker & Nolting, 1977, 1982 ; Baeyens et al, 1979a, 1979b ; Decadt et al, 1980 ; Gillain et al, 1979, 1980) and to attempts of modelisation of the heavy metal circulation in the Southern Bight of the North Sea (Duinker & Nolting, 1976 ; Elskens, 1976).

A basic requirement to describe the circulation pattern of a heavy metal is the knowledge of its distribution among the different compartments of the ecosystem and its spatial-temporal fluctuation in each of these compartments.

Although the heavy metals considered in this study (except perhaps Zn and Cu) do not play an essential function in the food chain, they may become accumulate into the higher organisms either through direct uptake from the dissolved phase (Bouquegneau et al, 1977) or indirectly after adsorption on detrital matter, nanoplankton, etc. and ingestion by organisms of the higher trophic levels. As a consequence, base line studies on the levels of these heavy metals (dissolved and particulate) in the water column are not only important for pollution control, but can also provide valuable information on the biogeochemistry of trace metals.

This paper deals with the relative importance of heavy metal concentrations in the dissolved and particulate phases of the water column and their spatial distribution patterns. An attempt has been made to discuss them in terms of external inputs.

MATERIALS AND METHODS

Sampling and analytical methods are described by Gillain et al (1982).

PRESENTATION OF THE RESULTS

Results described in this paper refer to samples collected during surveillance cruises along the Belgian coast. The stations are located along grid lines perpendicular to the coast (fig.1).
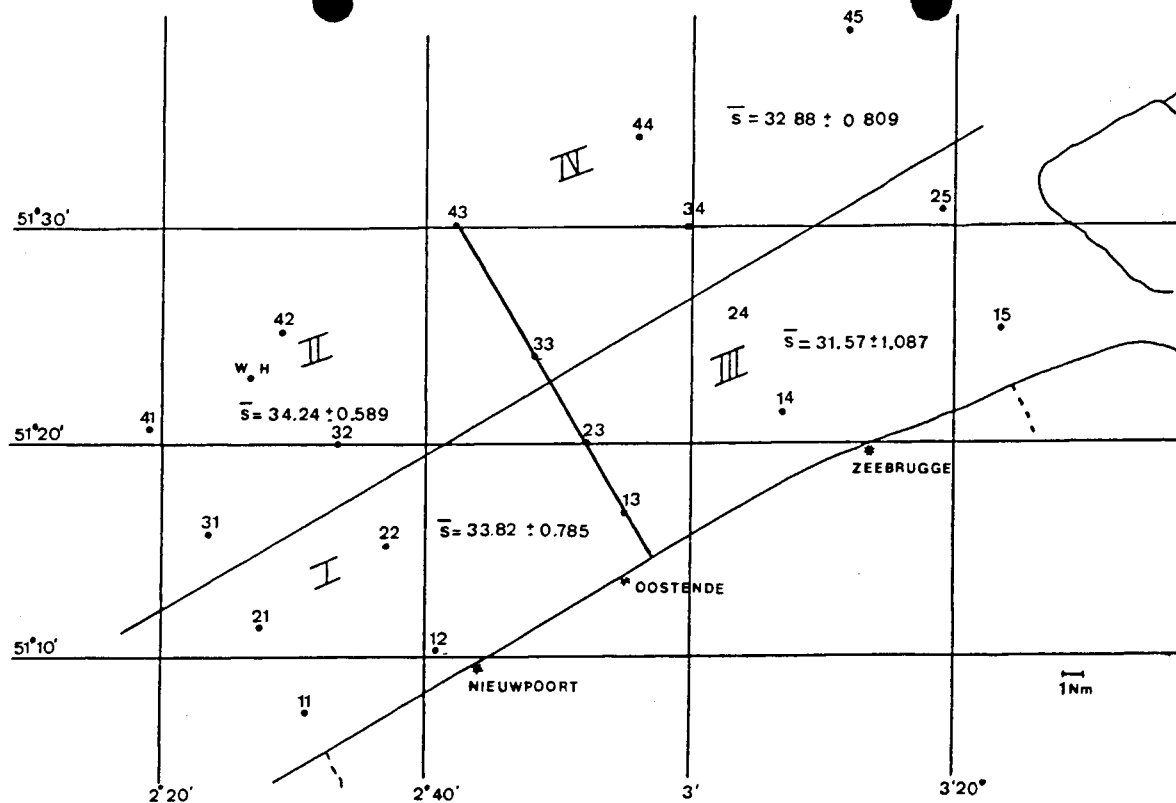
Fig. 1 : $\overline{S}$ = mean salinity during the period 1977–1981 (Unité de Gestion, Ministry of Public Health, personal communication).

Duinker & Nolting (1976) suggest that a number of distinct regions can be characterized by their values for the particulate Fe:Mn ratio. In the Southern Bight, they found a total particulate Fe:Mn ratio of 30 to 40 for inshore samples and of 60 to 85 for offshore samples. Fig.2 shows the relation between total iron and manganese for samples obtained in the Belgian coastal zone, during three cruises (May 1980, May and June 1981).

Fe and Mn were strongly correlated (r = 0.98). The mean Fe: Mn ratio of 32 indicates that we are most probably dealing with inshore samples. To be able to observe any possible influence of estuarine (Scheldt estuary) and coastal inputs on the heavy metal concentrations in the Belgian coastal zone, the monitoring network was divided into four sections (fig.1). This subdivision can be justified if one looks at the mean salinities observed in that area during the period 1977-1981 (fig.1), although salinity might not be correlated with heavy metal distribution.

Table I summarizes the mean values (arithmetic and geometric means) for Zn, Cd, Cu, Pb (dissolved and particulate) and Hg (total and particulate). Extremely high values, sporadically measured in our coastal zone, were not excluded.

Spatial distribution of Bi, Cu, Cd, Hg, Pb, Sb and Zn in the Belgian coastal zone.

a. Dissolved Zn, Cd, Pb and Cu

Data obtained by Jones (1972) and Duinker & Nolting (1982) for the Southern Bight, show a clear smooth dependence (concentration gradient similar but opposite to the salinity gradient) on the distance of the sampling site from the coast. Although zone III (zone under the influence of the river runoff) generally shows somewhat higher concentration levels than the other zones (table I), concentration gradients are not obvious. Several facts have to be taken into account. First, the wide scattering of the results in each of the individual subareas will mask largely the possible existence of smooth concentration gradients. Secondly, since our sampling area is too reduced (the maximum distance from the coast is about 30 km)   the region of maximum salinity (35‰), occurring in the central part of the Southern Bight, is not included in our sampling network (fig.1). The fact that we are greatly dealing with an inshore watermass, is corroborated by the remarkable constant particulate Fe:Mn ratio of 32 (Duinker et al, 1976). Thirdly, the existence of a gyre off the Belgian coast (Nihoul & Ronday, 1976) can also be a reason for a somewhat different and perhaps more homogenized system compared to other regions of the Southern Bight (Jones, 1972 ; Duinker et al, 1976).

The mean freshwater content in section I, II, III and IV is respectively 3.5, 2, 10 and 6% relative to the maximum salinity observed in the Southern Bight (35‰). The mean concentrations in box III are increased over the overall mean for the Belgian coastal area by respectively about 2 μg/l for Zn (30%), 0.04 μg/l for Cd (17%), 0.2 μg/l for Pb (5%) and 0.33 μg/l for Cu (15%).

Table 1

Mean heavy metal concentration in the Belgian coastal zone

Metal	Zone	Nb	Range ($\mu g.l^{-1}$)	Arithmetic mean		Geometric mean		Median
				$\bar{x}$	σ	$\bar{xg}$	σg	
Total dis-solved Zn	B.C.	83	1.7 −23.20	8.19	5.52	6.66	1.91	6.60
	I	18	2.35 −21.37	7.22	5.04	5.92	1.90	6.10
	II	17	2.4 −19.8	9.21	5.98	7.50	1.96	6.92
	III	15	1.7 −23.20	10.37	5.91	8.85	1.87	8.82
	IV	15	2.6 −20.40	6.98	4.73	5.96	1.73	5.70
Part. Zn	B.C.	46	0.15 −14.7	2.48	3.37	1.29	3.03	1.07
	I	11	0.56 −14.7	3.08	4.61	1.53	3.00	1.12
	II	12	0.15 − 1.24	0.52	0.31	0.44	1.83	0.45
	III	5	0.56 − 6.10	3.22	2.15	2.46	3.30	3.30
	IV	7	0.46 − 1.60	1.10	0.38	1.03	1.51	1.10
Total dis-solved Cd	B.C.	84	0.025−0.980	0.151	0.133	0.118	1.98	0.116
	I	18	0.025−0.480	0.160	0.112	0.127	2.07	0.129
	II	17	0.040−0.530	0.161	0.130	0.124	2.07	0.100
	III	15	0.074−0.980	0.205	0.224	0.156	1.91	0.140
	IV	16	0.035−0.330	0.106	0.070	0.091	1.71	0.083
Part. Cd	B.C.	45	0.005−0.095	0.026	0.019	0.020	2.07	0.021
	I	11	0.007−0.067	0.027	0.018	0.022	1.97	0.024
	II	12	0.005−0.040	0.014	0.011	0.011	1.87	0.010
	III	5	0.016−0.041	0.026	0.010	0.025	1.44	0.022
	IV	7	0.009−0.050	0.026	0.014	0.023	1.75	0.022
Total dis-solved Pb	B.C.	82	0.90 −13.87	4.61	2.75	3.86	1.86	3.97
	I	18	1.4 −13.87	5.00	3.22	4.19	1.83	3.99
	II	16	1.0 −10.95	5.15	2.99	4.13	2.15	4.73
	III	15	1.2 −13.80	4.79	3.08	4.06	1.82	4.00
	IV	15	0.9 − 8.30	3.86	1.89	3.40	1.73	3.40
Part. Pb	B.C.	46	0.033−5.8	0.781	1.105	0.365	3.61	0.370
	I	11	0.059−1.7	0.564	0.460	0.407	2.54	0.500
	II	12	0.033−0.44	0.172	0.121	0.133	2.19	0.160
	III	5	0.470−1.33	0.958	0.385	0.888	1.57	1.000
	IV	7	0.050−1.30	0.363	0.431	0.223	2.86	0.190

B.C. : Belgian Coast.

Table 1 (continued)

| Metal	Zone	Nb	Range (µg.1⁻¹)	Arithmetic mean		Geometric mean		Median
				$\bar{x}$	σ	$\bar{xg}$	σg	
Total dis-	B.C.	84	0.50 -21.8	2.82	2.66	2.21	1.96	2.30
solved Cu	I	18	1.10 - 5.15	2.43	1.13	2.21	1.57	2.08
	II	17	0.50 - 8.50	3.01	2.57	2.12	2.44	2.44
	III	15	1.20 -21.80	3.63	5.10	2.54	2.02	2.10
	IV	16	0.80 - 6.00	2.37	1.32	2.08	1.69	2.30
Part. Cu	B.C.	46	0.039-1.900	0.371	0.382	0.241	2.57	0.210
	I	11	0.118-0.780	0.301	0.212	0.248	1.88	0.200
	II	12	0.039-0.210	0.117	0.055	0.104	1.71	0.108
	III	5	0.386-0.790	0.614	0.200	0.586	1.43	0.710
	IV	7	0.075-0.450	0.224	0.121	0.195	1.80	0.220
Total Hg	B.C.	253	0.002-0.787	0.074	0.073	0.050	2.63	0.059
	I	55	0.004-0.255	0.062	0.061	0.037	3.02	0.046
	II	43	0.002-0.180	0.051	0.040	0.036	2.63	0.047
	III	58	0.020-0.787	0.120	0.112	0.095	1.95	0.092
	IV	47	0.009-0.234	0.061	0.041	0.049	2.09	0.052
Part. Hg	B.C.	69	0.003-0.570	0.060	0.081	0.035	2.75	0.040
	I	11	0.009-0.050	0.028	0.014	0.025	1.78	0.030
	II	11	0.003-0.054	0.026	0.020	0.018	2.57	0.014
	III	18	0.029-0.570	0.126	0.132	0.087	2.34	0.095
	IV	16	0.009-0.080	0.033	0.025	0.025	2.34	0.024
Suspended	B.C.	47	6 -100	24.1	18.9	19	1.97	18.2
matter	I	11	12.2 -31.7	21.1	6.0	20.3	1.35	20.2
	II	12	6.1 -13.9	9.1	2.3	8.9	1.28	8.4
	III	5	23.4 -50	42.7	11.2	41.2	1.38	48.8
	IV	7	9.3 -30.9	17.9	6.7	16.9	1.44	17.6

B.C. : Belgian Coast
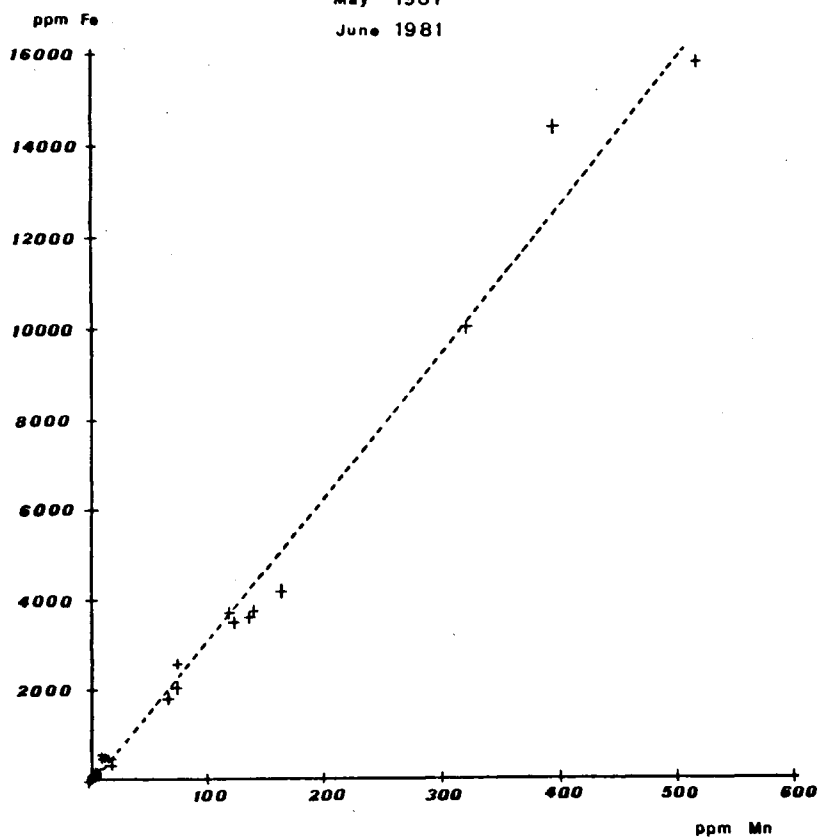
Fig. 2.

According to Baeyens et al (1982a), the annual dissolved heavy metals supply of the Scheldt estuary amounts to 28.2 T.year^{-1} for Zn, 6.6 T.year^{-1} for Cu, 2.3 T.year^{-1} for Pb and 0.98 T.year^{-1} for Cd. If we accept a conservative character for the dissolved element, as suggested by Duinker & Nolting (1976) in the case of Zn and using a mean residual outflow of 6 km^3.year^{-1}, calculated on the basis of the spatial distribution of the salinity, an adequate conservative parameter (Decadt et al, 1982), the Scheldt estuary supply would give a concentration increment of 1.5 µg/l for Zn, non detectable for Cu, non detectable for Pb and 0.12 µg/l for Cd.

The observed increments for Zn and Cd in box III can therefore be explained by the Scheldt estuary input while this is not the case for Pb and Cu. However, one has to keep in mind that the analytical techniques actually in use have a relative error of about 10%.

The sensitivity of the Belgian coast to the input from the Scheldt estuary can also be tested by a model suggested by Yeats et al (1978). The change in concentration of a particular dissolved metal (m) in the estuary, required to significant alter the metal concentration in coastal receiving waters ($\Delta m_{estuary}$) can be expressed as :

$$\Delta m_{estuary} = \Delta m_{coastal} \frac{D}{(1 - S_m)} \cdot \frac{F_t}{F_{est}}$$

where : $\Delta m_{coastal}$ = minimum detectable change in metal concentration in coastal water. Its value is based upon the confidence limit for all the samples at the 90% level.

D = size of the mixing ratio between fresh water and sea water (about 9 in our area).

F_t = total fresh water flux (4 km^3.y^{-1})

$F_{estuary}$ = estuary flux (3.3 km^3.y^{-1})

S_m = sources and sinks of the dissolved metal during transit through the coastal water body. We consider here the dissolved element, displays a conservative property and, as a consequence, $S_m = 0$.

The results of the calculations are shown in table 2.

Although these calculations are very crude, they prove that a very small concentration increase in the Belgian coastal area corresponds to a much larger increase in the estuarine heavy metal input corroborating the conclusions of Yeats et al (1978) that the precision with which trace metal levels in a coastal water body can be determined, is generally not high enough to detect increased levels of these trace metals due to anthropogenic activity.

In table 3, we make a comparison of our data with trace metal

Table 2

Compositional changes required in the Scheldt estuary to produce detectable changes in the Belgian coastal waters

		Zn	Cd	Pb	Cu
Mean concentration at the mouth of the Scheldt Estuary (Baeyens et al, 1982a)	$\mu g.l^{-1}$	11	0.39	0.93	2.6
Maximum concentration in the Scheldt Estuary (Baeyens et al, 1982a)	$\mu g.l^{-1}$	135	1.9	5	12.9
Minimal detectable change in the Belgian Coast (Δm, coastal)	$\mu g.l^{-1}$ %	1 15	0.03 25	0.51 13	0.48 22
Corresponding change in the Scheldt Estuary concentration (Δm, estuary)	$\mu g.l^{-1}$ % min-max	11 8-100	0.32 17-82	5.6 112-602	5.3 41-204
Change in estuarine metal flux	T/j	36.3	1.06	18.5	17.5

concentrations measured in adjacent regions. The levels in the
Belgian coastal zone are increased over the minimum values in the
central part of the Bight (maximum salinity area) by a factor 9
for Cu, 20 for Zn and 6 for Cd. The question arises whether we
can expect an increased input from the atmosphere in our coastal
area or not. Considering the data obtained at a marine platform
(West-Hinder, situated at the border of our monitoring network),
the global atmospheric fall-out (dry and wet) is even smaller or
equal to those observed for other regions in the North Sea
(Dehairs et al, 1982a). On the other hand, observations suggest
an increased emission with continental wind directions and a gra-
dual dry fall-out from land to sea (Dehairs et al, 1982b). It
might be that the real fall-out in the Belgian coastal zone is
underestimated comparing the measured fall-out at the West-Hinder
with that on a landstation (De Blanckaert).

We found indeed differences in dry and wet fall-out, although,
the total atmospheric fall-out on land is not quite different from
that at sea.

Consequently, other factors should be taken into account to
explain the increased concentrations in the Belgian coastal zone.

The main source of water supply to the Belgian coastal zone
is the Straits of Dover. However, due to the lack of sufficient
reliable data in the Straits of Dover and to the rather wide scat-
tering of the results, possible local effects such as dumping,
remobilization from the sediments or effects related to increased
biological activities are not evident.

From a restricted chemical point of view, extended intercali-
bration exercises for sampling might help to elucidate the origin
and fate of trace metal levels found in the Belgian coastal wa-
ters, simply to increase the reliability of the data given by dif-
ferent teams.

b. Particulate Zn, Cd, Pb, Cu and Hg

The distribution of the particulate trace metal concentrations
(µg/l) is similar to the distribution of suspended matter :

- a zone with relatively high concentrations situated near the
  mouth of the Scheldt estuary,

- a progressive diminution with the distance from the coast and
  the mouth of the Scheldt estuary outlet.

The trace metal concentrations in terms of particulate matter
(dry weight (µg/g)) are distributed in a more complex way ; the re-
sults are shown in table 4. No differences between the four sec-
tors are observed for Cu. The relative abundances of Pb and Zn
are higher in sector I and III than in sector II and IV. Hg
(table 5) and Cd show an inverse distribution pattern. More mer-
cury or cadmium is adsorbed per weight-unit of suspended matter
at low turbidity (zone II, most similar to an open-sea situation)
than at high turbidity (zone III, zone under the influence of the
Scheldt estuary). Each of these elements shows its proper beha-
viour. Therefore, to explain the observed distribution patterns,

Table 3

Mean and range of dissolved concentrations of Cu, Zn, Cd and Pb
for the North Sea and adjacent regions $(\mu g.1^{-1})$

Area	Cu	Zn	Cd	Pb	References	Anal. method
Min. values in the Southern Bight	0.2-0.3 0.5-1	0.3-0.4 2 - 4	0.02-0.03 0.1 -0.3	– –	Duinker & Nolting (1982) Dutton et al (1973)	GFAAS AAS
English East Coast (inhore)	1.4 (1.2-2.8)	6.3 (3.0-15.6)	0.5 (0.1-6.2)	–	Dutton et al (1973)	AAS
Straits of Dover	1.0 0.86 (0.06-3.6)	6-8 –	1.2 -1.6 0.14 (0.02-0.26)	– – –	Dutton et al (1973) Dehairs et al (1982)	AAS AAS
British Channel	0.34(±0.27) 0.22 (0.1 -0.4) 0.46 0.23-1.29	0.78(±0.28) 0.6 (0.3-0.9) 2.0 (1.2-3.8)	0.041(±0.19) 0.01 (0.01-0.02) 0.06 <0.01-0.38	– – 0.17 <0.05-1.1	Duinker & Nolting (1982) Jones in Topping et al (1979) Preston (1973)	AAS AAS AAS
North-East Atlantic	0.26 0.05-0.80	3.0 1.4-7.0	0.04 <0.01-0.41	–	Preston (1973)	AAS
Bristol Channel	2.07 1.02-4.74	9.98 3.57-21.42	1.13 0.28-4.20	1.18 0.35-5.00	Abdullah (1972)	ASV

Table 3 (continued)

Area	Cu	Zn	Cd	Pb	References	Anal. method
Belgian Coastal Area	2.21 (0.5-21.8) 0.34-2.00 0.6-2.4	6.66 (1.7-23.2) - -	0.118 (0.025-0.98) 0.024-0.11 0.1-0.4	3.86 (0.9-13.87) 0.1-2.6 -	This study Mart (1976) Duinker & Nolting (1977)	DPASV pH=1 + U.V. DPASV pH=2 AAS
Dutch Coastal Area	1.7 (1-2.5)	9.9 (3-20)	0.2 (0.1-0.3)		Duinker & Kramer (1977)	DPASV pH=2.7
Northern North Sea	1.0 (0.8-1.2) 0.26 (0.1-0.9) 2.7	1.0 (0.8-1.2) 2.7 (1.4-4.2) 5.7	0.03 (0.02-0.03) 0.07 (0.01-0.17) -	- - 1.2	Duinker & Nolting (1982) Jones in Topping (1979) Burda (1978)	AAS AAS X-Ray fluorescence
Western Atlantic shelfwaters	0.26	0.16	0.023	-	Bruland (1981)	AAS

Table 4

Mean relative abundances of trace metals in particulate matter ($\mu g \cdot g^{-1}$)

Metal	Zone	Nb	Range	Arithmetic mean		Geometric mean		Median
				$\overline{x}$	σ	$\overline{xg}$	σg	
	Belgian Coast	35	5.7 - 735	94	166	55	2.5	52
	I	11	5.7 - 735	169	280	61	2.4	53
Zn	II	12	23 - 155	57	35	49	1.7	57
	III	5	11 - 141	82	55	59	2.8	88
	IV	7	26 - 80	59	20	55	1.5	58
	Belgian Coast	36	0.10-3.90	1.27	0.85	1.00	2.1	1.03
	I	11	0.65-3.15	1.32	0.88	1.08	1.9	0.95
Cd	II	12	0.10-3.90	1.31	1.01	0.93	2.7	1.29
	III	6	0.32-1.55	0.80	0.43	0.71	1.7	0.74
	IV	7	0.50-2.45	1.55	0.76	1.35	1.8	1.80
	Belgian Coast	36	3.6 -57.3	21.6	14.2	17.0	2.1	18.6
	I	11	3.6 -41.0	23.0	12.8	18.5	2.2	23.8
Pb	II	12	4.1 -43.3	18.0	10.6	15.0	2.0	17.2
	III	6	9.4 -55.0	29.6	16.9	25.3	1.9	27.1
	IV	7	5.5 -57.3	18.4	18.5	13.2	2.3	10.5
	Belgian Coast	36	4.8 -31.6	13.8	6.5	12.3	1.6	14.2
	I	11	4.8 -31.6	14.5	8.6	12.3	1.8	15.8
Cu	II	12	6.2 -25.6	13.1	6.3	11.7	1.6	11.6
	III	6	7.7 -18.7	15.4	4.0	14.8	1.4	16.7
	IV	7	6.3 -22.1	12.4	5.4	11.4	1.5	13.6

Table 5

Relative abundances of mercury in particulate matter ($\mu g.g^{-1}$)

Period	Zone III - Scheldt Estuary zone - high turbidity (A)	Zone II - open sea zone - low turbidity (B)	B/A
November 1978	2.1	4.6	2.2
Oktober 1979	0.7	1.5	2.0
May 1980	1.0	-	-
June 1980	0.5	1.2	2.4

Table 6

Dissolved mercury concentrations in the Belgian Coastal Zone
(May 1981)

Station	ng Hg.1^{-1}	Salinity (‰)
15.05.120581.0950	13.5 ± 1	30.27
25.05.120581.1120	8.5 ± 0.4	31.26
35.05.120581.1210	13.3 ± 0.2	31.30
45.05.120581.1255	10.7 ± 0.3	31.62
54.05.120581.1435	6.2 ± 0.6	33.64
44.05.120581.1444	5.9 ± 1.8	32.59
34.05.120581.1650	7.9 ± 1	31.07
24.05.120581.1740	10.9 ± 0.9	30.07
14.05.120581.1830	16.9 ± 0.7	29.64
12.05.130581.0920	19.3 ± 0.1	32.99
22.05.130581.1010	20.7 ± 0.2	33.52
32.05.130581.1050	15.1 ± 0.3	33.36
42.05.130581.1140	14.4 ± 0.2	33.76
43.05.130581.1235	16.9 ± 0.4	33.52
33.05.130581.1345	24.4 ± 0.4	32.39
23.05.130581.1440	21.7 ± 0.2	31.38
13.05.130581.1500	19.5 ± 0.5	31.18
11.05.140581.0850	13.4 ± 0.1	33.20
21.05.140581.1220	6.6 ± 0.4	33.52
31.05.140581.1310	–	–
41.05.140581.1400	–	–

one must also study the characteristics of the suspended matter
such as grain size, chemical and mineralogical composition as
well as specific interactions between the metal and the suspen-
ded material in function of these characteristics (see e.g. the
study of mercury interactions with suspended matter from the
Scheldt estuary by Baeyens et al (1982).

c. Total and dissolved mercury

The spatial distribution of total mercury is completely ana-
logous to the distribution of particulate mercury. The mean ob-
served particulate and total mercury concentrations indicate that
an important fraction of the mercury is attributed to the parti-
culate phase and that dissolved mercury concentrations must be
very low.

Table 6 shows results obtained during a cruise in May 1981.

Measured values of dissolved mercury range between 6.2 and
24.4 ng Hg/l. These results agree fairly well with those obser-
ved by Burton & Leetherland (1971) in British coastal waters ran-
ging from 11 to 21 ng/l.

d. Bismuth and Antimony

Total concentrations range between 0.08 µg/l and 0.3 µg/l for
Sb and between non detectable amounts to 0.1 µg/l for Bi (table
7). Data on Sb and Bi are scarce and comparison can only be made
with results obtained with other analytical techniques and in ve-
ry different geographic localities. Nevertheless, the same order
of magnitude was found by Schutz (1965) in the Atlantic Ocean and
by Portmann (1966) in the Irish Sea.

The data for Bi show concentrations often below detection li-
mit (< 0.05 µg/l) ; few results have been obtained on samples
close to the coast and in the vicinity of the mouth of the Scheldt
estuary. They might indicate that Bi diffuses from the coast and
is rapidly diluted or removed by unknown processes from the wa-
ter column offshore.

Metal speciation (Zn, Cd, Pb, Cu, Sb and Bi)

Besides its very high sensibility, DPASV has another advanta-
ge (see part I) as it allows an approach to speciation. As an
illustration of this speciation approach, we provide some results
obtained during a cruise in October 1979, in table 7.

The fraction detected in step I at in situ pH refers rather
arbitrarily to ionic species since very labile complexes (proba-
bly inorganic) can also be involved. The difference between the
results obtained in step IIa (acid pH) and I corresponds to weak
complexes. Finally, step III gives us the total concentrations.
The difference between III and IIa corresponds to strong comple-
xes. This concerns Zn, Cd, Pb and Cu. The content of Zn, Cd,
Pb and Cu involved in organic complexes represents frequently an
important fraction of the total concentration but shows strong

Table 7

Speciation of dissolved heavy metals in seawater ($\mu g.l^{-1}$). October 1979

Stations	Zn			Cd			Pb		
	pH in situ I	pH acid IIa	UV III	pH in situ I	pH acid IIa	UV III	pH in situ I	pH acid II	UV III
11	0.15	0.95	2.97	0.12	0.18	0.30	0.05	1.10	2.21
21	0.21	2.70	4.15	0.03	0.08	0.14	0.22	1.00	2.20
31	0.10	1.10	3.37	0.02	0.14	0.25	0.07	0.40	1.13
41	0.10	0.70	6.37	0.02	0.05	0.27	0.05	0.61	1.03
12	0.50	1.10	6.10	0.05	0.05	0.20	0.10	0.30	3.15
22	0.75	1.90	3.40	0.08	0.08	0.16	0.05	0.30	1.40
32	0.36	1.30	2.40	0.04	0.05	0.10	0.05	0.35	1.00
42	0.10	2.25	4.16	0.02	0.06	0.13	0.05	0.36	3.02
13	0.50	1.23	2.38	0.06	0.10	0.26	0.14	0.75	1.31
23	0.30	1.50	2.05	0.04	0.04	0.06	0.11	0.80	1.22
33	0.50	2.12	3.10	0.05	0.10	0.15	0.16	0.80	1.80
43	0.20	1.20	3.50	0.05	0.08	0.18	0.08	0.20	1.60
14	0.54	1.42	1.70	0.08	0.08	0.10	0.16	0.44	1.20
44	0.30	2.00	4.30	0.03	0.03	0.06	0.05	0.30	1.80
15	0.80	4.50	7.90	0.02	0.08	0.18	0.05	1.20	1.80
25	0.30	5.08	5.80	0.05	0.06	0.13	0.07	1.54	3.90
35	0.50	3.65	6.70	0.02	0.10	0.16	0.08	1.23	3.40
45	0.30	2.25	7.18	0.02	0.05	0.14	0.08	1.88	3.23

I   = free ions + very labile complexes
IIa = free ions + weak organic and inorganic complexes (for Sb, IIa = Sb^{III})
IIb = Sb^V + Sb^{III}
III = total concentration

Table 7 (continued)

Stations	Cu			Sb				Bi	
	pH in situ I	pH acid IIa	UV III	pH acid IIa	pH acid+SO$_2$ IIb	UV + SO$_2$ III		pH acid IIa	UV III
11	0.11	1.05	1.30	N.D.	0.17	0.17		N.D.	N.D.
21	0.20	1.14	1.85	N.D.	0.08	0.10		0.14	0.20
31	0.10	0.25	0.82	N.D.	0.12	0.14		N.D.	N.D.
41	0.06	0.12	0.70	N.D.	0.12	0.12		N.D.	N.D.
12	0.15	0.40	1.65	N.D.	0.10	0.15		N.D.	N.D.
22	0.25	0.60	1.20	N.D.	0.14	0.20		N.D.	0.08
32	0.10	0.40	0.80	N.D.	0.10	0.15		N.D.	N.D.
42	0.10	0.10	0.50	N.D.	0.12	0.15		N.D.	0.07
13	0.20	0.40	0.80	N.D.	0.17	0.25		N.D.	0.05
23	0.60	0.90	1.20	N.D.	0.12	0.18		N.D.	N.D.
33	0.30	0.80	1.60	N.D.	0.05	0.08		N.D.	N.D.
43	0.06	0.20	0.60	N.D.	0.15	0.25		N.D.	N.D.
14	0.30	0.84	1.32	N.D.	0.26	0.30		N.D.	0.05
44	0.10	0.30	1.20	N.D.	0.18	0.28		N.D.	N.D.
15	0.12	1.50	2.90	N.D.	0.20	0.23		N.D.	0.10
25	0.54	1.12	1.90	N.D.	0.25	0.26		N.D.	0.08
35	0.15	0.80	0.80	N.D.	0.16	0.20		N.D.	N.D.
45	0.15	0.80	1.42	N.D.	0.10	0.25		N.D.	N.D.

I   = free ions + very labile complexes
IIa = free ions + weak organic and inorganic complexes (for Sb, IIa = Sb^{III})
IIb = Sb^{V} + Sb^{III}
III = total concentration

variations from one sampling site to another : 12 to 87% for Zn, 20 to 80% for Cd, 33 to 87% for Pb and 20 to 83% for Cu. More results are necessary to look at possible links with other important water quality parameters such as nutrients, DOC, Chl.A and processes such as primary production, grazing, etc.

Sb and Bi cannot be measured at in situ pH because of hydrolysis of their salts under these conditions. As a consequence, the ionic form cannot be dissociated from weak complexes and step IIa of table 7 gives the sum of the two forms. The IIb data for Sb corresponds to the sum of Sb^{III} and Sb^V. The results for Sb lead to the conclusion that Sb^V is the main dissolved form of this metal. The percentage of Sb complexed by organic matter can be estimated to vary between 20 and 40% of the total concentration.

Compartmental distribution of Zn, Cd, Pb, Cu and Hg

Up to 90% of the total content of Zn, Cd, Pb, and Cu is found in the dissolved phase (table 1). This may suggest that the largest part of these metals are transported out of the Belgian coastal area and that only a minor fraction is involved in the sedimentation cycle. The behaviour of mercury however is completely different : the dissolved phase represents only about 30% of the total content in the Belgian coastal waters. Practically all the mercury is associated with the suspended matter in the Scheldt estuary zone (zone III). The dissolved mercury-particulate mercury ratio increases with the distance from the coast. This seems quite acceptable since in the very turbid Belgian coastal waters, dissolved mercury has been scavenged by particulate suspended matter (Reimers, 1974 ; Baeyens et al, 1977, 1979a, 1979b and 1982) while mercury data for open ocean regions reveal that, due to the very low particulate matter content, the dissolved phase is the major compartment.

DISCUSSION

Little information is available about the distribution of Bi in the explored zone. But, the present results indicate that the distribution of Bi along the coast is primarily a coastal problem. The Bi is possibly derived entirely from domestic effluent (including the estuary), as there are no known large natural and industrial Bi sources in the region.

Dissolved mercury shows a smooth decreasing dependence on the distance from the coast.

The spatial distribution patterns of total dissolved Zn, Cd, Pb, Cu and Sb exhibit no analogy with those of salinity. It is most probably determined by the intensity of life processes and the cumulative effect of many small or large sources of contamination (ship traffic, industrial dumping, estuarine area, Dover straits inputs as well as outputs depending on residual currents).

Data on "organically bound" metal ions (representing up to 80% of the total dissolved metal content) show effectively that organic binding may play a major role in "controlling" the concentrations of these elements, at least in this zone characterized by high biological productivity. It must however be clear that the survey described here are limited in time and space and that different patterns might appear if long time averages (many years) are taken (see part 6).

The availability of the metals to living cells or adsorption by particulate matter obviously affect the ratio of the different metal species (ionic, inorganic and organic fractions).

Further evidence for this hypothesis is the observed correlation of the different fractions of metal concentrations with an indicator of productivity e.g. chlorophyll concentrations and ^{14}C uptake.

Particulate metal distributions are similar but opposite to the salinity gradient and follow clearly the turbidity distribution.

The dissolved phase (free metals, inorganic and organic soluble species) seems to be the main compartment for heavy metals in the explored region, except for mercury.

Our results seem to be comparable with those found in other coastal areas.

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