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BOUNDARY CONDITIONS FOR HEAVY METALS
AT THE AIR-SEA INTERFACE

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Abstract

During 1980 and 1981 the aerosol burden as well as the wet
and dry atmospheric fall-out of Cu, Cd, Pb, Zn, Fe and Mn to the
sea have been studied in the Belgian coastal area. Atmospheric
Cu, Zn and Cd are observed to be introduced into the sea mainly
by wet fall-out, while Fe, Mn and also Pb have a dry and wet
fall-out of similar magnitude. Of these elements, Cu, Zn and
Cd have the highest washout factors. Furthermore, for all
elements, excepted Mn, discrepancies exist between washout
factors above land and sea, with values up to 5 times larger
above the sea.
On the scale of the North Sea, atmospheric fall-out of Cu, Zn,
Pb and Cd exceeds by one order of magnitude the combined input
of the rivers Scheldt, Rhine and Meuse, while fall-out of Fe and
Mn is of similar magnitude as river input. As concerns the
Belgian coastal area, fall-out of Cu, Zn, Pb and Cd is still
larger than, but remains within one order of magnitude of the
input by the river Scheldt. Here Fe-inputs are of similar
magnitude, while fall-out of Mn is 10 times smaller than river
input. In this coastal region, characterized by a large resi-
dual flow of water coming from the Channel, the total annual
input of Cu, Zn, Pb and Cd from the atmosphere and the river
Scheldt represents only from 0.8 (Pb) to 3.4 % (Zn) of the
annual flow-through of these heavy metals. Furthermore, it is
observed that measured enrichments of the sea-surface microlayer,
as sampled with the screen method, can support out-fluxes of
heavy metals to the atmosphere which are only < 0.1 % of the
atmospheric fall-out to the sea.

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Introduction

During the past decade, the atmospheric aerosol burden and the atmospheric fall-out have been studied in the North Sea area from a series of shore based, coastal sampling platforms and a single maritime platform (Peirson et al., 1974; Cambray et al., 1975 and 1979; Kretzschmar and Cosemans, 1979). The importance of the atmosphere as a main transport route of heavy metals to the sea has been stressed by Cambray et al. (1975 and 1979). The predominant source of these heavy metals in the North Sea area is shown to be the industrial activity on the mainland (Kretzschmar and Cosemans, 1979).
In open ocean areas, evidence exists that winddriven material output from the enriched sea surface microlayer to the atmosphere can to some extent determine the composition of the marine aerosol (see for instance Duce et al., 1976; Lantzy and Mackenzie, 1979). However, also as concerns the North Sea, Peirson et al. (1975) consider the winddriven formation of a heavy metal enriched sea spray, as the most plausible process responsible for the increased Na and heavy metal contents in rainwater above the sea, as compared to rainwater above the mainland. Analysis of screen-sampled microlayer and of sea spray artificially produced in situ in the North Sea, point towards important enrichments of some heavy metals relative to Na, at the air sea interface (Hunter, 1977; Pattenden et al., 1980).
For the southernmost part of the North Sea and specifically for the Belgian coastal area, no data exist concerning (1) the composition of the marine aerosols, as sampled above the sea and (2) air-sea exchanges in general.

From January 1980 on we occupied two sampling platforms on an intermittent basis in the Southern Bight and in the Straits of Dover (Dedeurwaerder et al., 1981). Both marine aerosols and atmospheric fall-out were sampled in order to assess: (1) the impact of the industrial activities in the surrounding countries (Belgium, France, Great-Britain) on the Cu, Cd, Pb, Zn, Fe and Mn content of the aerosols above the southernmost part of the North Sea and (2) the importance of the atmosphere as a transport route of heavy metals to the sea.

Furthermore, the sea-surface microlayer was sampled in the close vicinity of the atmospheric sampling platforms in order to study enrichments of Cu, Pb, Cd and Zn relative to the bulk sea water and to allow an estimation of the sea to air flux for these heavy metals.
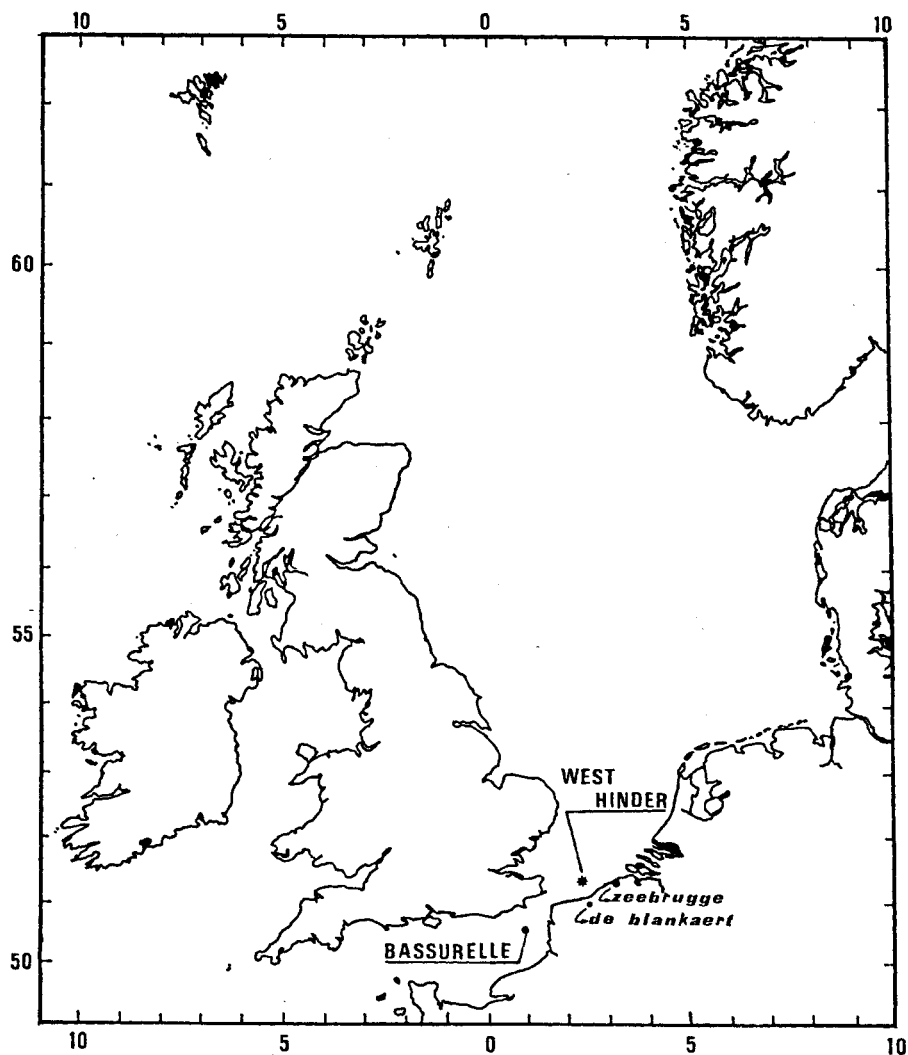
fig. 1.

Positions of both maritime sampling platforms
West-Hinder (51° 23' 30" N – 2° 21' 30" E) and
Bassurelle (50° 33' 24" N – 0° 54' E).

The sampling and analysis

Sampling location:

The positions of both aerosol sampling platforms and micro-layer collection sites are given in Figure 1. Most samples of marine aerosols and all samples of atmospheric fall-out were taken aboard the Light-Vessel "West-Hinder", anchored in the Southern Bight (position: 51° 23.5'N - 02° 21.5'E). On a few occasions marine aerosols were sampled from the Research Vessel "Mechelen" anchored in the close vicinity of the Light-Vessel "West-Hinder" and also in the Straits of Dover (Bassurelle light-buoy, position: 50° 33.'4N - 00° 54'E; Figure 1).

Aerosol sampling devices and analysis:

Total aerosol burden is sampled with hi-vol samplers ($\sim$ 20 m^3 . h^{-1}; velocity of air through the filter 58 cm . s^{-1}) by pumping up to 200 m^3 of air through Whatman 41 cellulose filters. Size fractionated aerosol samples are taken with 6 stage hi-vol cascade impactors (model Sierra-235).
Aerosol collection occurs on 5 slotted Whatman 41 cellulose substrates and one Whatman 41 cellulose back-up filter. Up to 1000 m^3 of air are sampled for this purpose.
According to the manufacturer, for an air flow of 40 CFM, these impactors separate the particles in the following equivalent aerodynamic diameter classes: > 7.2; 7.2 - 3.0; 3.0 - 1.5; 1.5 - 0.95; 0.95 - 0.49; < 0.49 μm.
The Whatman 41 cellulose substrates are subsequently acid mineralized and the heavy metal contents determined by flame- and electrothermal- AAS.
Up to now 10 sampling campaigns of 2 full weeks each were conducted aboard the Light-Vessel "West-Hinder", providing us with a total of 78 samples.

Fall-out sampling and analysis

The atmospheric dry fall-out is collected on vertically suspended vaselinated plexiglass surfaces of 400 cm^2 for periods of 12 days. In the laboratory the vaseline is transferred to a Whatman 41 cellulose filter and is extracted with petroleum ether in a soxhlet apparatus. The Whatman filter with the collected atmospheric dust is then acid mineralized and analyzed by flame- and electrothermal- AAS.
Wet atmospheric fall-out is manually collected in acid cleaned polyethylene funnels ($\emptyset$ 18 cm) and containers. No attempt was undertaken to filter the rain water as evidence exists that the dissolved phase is the predominant one for all heavy metals of interest (Nguyen et al., 1979). Heavy metal content is measured directly on the untreated rain water samples by flame- or electrothermal- AAS.

Table I: Heavy metal content in air and rainwater and heavy metal wet- and dry fall-out above the Southern Bight.

Element	1 Concentration in air		2 Concentration in rain		3 Dry fall-out		4 Wet fall-out
	$ng.m^{-3}$	N	$\mu g.\ell^{-1}$	N	$ng.cm^{-2}.yr^{-1}$	N	$ng.cm^{-2}.yr^{-1}$
Cu	6.5	77	39.5	15	74	8	1,509
Zn	86.6	72	193.6	12	411	8	7,396
Pb	82.6	75	13.0	10	507	8	497
Cd	2.7	53	3.0	11	4.5	7	114
Fe	250	78	158.9	15	6,883	7	6,070
Mn	14.6	71	9.5	11	135	8	363

N = number of samples.

Up to now 8 dry fall-out samples and 15 rainwater samples were taken aboard the West-Hinder.

Microlayer sampling and analysis

The microlayer is sampled using the Garrett screen technique (Garrett, 1967). The screen consists of an all plexiglass frame stretching a nylon net with a mesh aperture of 400 µm and a fabric thickness of 440 µm.
The sampling is done from a rubber boat at about 1 km upstream from the Research-Vessel. The operator wears polyethylene gloves and touches the sea surface with the screen in horizontal position.
The collected fractions (about 50 ml each) are then drained into acid cleaned polyethylene containers. For each sampling about 2 liter of microlayer are collected in this way. At each microlayer sampling site the watercolumn is sampled by immersion of polyethylene containers at -30 cm.
Once aboard the samples are immediately deep-frozen.
For the analysis mode of the dissolved and particulate microlayer and bulk sea water phases, see G. Gillain et al. (1982) and Dedeurwaerder et al. (1981).

Results

1. Wet and dry fall-out

The mean values (geometric means) of heavy metal concentrations in marine aerosols (total aerosol and cascade impactor samples for 1980 and 1981 combined) and in rainwater collected at sea are given in Table I, columns 1 and 2.

The annual wet fall-out is given by the product of the mean concentration in rainwater with the annual precipitation above the sea. It is this latter variable which induces most of the uncertainty in the values of heavy metals wet fall-out. Indeed, since no systematic record of precipitation at sea exists for the Southern Bight and since our samplings were only done intermittently, no complete and satisfactory information exists on this matter.
To our knowledge the only continuous, one year lasting record of rainfall over the North Sea was done by Cambray et al. (1975). These authors observed that rainfall at sea was only about 55 % of the amount collected at land-based stations located at similar latitude. The Royal Meteorological Service of Belgium recorded for 1980 at the Coastal stations Zeebrugge and Kokzijde respectively a precipitation of 731 mm and 659 mm. Taking 55 % (see Cambray et al., 1976) of these values gives an annual precipitation at sea of 362 to 402 mm, with a mean value of 382 mm. Using this mean value and our mean data for heavy metal concentrations in rainwater, we calculated the wet fall-out for the different heavy metals. (Table I, column 4).

Table II: Calculated dry and total (wet + dry) deposition velocities, wash-out factors and observed mean mass median diameters (MMD) for the considered heavy metals.

Element	1 Dry deposition velocities cm.sec^{-1}	2 Total (wet + dry) deposition velocities; cm.sec^{-1}	3 Mean M.M.D.; μm	4 Wash-out factor x 10^6
Cu	0.36	7.75	0.59	6.11
Zn	0.15	2.85	0.28	2.24
Pb	0.19	0.39	0.71	0.16
Cd	0.05	1.40	0.53	1.12
Fe	0.87	1.60	1.58	0.64
Mn	0.29	1.08	0.72	0.65

The measured dry fall-out is given in Table I, column 3.
From Table I, it appears that Pb, Fe and Mn have wet- and dry
fall-out rates, which are similar (Pb, Fe) agree within one.
order of magnitude (Mn).
For Cu, Zn and Cd wet fall-out is one order of magnitude larger
than dry fall-out. This situation is also reflected in the
wash-out factors, being the ratios of rainwater over air con-
centrations of the different heavy metals. For Pb, Fe and Mn,
wash-out factors are $< 1 \times 10^6$, while for Cu, Zn and Cd they
are $\geqslant 1 \times 10^6$ (Table II, column 4).

It is furthermore observed that those elements with the
largest wash-out factors (Cu, Zn, Cd) have smaller Mass Median
Diameter (MMD) values, as deduced from our cumulated aerosol
mass distributions, (Table II, columns 3 and 4).

Although it appears that differences exist between elements
as concerns the efficiency of their rain-out, the clean-up of
the atmosphere is done mostly by the very first fraction of
rainfall. Indeed, an exponential-like decrease of heavy metal
concentration with increase of precipitation was observed
(Figure 2). This also indicates a continuous dilution of the
concentrated primary rainfall, such as observed by others
(see for instance Nguyen et al. (1979)).

Dry deposition velocities and total (wet + dry) deposition
velocities given by the ratio of dry and total fall-out over the
content in air, are given in columns 1 and 2 of Table II. Dry
deposition velocities range from 0.15 (Zn) to 0.87 (Fe) cm.sec^{-1}
and total deposition velocities from 0.39 (Pb) to 7.75 (Cu) cm.
sec^{-1}.
From their studies on the ^{7}Be distributions in the surface
waters of the world oceans and the lower troposphere, Young and
Silker (1980) emphasized the important role of the aerosols as
the carriers of ^{7}Be to the ocean surface. By assuming the
validity of the steady state assumption that radioactive des-
integration of ^{7}Be in the watercolumn is compensated for by
wet and dry fall-out to the oceans of ^{7}Be associated with the
smaller aerosols ($<1\mu$m), Young and Silker deduced a mean aero-
sol deposition velocity of 0.85 cm.sec^{-1}.
From Table II it appears that it are only Pb, Cd, Fe and Mn,
which have total deposition velocities close to the ^{7}Be value
(deviatons are not larger than a factor 2). On the contrary,
Zn and Cu have total deposition velocities which are respecti-
vely 3.4 and 9.1 times larger than the ^{7}Be value. These two
elements also have the largest wash-out factors.
However, from Table II (column 4) it is apparent that all ele-
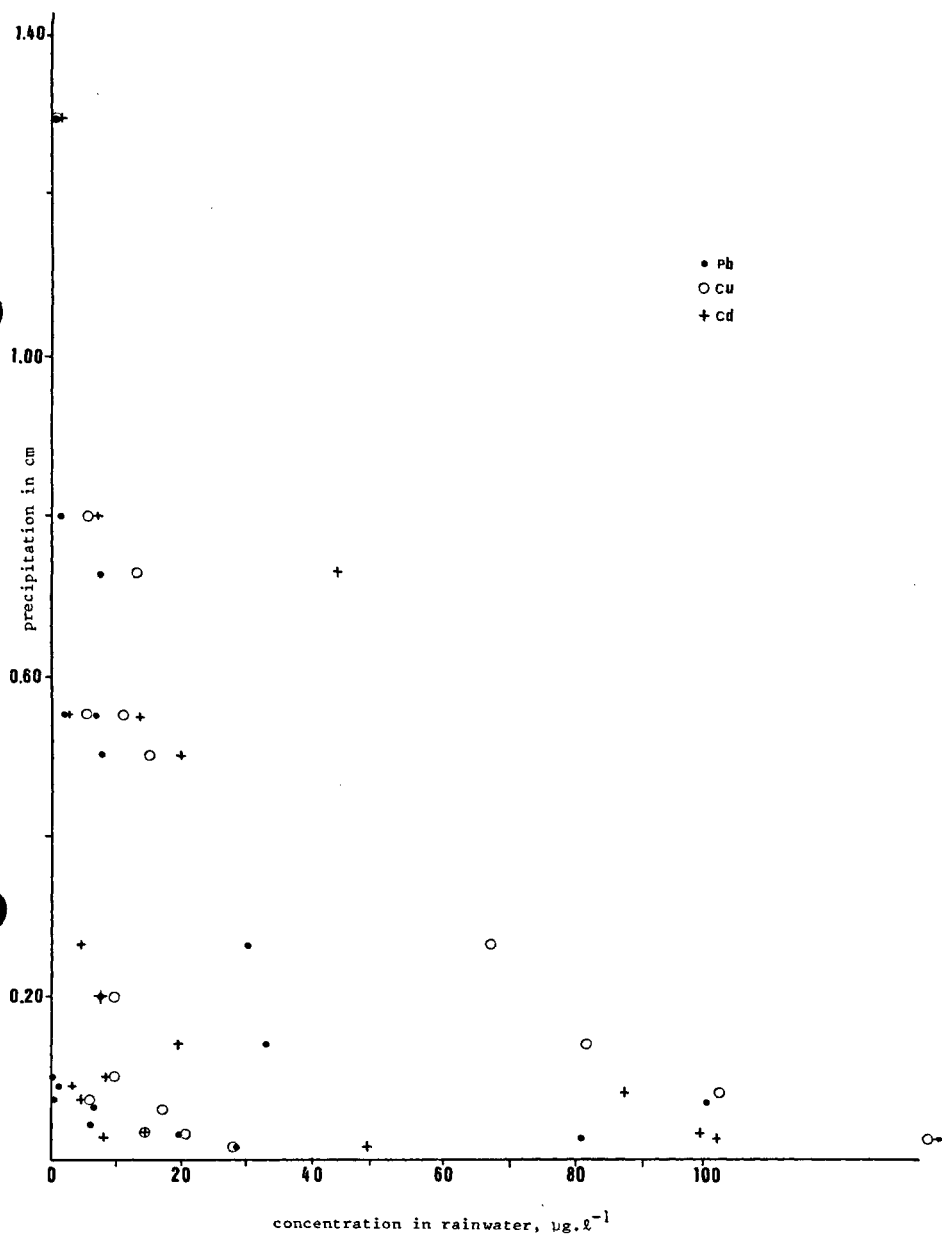ments, with the exception of Fe, have MMD values $<1\mu$m as
required the ^{7}Be model.

Figure 2: concentrations of dissolved Pb, Cu and Çd in
rainwater (in µg.ℓ$^{-1}$) against collected precipitation

Table III: Comparison between heavy metal content (geometric mean values) in rainwater and wash-out factors above land and sea.

Site	Cu	Zn	Pb	Cd	Mn	Fe	Na
			Concentration in rainwater	(μg.ℓ^{-1})			
Sea: West-Hinder (N=15)	39.5	194	13	3	9.5	159	17,154
Land: De Blankaert (N=8)	5.9	91.5	3	1.5	8.9	44.6	446
			Wash-out factors	($\times 10^6$)			
Sea: West-Hinder	6.10	2.24	0.16	1.11	0.65	0.64	9.38
Land: De Blankaert	1.02	1.20	0.05	0.63	0.46	0.12	--

It therefore appears that essentially 2 factors determine the "fitting" of an element to the ^{7}Be-model: (1) the MMD value and (2) the solubility of the element in rainwater. Those elements which fit best to the ^{7}Be-model not only have a MMD <1µm, but are also relatively poorly soluble in rainwater; this is the case for Pb and Mn.

2. Rain above land and sea: differences in heavy metal content

During June and September 1981 the sampling campaigns aboard the West-Hinder were paralelled by sampling campaigns on land (station "De Blankaert", Figure 1), at 25 Km from the coast-line.
Although concentrations of Cu, Zn, Cd, Pb, Fe and Mn in air above sea are similar or lower than above land, it is observed that such as for Na, the rainwater content of these elements is higher above sea than above land, with the exception of Mn which shows similar concentrations (Table III).
A similar discrepancy between land- and sea-based sampling platforms was observed in the North Sea by Peirson et al. (1974) and Cambray et al. (1975). These authors considered that the reduced rainfall at sea alone could not account for the magnitude of the observed enrichments. Therefore, they attributed the enhanced heavy metal content in rainwater above the sea to a contribution from sea spray as indicated by the much enhanced Na content. They concluded that this sea spray should be derived from a strongly enriched sea-surface microlayer. However, as discussed below under point 4, the heavy metal output from the sea-surface to the atmosphere, as based on our microlayer enrichment data is negligible compared to the atmospheric input. Therefore, other processes must be considered in order to explain the higher rainwater contents above sea.

When comparing the wash-out factors we obtained for the sea-based station with those obtained for the land-based station (Table III) it appears that these factors are larger at sea for all considered elements, excepted again Mn. This suggests a greater solubility of the aerosols above sea. Therefore, considering the fact that the largest fraction of the marine aerosols are in fact land-derived, it might well be that the chemical transformation the aerosols undergo during their aging process, as well as differences in physico-chemical characteristics of rainwater above land and sea are responsible for this enhanced solubility.
The way to handle this problematic would be to compare the chemical composition of the discrete aerosols particles and the rainwater characteristics above land and sea.

3. The atmospheric heavy metal input into the Belgian coastal zone, as compared to river input

   In Table IV the atmospheric fall-out (wet + dry) to the entire North Sea (surface: 5.3 x 10^5 Km^2; Cambray et al. 1975) is compared with inputs through the rivers Rhine, Scheldt and Meuse, as given in the literature.
   Our fall-out data are compared with those obtained by Cambray et al. (1975) for the North Sea area. Both sets of data agree within a factor 3, justifyring the extrapolation of our fall-out data to the entire North Sea.
   From Table IV it appears that atmospheric fall-out for Cu, Zn, Pb and Cd is up to one order of magnitude larger than the input by the main rivers entering the North Sea. On the contrary fall-out of Fe and Mn is of the same order of magnitude as river input.
   We have also compared the relative inputs by the atmosphere and river run-off in the Belgian coastal environment. The considered area consists of zone 1S and half of zone 2 of the sampling network of the former "National R.D. program SEA" (Figure 3; Podamo, 1973). The area covers 11050 Km^2 and includes the Scheldt estuary. The residual flow for zone A (mean depth 15 m) is 1438 $Km^3.yr^{-1}$ and for zone B (mean depth 30 m) 3250 $Km^3.yr^{-1}$ (see Figure 3; Podamo, 1973).
   The product of this residual flow with the mean particulate plus dissolved heavy metal load in the Belgian coastal environment (Table V, column A) gives the heavy metal transport through the considered zone (Table V, column B). The values of the combined dissolved and suspended loads of Cu, Zn, Pb and Cd used here are the geometric means of the values found for zones II and IV in Decadt et al. (1982). Since no sufficient data exist for the watercolumn load of Mn and Fe in the Belgian coastal area, the transport of these elements resulting from the residual flow was not considered. From Table V, columns C and D it is seen that the atmospheric impact is much less apparent in this reduced environment affected by the run-off of the river Scheldt. Nevertheless it is clear that even in this environment the atmospheric fall-out of Cu, Zn, Pb and Cd is still up to 5 times larger (case of Cd) than river input. On the contrary for Fe and Mn atmospheric fall-out is similar (Fe) or one order of magnitude lower (Mn) than the river input.

4. The heavy metal output from the sea-surface microlayer to the atmosphere

A. The heavy metal enrichment in the seasurface microlayer

   Particulate output from the sea to the atmosphere occurs by sea spray formation. As this process affects the sea-surface microlayer it is important to know the extent of the element enrichment in this layer. During 1980 and 1981 the microlayer was sampled in the vicinity of the West-Hinder and the Bassurelle sampling platforms.
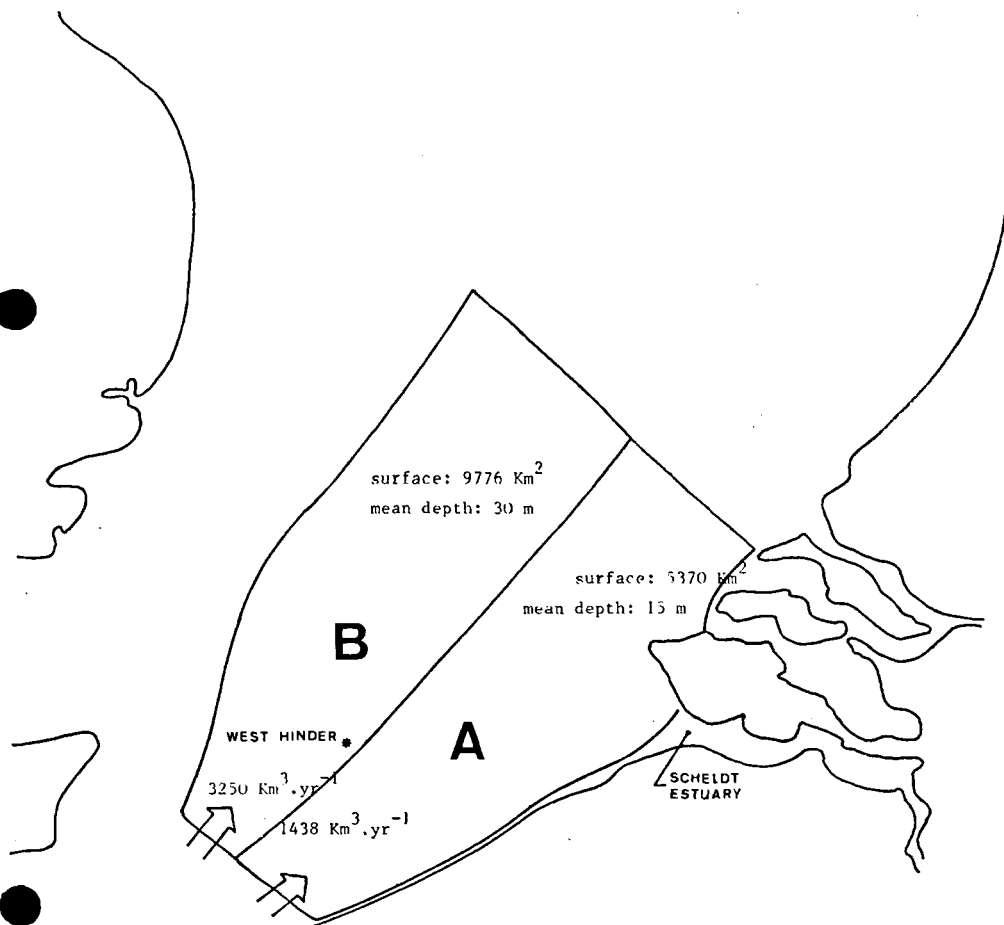
fig. 3.

Characteristics (residual flow, mean depth and surface) of the coastal environment in the Southern Bight for which the impact of atmospheric fall-out and river input is compared to the magnitude of the heavy metal flow through due to the residual flow.

Table IV: Heavy metal input in the North Sea (surface = 5.3×10^5 Km^2, Cambray et al. 1975); comparison between atmospheric contribution and river contribution; values of atmospheric fall-out are based on the data in Table I.

Element	Wet + dry atmospheric fall-out ton.yr^{-1}		River input in ton.yr^{-1}				Input by rivers in ton.yr^{-1}	
			Scheldt A		Rhine B	Rhine + Meuse C		
	This work	Cambray et al. (1975)	(1)	(2)	(3)	(4)	min.	max.
Cu	8,390	4,850(+)	12	62	730	389	401	792
Zn	41,234	47,435	28(*)	320(200*)	7,060	3,015	3,335	7,380
Pb	5,321	14,045	12	31	2,000	444	456	2,031
Cd	628	228(++)	2.1	1.6(*)	77	53	55	79
Fe	68,651	134,100	1,458	2,122	46,080	--	47,538	48,202
Mn	2,639	4,876	103(**)	700(400**)	6,000(5)	--	6,700	--

(-)   no data
(1)   Baeyens et al. (1982); dissolved + suspended load
(2)   Wollast (1976) and Duinker et al. (1979); dissolved + suspended load
(3)   Based on data of Duinker and Nolting (1976 and 1979); dissolved + suspended load
(4)   Based on data of Salomons and Eysink (1979); dissolved + suspended load
(5)   Weichart (1973)
(*)   Dissolved load only
(**) Suspended load only
(+)   max. value
(++) min. value

Table V: Impact of the atmospheric heavy metal fall-out and the heavy metal input through the river Scheldt on the watermass in the Belgian coastal area.

Element	A Average dissolved + particulate conc. in the watercolumn (1) $\mu g.\ell^{-1}$=ton.Km^{-3}	B Flow through zones A + B (Figure 3) (2) ton.yr^{-1}	C Atmospheric input (3) (this study) ton.yr^{-1}	C/B in %	D River Scheldt input (dissolved + particulate) (4) ton.yr^{-1}	D/B in %
Cu	2.23	10,454	175	1.7	62	0.6
Zn	7.330	34,363	859	2.5	320	0.9
Pb	3.921	18,382	111	0.6	31	0.2
Cd	0.121	567	13	2.3	2.1	0.4
Fe	--	--	1,431	--	2,122	--
Mn	--	--	55	--	700	--

(1) data from Decadt et al. (1982)

(2) The water flow is 4688 Km^3 (see text; Podamo (1973))

(3) The considered surface is 11050 Km^2 (see Figure 3)

(4) data from Wollast (1976) and Baeyens et al. (1982); see Table IV

(-) no data

The enrichment of the microlayer relative to the bulk sea water is discussed elsewhere (Dehairs et al., 1982).
In Table VI the observed average heavy metal concentrations (dissolved + particulate) are given relative to a constant Na content.

B. The heavy metal output from the sea-surface microlayer to the atmosphere

The heavy metal flux from the sea-surface to the atmosphere can be deduced from the known metal concentrations in the micro-layer and from the Na amount emitted from the sea-surface.
To estimate the emitted Na amount from the sea-surface, we can assume as a first approximation that the largest fraction of the emitted amount reenters the sea by dry and wet fall-out (Chesselet and Buat-Menard, 1972).
Similarly, for the area of interest we have observed that for the land based station "De Blankaert" Na in rainwater is in average only 2 % of the Na content collected in rainwater at sea in the same period. Our data on the Na content in rain-water and on the dry deposition of Na collected at sea, allow to compute a Na fall-out >0.65 and $\leqslant 1.03$ $mg.cm^{-2}.yr^{-1}$. This flux is similar to the average value found by Cambray et al. (1979) for total Na fall-out in the North Sea area (1.1 $mg.cm^{-2}.yr^{-1}$) and to the value of Na-emission from the sea-surface (1 $mg.cm^{-2}.yr^{-1}$) given by Erikson (1959). Therefore we will consider here a Na emission of 1 $mg.cm^{-2}.yr^{-1}$.
The heavy metal outflux is thus calculated as:

$$(\; [Element]/[Na] \;)_{ML} \; x \; Na\text{-}outflux$$

It is assumed here that no fractionation between heavy metals and Na occurs during sea spray formation. The outflux values are given in Table VI. They are about 4 orders of magnitude smaller than our atmospheric fall-out values. However, it is probable that our observed enrichments in the microlayer are underestimated, due to possible dilution of the samples with bulk sea water during the sampling and which is inherent to the Garret-screen sampling technique. Indeed, other micro-layer sampling methods, using bubble-burst techniques suggest for Pb and to a lesser extent for Zn in the North Sea micro-layer, enrichments relative to Na which are respectively 100 and 5 times greater than our values (Pattenden et al., 1981).

Table VI: Estimated flux of heavy metals from the sea-surface to the atmosphere.

Element (Number of samples)	Ratio of dissol- ved + particu- late conc. over Na conc. in the microlayer $\times 10^{-8}$ (1)	Enrichment (ML/BSW) of total concen- trations (1)	Sea-surface to atm. output $(=\dfrac{\text{element}}{\text{Na}} \times \text{Na output})$ $ng.cm^{-2} . yr^{-1}$	Ratio of sea-surface output over total atm. input (see Table I) $\times 10^{-4}$
Cu (17)	39	7.9	0.39	2.5
Zn (2)	260	5.3	2.6	3.3
Pb (Ndiss.= 2) (Npart.= 17)	32	5.1	0.32	3.2
Cd (17)	3.9	3.9	0.039	3.3
Hg (12)	0.49	1.7	0.0049	--

(1) as given in Dehairs et al. (1982)

Na content $\approx$ 109/liter

Na output taken as 1 $mg.cm^{-2} . yr^{-1}$ (see text)

ML = microlayer
BSW= bulk seawater

Conclusions

This study has shown that the atmospheric input of the heavy metals Cu, Zn, Pb and Cd to the North Sea exceeds the river input, even in a restricted, coastal environment fed by river run-off. For Fe the inputs from rivers and atmosphere are of similar strength, while atmospheric input of Mn is observed to be less important than river input in the coastal environment.

For Cu, Zn and Cd, the atmospheric input to the sea is essentially carried by wet fall-out, while for Pb, Fe and Mn wet and dry fall-out are of similar strength.

The fact that Cu, Zn and Cd leave the atmosphere mainly by wet fall-out is due to their greater solubility in rainwater as indicated by their larger wash-out factors. Some evidence exists that this greater solubility may in part be favored by the association of Cu, Zn and Cd are with the smaller aerosols (MMD's are $\leqslant 0.59\mu m$), as compared to Pb, Fe and Mn (MMD's are $\geqslant 0.71\mu m$). Besides differences in rainwater solubility between elements, there also exist land to sea differences in wash-out factors for the individual elements, with the exception of Mn. Although this can partly be explained by the fact that rainfall is less at sea, and should therefore be more concentrated in heavy elements than rainfall above land, other factors, such as a varying chemical composition of the aerosol and varying physico-chemical characteristics of rainwater itself, should be considered.

The enhanced heavy metal content of rainwater above the North Sea is not likely to result mainly from the incorporation in rainwater of a heavy metal enriched sea-spray, derived from the enriched sea-surface microlayer, as proposed by others. Evidence for this is given by the relatively small enrichments we observed in the microlayer in this part of the North Sea and the resulting small heavy metal outflux to the atmosphere compared to the atmospheric input (output <0.1 % of input). However, the question concerning the real microlayer enrichments is still unresolved, as evidence exist from other studies in the North Sea that microlayer enrichments based on the screen sampling method used here might be underestimated.

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