

Trace metals
North Sea
Residual flows
Diffusion
Métaux en traces
Mer du Nord
Flux résiduel
Diffusion

Trace metals in the eastern part of the North Sea. II: Flows of Cd, Cu, Hg, Pb and Zn through the coastal area

Willy BAEYENS ^a, Gérard GILLAIN ^b, François RONDAY ^c, Frank DEHAIRS ^a

^a Laboratorium voor Analytische Chemic, Vrije Universiteit Brussel, Pleinlaan 2, 1050-Brussel, Belgium.

^b Laboratoire d'Océanologie, Institut de Chimie, Université de Liège, Sart-Tilman, 4000-Liège, Belgium.

^c Geohydrodynamics and Environmental Research, Université de Liège, Sart-Tilman, 4000-Liège, Belgium.

Received 29/8/86, in revised form 18/11/86, accepted 20/11/86.

ABSTRACT

The residual flow lines off the Belgian coast are more or less parallel to the coast except in the area where the northeasterly flowing watermass coming from the Channel encounters the southwesterly-oriented Scheldt outflow. The result is a residual hydrodynamical front with, at the northern side, a less saline estuarine watermass, and at the southern side a more saline marine watermass. From the steady-state salinity pattern, diffusion coefficients perpendicular to the residual flow were deduced; they ranged from 21 to 108 m².s⁻¹.

The steady-state profiles of dissolved metals versus salinity indicate a dilution effect in the coastal-estuarine watermass and an almost constant concentration in the marine watermass. Offshore fluxes of Cd, Cu, Hg, Pb and Zn based on diffusive and mixing processes are calculated. They can explain the concentration increases in the coastal flow tube (315 km³.y⁻¹), but are insignificant beyond that flow tube. The ratios of the Scheldt output to the offshore flux vary from 38 to 85%, depending on the kind of metal. The ratio of the Scheldt output to the metal flow parallel to the coast is smaller than 1%.

The steady-state concentration profiles of particulate metals versus salinity are fairly constant in the coastal-estuarine and marine watermasses, but decrease very abruptly from the first to the second watermass. Assuming a conservative behaviour of the particulate metals, offshore fluxes and the resulting concentration increases in the coastal flow tube were deduced. These calculated concentration increases agree fairly well with the observed values. The contribution of the Scheldt estuary to the flows parallel to the coast ranges from 1.6 to 3.3%.

Oceanol. Acta, 1987, 10, 3, 301-309.

RÉSUMÉ

Métaux en traces dans la partie est de la Mer du Nord. II : Flux de Cd, Cu, Hg, Pb et Zn à travers la zone côtière

Les lignes de courant résiduel en face de la côte belge sont plus ou moins parallèles à cette côte, sauf dans la région où le courant Nord-Est en provenance de la Manche se heurte au flux de l'Escaut qui est orienté Sud-Ouest. Il en résulte un front hydrodynamique séparant une masse d'eau estuarienne moins salée (au nord du front), d'une masse d'eau marine plus salée (au sud du front). La distribution moyenne de la salinité nous permet de déduire les coefficients de diffusion perpendiculaires au courant résiduel; les valeurs varient de 21 à 108 m².s⁻¹.

Les courbes de concentrations moyennes en métaux dissous en fonction de la salinité moyenne font apparaître un effet de dilution dans la masse d'eau côtière-estuarienne et une concentration invariante dans la masse d'eau marine. Les flux de Cd, Cu, Hg,

Pb et Zn vers le large ont été calculés en se basant sur des processus de mélange et de diffusion. Ils permettent d'expliquer les augmentations de concentration dans la ligne de courant côtière ($315 \text{ km}^3 \cdot \text{an}^{-1}$), mais n'ont aucune signification en dehors de cette ligne de courant. Les rapports flux de l'Escaut sur flux vers le large varient entre 38 et 85%, en fonction du métal. Les rapports flux de l'Escaut sur flux parallèle à la côte sont inférieurs à 1%.

Les courbes de concentration moyennes en métaux particuliers, par rapport à la salinité moyenne, sont invariantes dans les masses d'eau côtière-estuariennes et marines mais décroissent abruptement de la première masse d'eau vers la seconde. En supposant un comportement conservatif des métaux particuliers, nous avons pu calculer les flux de métaux particuliers vers le large ainsi que l'augmentation des concentrations dans les lignes de courant qui en résulte. Les augmentations calculées ainsi sont en bon accord avec les valeurs observées expérimentalement. La contribution du flux de l'estuaire de l'Escaut au flux parallèle à la côte varie entre 1,6 et 3,3%.

Oceanol. Acta, 1987, 10, 3, 301-309.

INTRODUCTION

Unlike the open ocean, coastal systems such as the North Sea have attracted considerable attention where trace metal studies are concerned. The explanation appears to be related to several factors. Coastal waters are relatively accessible; the type of research vessel required for most work is relatively unsophisticated; trace metal levels in these waters are sufficiently enhanced; most important, there has been a growing concern over the last decade regarding the effects of industrial discharges on trace metal levels in nearshore waters and estuaries.

The review of trace metal studies in coastal areas has indicated that most studies over the last 10 years have fallen into the category of "snap shot" studies (Topping *et al.*, 1980). Such short-term metal distributions are not sufficient to derive metal flows through a coastal system. The time scales of the hydrodynamical and chemical data need to be matched, so when one uses, for example, a stationary winter flow, the metal distribution over the same period also needs to be known.

The metal flows through the Belgian coastal area can thus only be derived if information exists about: 1) the residual, steady-state current; 2) the diffusion coefficients related to these residual currents; and 3) the steady-state metal distributions. In this paper we will discuss these three items.

RESIDUAL FLOWS

Residual currents are calculated by solving, with appropriate inflow-outflow boundary conditions, averaged equations over a time sufficiently long to cover several tidal periods and thus to cancel out most of the tidal contributions. The non-linear residual effect of mesoscale motions is in these equations explicitly taken into account in the so-called Mesoscale Reynolds Stress or Tidal Stress (*e.g.* Nihoul, Runday, 1976; Nihoul, 1980). This model is fundamentally different from the "Long Wave Residue" models. In the latter, a solution is sought of the time-dependent hydrodynamic equations

which describe both macroscale and mesoscale motions. The residual macroscale part is then obtained by averaging the solution over the chosen time. Nihoul (1980) has argued that this method could lead to a 100% error on the residual circulation.

Djenidi and Runday (1985) applied the mesoscale Reynolds Stress model to the North European Continental shelf including the Skagerrak, the North Sea, the English Channel, the Celtic Sea, the Irish Sea and bounded at the Atlantic side by the 200 m isobath. Depths are less than 100 m in the major part of this area except in the Norwegian trench and on the continental slope. For that reason, and due to the strength of mesoscale mixing, vertical homogeneity was assumed and a depth integrated shallow water equation was used (*e.g.* Runday, 1976; Nihoul, 1980). A grid mesh of $10' \times 10'$ was selected for the computation.

To solve this equation, boundary conditions must be prescribed. They were derived from current, salinity and caesium 137 measurements reported in the literature. Djenidi and Runday (1985) estimated flows of $150.000 \text{ m}^3 \cdot \text{s}^{-1}$ through the Dover Strait, $60.000 \text{ m}^3 \cdot \text{s}^{-1}$ through the North Channel, $300.000 \text{ m}^3 \cdot \text{s}^{-1}$ between the Shetlands and Norway. A greater uncertainty was present at the western and southern open sea boundaries of the model; several scenarios of exchanges with the Atlantic Ocean were conceived, showing that the influence of those conditions remains limited to the west of Ireland and in the Celtic Sea, with very slight changes in the residual velocities for the second area.

The wind field has an important effect on the residual displacement of water masses. Therefore, Djenidi and Runday (1985) selected two situations, one typical of winter and the other of summer. The mesoscale Reynolds stress was calculated for these two situations with transient wind stress; then the residual circulation was calculated, using the mesoscale Reynolds stress over one week, and applying the mean wind stress. Results for the North Sea are shown in Figure 1; we have combined these two situations into an average situation over the year, to correspond in time scale with the salinity and trace metal data (this time scale covers several winter and summer periods).

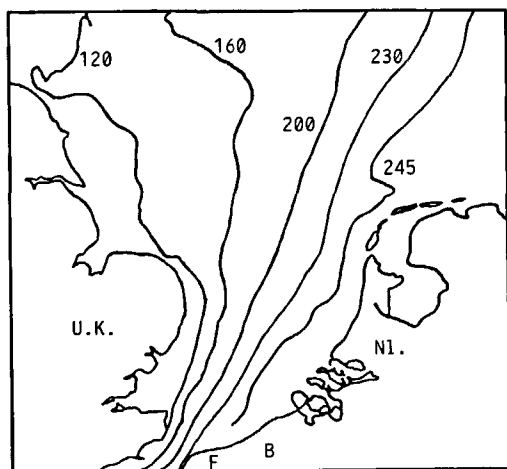


Figure 1
Residual flows in the Southern Bight of the North Sea. Summer situation. Flows in $10^3 \text{ m}^3 \cdot \text{s}^{-1}$.

The grid mesh which was used to carry out these calculations is, however, too coarse to represent the finer structure of the circulation in the vicinity of the Scheldt estuary. This information was therefore extracted from a smaller scale model ($500 \text{ m} \times 500 \text{ m}$) covering the zone off Zeebrugge (Fig. 2). The resulting circulation pattern in the Belgian coastal area is represented at Figure 3. Two flow lines separate a flow rate of $10,000 \text{ m}^3 \cdot \text{s}^{-1}$ or $315 \text{ km}^3 \cdot \text{y}^{-1}$, except the first streamtube which is subdivided into one tube of $85 \text{ km}^3 \cdot \text{y}^{-1}$ closest to the coast, and a second one of $230 \text{ km}^3 \cdot \text{y}^{-1}$, for a better assessment of the exchange of material from inshore to offshore watermasses. The flow lines are more or less parallel to the coast except in the zone around stations 13 and 23. Here, the northeasterly flowing watermass coming from the Channel encounters the southwesterly oriented Scheldt outflow. As a result, a residual hydrodynamical front is established with, at the northern side, a less saline estuarine watermass, and at the southern side a more saline marine watermass. Once the coastal-estuarine watermass has turned at the hydrodynamical front, it progressively mixes with the adjacent streamtube I of $85 \text{ km}^3 \cdot \text{y}^{-1}$, which increases then to $89.4 \text{ km}^3 \cdot \text{y}^{-1}$. The

composition of streamtube I can be modified: in the upstream part (south of the front) by coastal outfalls and the river Yser ($0.4 \text{ km}^3 \cdot \text{y}^{-1}$), at the hydrodynamical front (close to station 13) by diffusion processes with the coastal-estuarine watermass, and north of this front by mixing with the coastal-estuarine watermass. Exchange of matter between streamtubes I and II and also between further streamtubes can only occur through diffusion, since the flow lines are parallel to the current.

The residual current appears to be fairly constant over the whole area and amounts to $850 \text{ km} \cdot \text{y}^{-1}$ or $2.7 \text{ cm} \cdot \text{s}^{-1}$. The residence time of the watermasses flowing through our coastal zone (length of 70 km) is then of the order of 1 month.

SALINITY

Twenty-three cruises in the period 1978 to 1982 were chosen, in order to determine the average or steady-state salinity pattern in the Belgian coastal zone. The seasonal repartition of these cruises was taken into account (4 in winter, 7 in spring, 4 in summer and 8 in fall), and each station was measured at least 21 times.

The salinity pattern is strongly influenced by the residual circulation pattern. The isohalines run parallel to the residual flow lines except downstream of the hydrodynamical front, where the streamtubes I and II (85 and $230 \text{ km}^3 \cdot \text{y}^{-1}$ respectively) show a decrease in salinity (Fig. 4). As mentioned in the previous paragraph, the salinity may be influenced in the $85 \text{ km}^3 \cdot \text{y}^{-1}$ streamtube by coastal inputs downstream of the hydrodynamical front, by diffusion at the front and by mixing with the coastal-estuarine watermass north of the front. Coastal freshwater inputs downstream of the front are estimated at $0.4 \text{ km}^3 \cdot \text{y}^{-1}$. Their salt content is almost zero, hence they will decrease the salinity in the coastal streamtube by about 0.2. This value corresponds approximately to the salinity decrease observed between stations 11 and 12; the further decrease to station 13, however, equals 1.4 and is thus much larger. Mixing of the coastal estuarine watermass

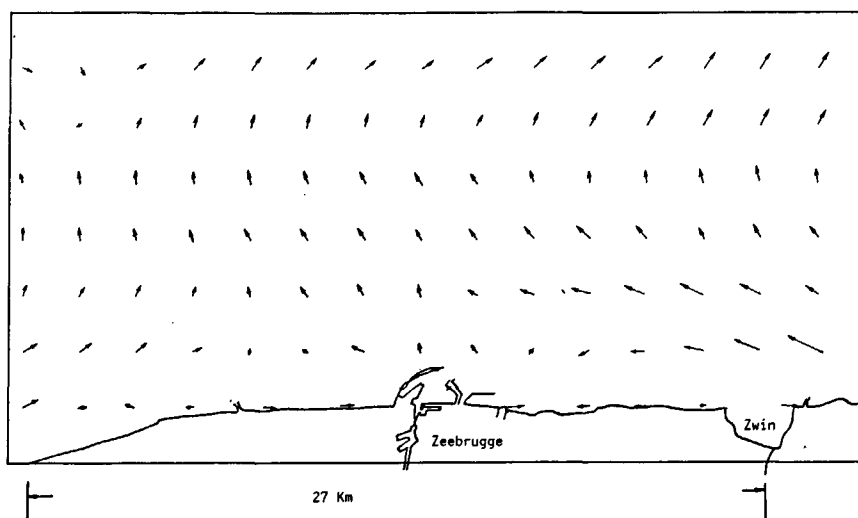


Figure 2
Residual currents off the harbour of Zeebrugge.

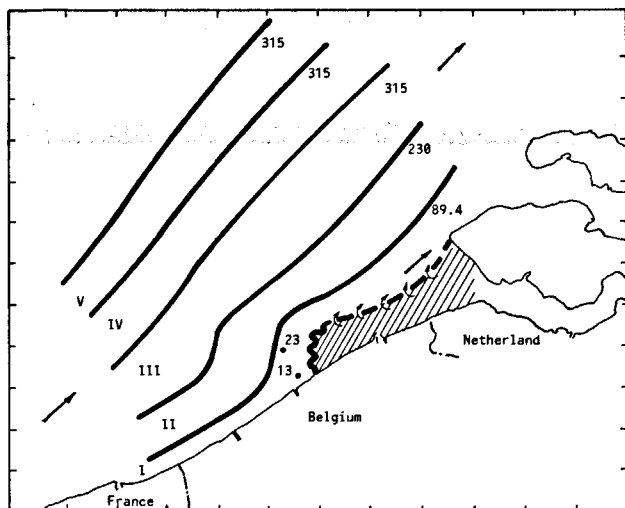


Figure 3

Residual flows through the Belgian coastal area ($\text{km}^3 \cdot \text{y}^{-1}$). The shaded area indicates the coastal-estuarine watermass and the undulating line the residual hydrodynamical front.

($4.4 \text{ km}^3 \cdot \text{y}^{-1}$, $S=30.55$), with the $85 \text{ km}^3 \cdot \text{y}^{-1}$ ($S=31.86$) streamtube results in a salinity decrease of 0.1. Diffusion should thus be the dominant process influencing the salinity in the streamtubes. The diffusion coefficient in the mouth of the Scheldt estuary (along line A on Fig. 4) can be estimated from the balance between diffusive and advective residual transport of salt. This calculation yields a diffusion coefficient of $180 \text{ m}^2 \cdot \text{s}^{-1}$. Diffusion coefficients perpendicular to the streamtubes (for example along lines B, C and D on Fig. 4) can not be estimated in this way. However, the fact that isohalines and streamtubes run parallel, except downstream of the hydrodynamical front, implies that the diffusion fluxes into and out of the streamtubes are fairly well balanced. If we are thus able to estimate one diffusion coefficient, then diffusion coefficients in other areas can be calculated from the balance of salt diffusion. Diffusion across the hydrodynamical front can at the very most account for the total

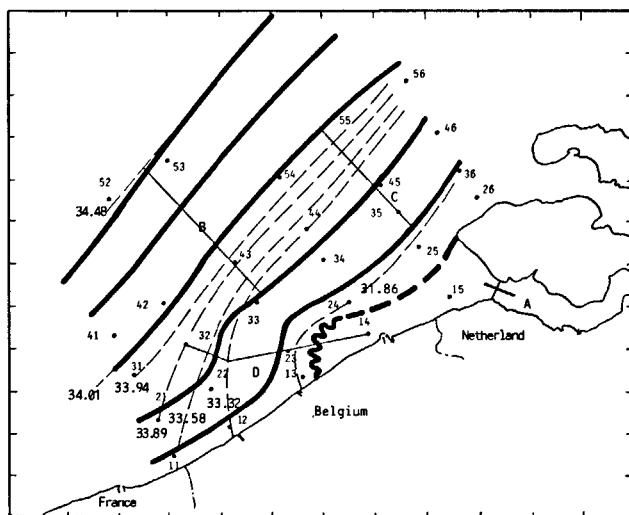


Figure 4

Salinity patterns (---) and residual flow lines (—) in the Belgian coastal area.

increase of salinity observed in the coastal estuarine watermass flow: $(31.50-29.13=2.37) \text{ psu} \cdot 4.4 \text{ km}^3 \cdot \text{y}^{-1} = 10.43 \text{ psu} \cdot \text{km}^3 \cdot \text{y}^{-1}$. The concentration gradient across the front (along line D) equals $6.8 \cdot 10^{-2} \cdot \text{km}^{-1}$ and the cross section 0.15 km^2 . This yields a diffusion coefficient of $1018 \text{ km}^2 \cdot \text{y}^{-1}$ or $32 \text{ m}^2 \cdot \text{s}^{-1}$. Then along line B diffusion coefficients of $108 \text{ m}^2 \cdot \text{s}^{-1}$ and $40 \text{ m}^2 \cdot \text{s}^{-1}$ between the isohalines of $S=34.48-34.01$ and of $S=34.01-33.32$ respectively are obtained. Along line C we find diffusion coefficients of $37 \text{ m}^2 \cdot \text{s}^{-1}$ and $28 \text{ m}^2 \cdot \text{s}^{-1}$ between isohalines of $S=34.01-33.32$ and of $S=33.32-31.86$ respectively. Along line D the diffusion coefficients amount to $40 \text{ m}^2 \cdot \text{s}^{-1}$, $21 \text{ m}^2 \cdot \text{s}^{-1}$ and $32 \text{ m}^2 \cdot \text{s}^{-1}$ between the isohalines of $S=33.89-33.32$, of $S=33.32-31.86$ and of $S=31.86-30.70$ respectively. These values are somewhat lower than the diffusion coefficient of $150 \text{ m}^2 \cdot \text{s}^{-1}$ estimated off the Dutch coast (Van Pagee, pers. comm.).

METALS

Short-term trace metal distributions in the Belgian coastal waters may be quite different from other coastal areas. Duinker and Nolting (1982) reported that although the concentration gradients of dissolved metals in the transects perpendicular to the Dutch and Belgian coasts are similar (but opposite) to the salinity gradient, they differ quantitatively off the Belgian coast where a tongue of increased metal concentration occurs. We have also observed higher offshore data as mentioned in our previous paper (Baeyens *et al.*, 1987). Possible sources are local inputs (dumping or contributions from bottom sediments), variations in the composition of the mixing end-members or atmospheric input. Wollast (1976) and Mommaerts *et al.* (1984) suggested that particles derived from the Scheldt containing increased levels of trace metals and organic matter may accumulate in bottom sediments off the Belgian coast as a result of particular current conditions. Under certain conditions of wind field, and watermass supply from the English Channel and the river Scheldt, a residual gyre develops off the Belgian coast, increasing strongly the residence time of material included (*e.g.* Nihoul, 1980). The good correlation between trace metals and organic matter in the sediment column (Wollast, 1976) may indicate that metals are mobilized from the sediments after diagenetic transformation of organic matter. This may lead to an increase of trace elements in the watercolumn; the relative importance may, however, differ between metals and the effects may be time-dependent.

The simultaneous assessment of all of these possible sources influencing the short-term metal distribution in our sampling area is a quite ambitious, difficult and complex task. Averaging the system over a time period corresponding to that of the residual currents and the steady-state salinity distribution, firstly smooths out or even eliminates all time-dependent effects on the metal distribution, and secondly permits the quantification of metal flows through the coastal zone. Like the salinity the steady-state metal distribution is obtained by avera-

ging the results obtained during eleven cruises in the period 1981-1983. A station which was less than six times sampled is not considered. An exception is made for the element mercury which was less frequently measured, and the conclusions concerning this metal are thus rather tentative.

Mixing curves of dissolved and particulate metal concentrations plotted against a suitable index of mixing such as salinity make it possible to distinguish between conservative and non-conservative behaviour. In a previous paper (Baeyens *et al.*, 1987) we had major problems in interpreting such curves, due to *e.g.* fluctuations in end-member concentrations. The steady-state approach eliminates these fluctuations. The coefficient of variation which is a measure of these fluctuations in time is:

— for dissolved metals of the order of 78% (Zn), 60% (Pb), 41% (Cu), 62% (Cd), 44% (Hg) in the coastal-estuarine stations and 83% (Zn), 65% (Pb), 54% (Cu), 43% (Cd), and 41% (Hg) in the offshore stations;

— for particulate metals of the order of 66% (Zn), 106% (Pb), 56% (Cu), 80% (Cd), 59% (Hg) in the coastal-estuarine stations and 99% (Zn), 127% (Pb), 96% (Cu), 112% (Cd), and 58% (Hg) in the offshore stations.

Dissolved metals

The dissolved metal versus salinity profiles all resemble each other (Fig. 5 and 6), and may further be subdivided into two parts: 1) The concentration profiles progressively decrease from coastal station 15 with lowest

salinity ($S=30.4$) to station 46 with a salinity of about 32.4. The concentrations at station 15 are approximately the same as the average concentration in the mouth of the river Scheldt. These latter values rely, however, on a smaller number of measurements. For all metals, except for Cd, the ideal dilution line from $S=30.4$ to 32.4 (indicated by a dashed line on Fig. 5 and 6) and the fitted curve through the experimental data points, are in a good agreement. The hydrodynamical front (about $S=31.8$) is also located in this salinity range. 2) In the marine watermass the concentrations of Cd, Hg and Pb remain almost constant, while those of Zn and Cu show a maximum. These maxima are due to the relatively higher values observed in nearshore stations 11 and 12, where concentrations may be influenced by inputs from the area around Dunkerque and the river Yser. The concentrations at the offshore station 45 are much higher than at surrounding stations 33, 34 and 46 and this for all metals. Dumping activities and accompanying processes such as dissolution and desorption of particulate metals may explain this aberrant result. Indeed, several hundred thousand tons of waste material from TiO_2 industries are dumped in the area each year.

The levels in the coastal estuarine watermass are increased over the lower values in the marine watermass with a factor of 2 (Cu), 1.7 (Zn), 1.8 (Pb), 2.3 (Cd) and 2 (Hg). These factors are much smaller than for particulate metals as we will see further. The impact of anthropogenic coastal discharges seems to be limited to the coastal-estuarine watermass, and barely affects the marine watermass concentrations.

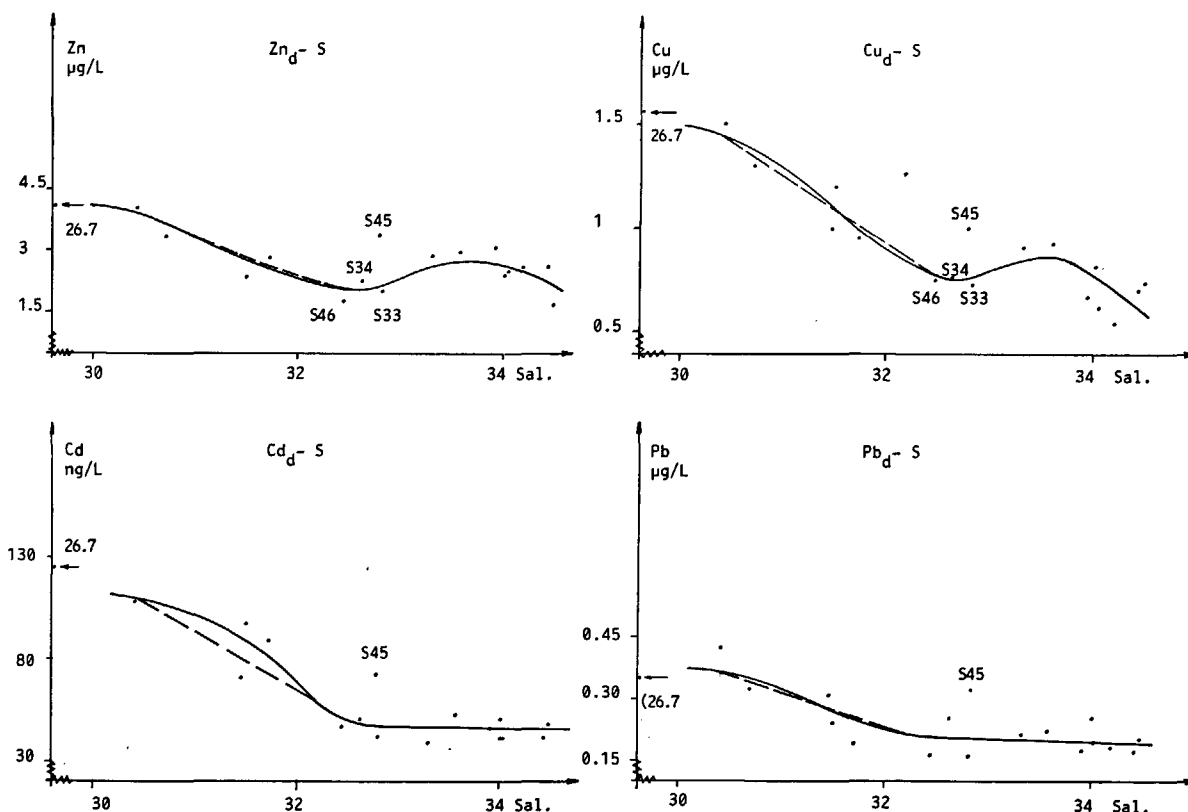


Figure 5
Stationary dissolved metal-salinity plots for the data of surveys between 1981 and 1983.

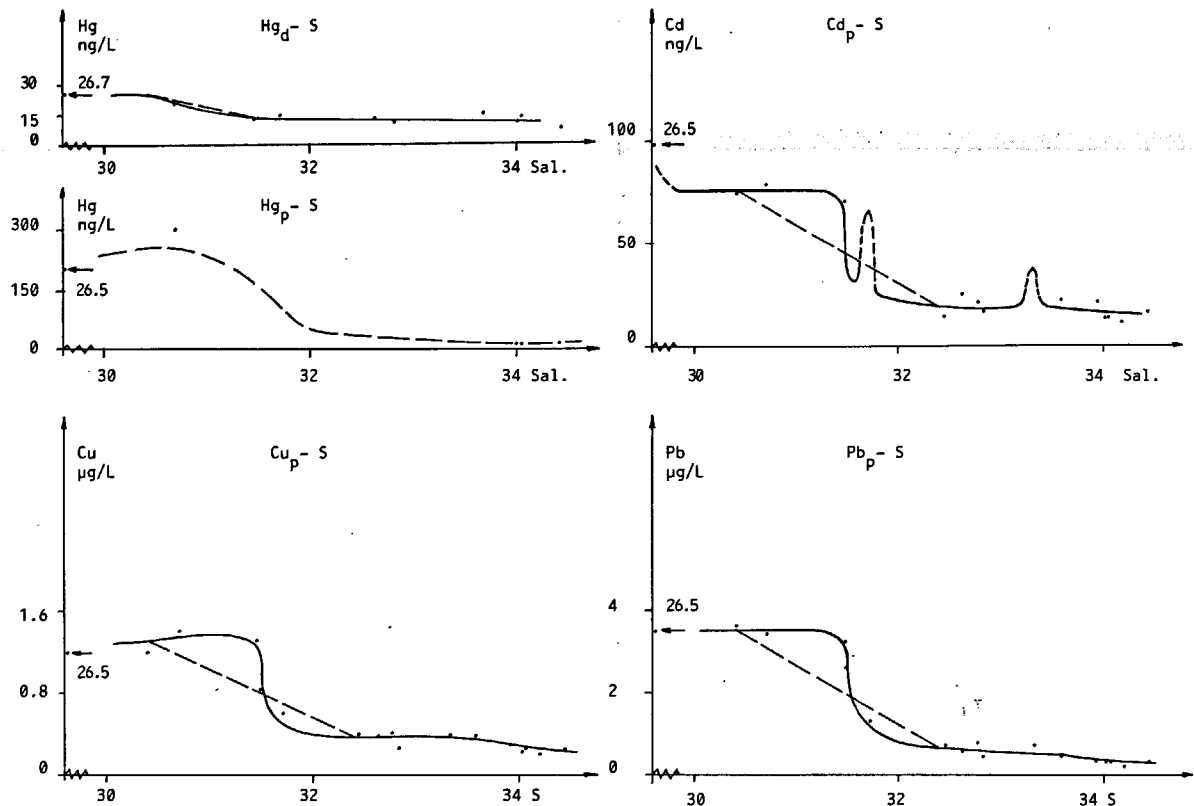


Figure 6
Stationary dissolved and particulate metal-salinity plots for the data of surveys between 1981 and 1983.

Offshore transport

As discussed in the section on residual currents, three processes may affect the concentrations in streamtube I: 1) coastal inputs upstream the hydrodynamical front; 2) diffusion through the front; and 3) mixing with the coastal-estuarine watermass downstream of the front.

Coastal inputs

These only seem to be important for Cu and Zn. However, no quantified data of such inputs exist.

Diffusion

For the calculation of the concentration gradients at the hydrodynamical front, we made use of the salinity at the stations at each side of the front and the corresponding metal concentrations inferred from the metal-salinity best fit curve. The concentration gradients at the front then amount to 0.0014 (Cd), 0.022 (Cu), 0.065 (Zn), 0.0059 (Pb) and 0.00047 (Hg) in tons.km^{-4} . Using the diffusion coefficient deduced for salinity at the front ($1018 \text{ km}^2.\text{y}^{-1}$ or $32 \text{ m}^2.\text{s}^{-1}$), diffusion fluxes of 0.22 (Cd), 3.3 (Cu), 9.9 (Zn), 0.90 (Pb) and 0.072 (Hg) in tons.y^{-1} , over the length of the front (about 10 km) are obtained. These diffusion fluxes represent between 40 and 65% of the dissolved metal supply by the river Scheldt. The resulting increases in streamtube I are 0.0025 (Cd), 0.039 (Cu), 0.12 (Zn), 0.011 (Pb) and 0.00085 (Hg), in $\mu\text{g.l}^{-1}$.

Mixing

The increases in streamtube I due to mixing with the adjacent coastal-estuarine watermass ($4.4 \text{ km}^3.\text{y}^{-1}$ and

Table 1

Comparison of observed and calculated dissolved metal concentrations in streamtube I.

	Observed concentration at $S=31.5$ (station 26) $\mu\text{g.l}^{-1}$	Calculated concentration after diffusion and mixing ($S=31.5$) $\mu\text{g.l}^{-1}$	Ratio of Scheldt flux/diffusion + mixing flux %
Cd	0.0885	0.0892	90
Cu	1.085	1.096	86
Zn	2.70	2.76	82
Pb	0.270	0.275	73
Hg	0.0130	0.0135	85

metal concentrations observed at $S=31.46$) yield 0.0047 (Cd), 0.057 (Cu), 0.14 (Zn), 0.014 (Pb) and 0.00067 (Hg), in $\mu\text{g.l}^{-1}$. These mixing fluxes represent between 52% and 79% of the dissolved metal supply by the river Scheldt.

When we compare now the concentrations observed at station 13 ($S=31.72$), increased by the contributions from diffusion and mixing calculated above, with the concentrations at station 26 ($S=31.5$), we find a very good agreement (Tab. 1). In addition, the input flux from the river Scheldt can almost account (between 73% and 90%) for the total supply (diffusion + mixing) from the coastal-estuarine watermass to streamtube I.

Exchange of material between streamtube I ($85 \text{ km}^3.\text{y}^{-1}$) and streamtube II ($230 \text{ m}^3.\text{y}^{-1}$) is only possible through diffusion. Metal concentration gradients upstream of station 13 are very small and diffusion is negligible. The diffusion fluxes downstream of station 13 amount to 0.83 (Cd), 10.7 (Zn), 1.07 (Pb),

5.22 (Cu) and 0 (Hg), in tons.y^{-1} . They are calculated analogous to the diffusion fluxes from the coastal-estuarine watermass to streamtube I, but now over a length of 30 km and using the concentration gradients between stations 13 and 33. The resulting increases in streamtube II are then 0.004 (Cd), 0.05 (Zn), 0.005 (Pb), 0.02 (Cu) and 0 (Hg), in $\mu\text{g.l}^{-1}$, and represent a concentration increase in streamtube II of less than 3%, except for Cd (8%). The input of the river Scheldt is between 1.4 and 1.7 times larger than the diffusion flux to streamtube II, except for Cd (only 0.7 times this diffusion flux). Since the total dissolved metal input of the Scheldt estuary is required to balance the metal supply to streamtube I, an additional source (atmosphere, bottom,...) is necessary to support the flows to streamtube II. Diffusion to the outer streamtubes (III, IV, V) is insignificant as a result of negligible concentration gradients.

Transport parallel to the coast

The total flow through streamtubes I to V (see Fig. 3) equals $1260 \text{ km}^3.\text{y}^{-1}$. This means about 25% of the flow entering the Southern Bight of the North Sea through the English Channel. The cumulative dissolved metal flow through streamtubes I to V equals 3000 (Zn), 250 (Pb), 900 (Cu), 59 (Cd) and 13 (Hg) in tons.y^{-1} . The contribution of the Scheldt to this flow is very small and ranges from 0.6 to 0.9%.

To obtain an idea of the magnitude of these metal flows, we compared them with dissolved metal flows through the English Channel, and the northern North Sea, normalized to a flow of $1260 \text{ km}^3.\text{y}^{-1}$. Trace metal data are obtained from Jones in Topping *et al.* (1980), Duinker and Nolting (1982) and our measurements in the considered areas. It appears from Table 2 that the metal flows through the English Channel are always lower than those through the Belgian coastal area, which are of the same magnitude as those through the northern North Sea. Much larger inputs than the Scheldt estuary are, however, required to explain the increase of dissolved metals in the northern direction.

Particulate metals

Rather than showing a progressive decrease in concentration from the mouth of the river Scheldt to the marine watermass, as is the case for dissolved metals,

Table 2

Dissolved metal flows parallel to the coast (in tons.y^{-1}) for a water flow of $1260 \text{ km}^3.\text{y}^{-1}$.

	Scheldt	Belgian coast	English Channel		Northern North Sea			
			(1)	(2)	(1)	(2)	(2)	
Zn	18	3000	760	980	930	3400	1300	2500
Pb	1.5	250			180			300
Cu	7.0	900	280	430	530	330	1300	690
Cd	0.55	59	13	52	38	88	38	39
Hg	0.11	13			16			

(1) Jones, in Topping *et al.* (1980).

(2) Duinker and Nolting (1982).

particulate metal concentrations remain almost constant in the coastal-estuarine watermass (stations 14, 15 and 25) and abruptly decrease in the salinity range of 31.4-31.8 to the much lower values of the marine watermass (Fig. 6 and 7). To illustrate this sharp decrease in concentration, the ideal dilution line from $S=30.4$ to 32.4 is also shown in Figures 6 and 7. Even less than in the case of for dissolved metals, do particulate matter and metals from the coastal-estuarine watermass seem to reach stations beyond the adjacent streamtube I; their offshore transport range seems to be still more limited.

The particulate concentrations of Zn, Cu and Pb in the coastal-estuarine watermass stations ($S=30.7$ to 31.4) are also comparable to the average concentrations in the mouth of the Scheldt ($S=26.5$), with the remark that these latter values rely on a smaller number of measurements. The suspended matter content, however, increases slightly from 40 mg.l^{-1} (at the mouth of the estuary) to 57 mg.l^{-1} ($S=31.46$, station 15), which can be attributed for example to local differences in sedimentation and erosion characteristics (*e.g.* Adam *et al.*, 1981). This implies a slight decrease in metal concentration in the suspended matter ($\mu\text{g.g}^{-1}$). In the marine watermass ($S>32.4$), particulate Zn, Pb and Cu follow the same pattern as the turbidity, smoothly decreasing with increasing salinity. The fluctuations around this curve are much smaller than in the case of dissolved metals. The general behaviour shown by Pb, Cu and Zn is also followed by mercury. Particulate Cd differs somewhat from the other metals, two coastal stations (12 and 13) off the harbours of Nieuwpoort and Oos-

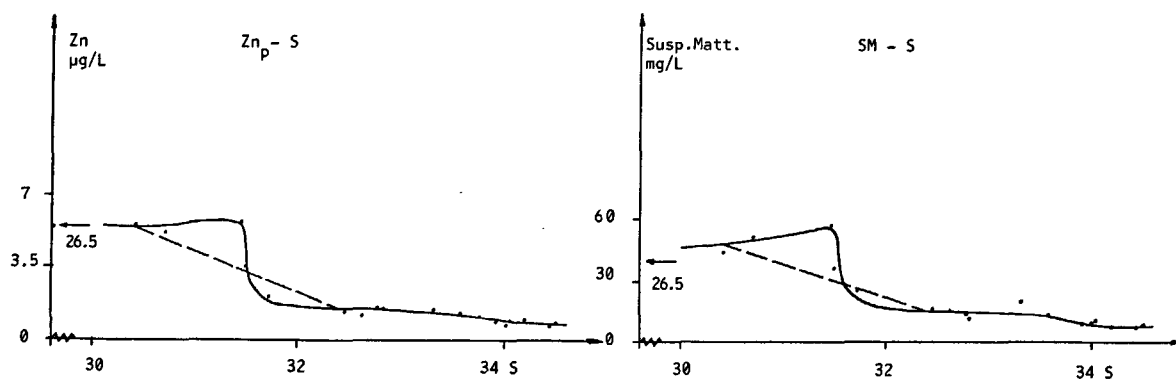


Figure 7

Stationary particulate metal and suspended matter-salinity plots for the data of surveys between 1981 and 1983.

tende and the station in the mouth of the river Scheldt showing substantially higher concentrations than we might expect from the behaviour of the other metals (these high values are indicated on Figure 6 by dotted lines). In this case, additional sources such as direct coastal inputs or dumping of dredged sludge cannot be ruled out. The levels in the coastal-estuarine watermass exceed the lower values in the marine watermass by factors of about 5 to 6 for Cd, Cu and Zn, comparable to the turbidity, but of 12 for Pb and of 20 for Hg. Pb and Hg differ from the other metals in that they are predominantly present in the particulate phase. Their K_D ratios (particulate to dissolved metal concentration) change more than those of the other metals from inshore to offshore waters (Baeyens *et al.*, 1987). Pb, for example, seems to be associated with iron and manganese hydrous oxides and these kind of particles, introduced in the coastal system via the estuary, are not found in the marine watermass.

Offshore transport

The offshore flux of the particles can be estimated, assuming they behave in a similar way to the fluid in which they are suspended. Three processes affect the metal concentrations in streamtube I: coastal inputs (upstream area, south of the front); diffusion (at the hydrodynamical front); mixing (downstream area, north of the front).

Coastal inputs

These only seem to be important for Cd, but there exist no quantified data.

Diffusion

The concentration gradients and the diffusion fluxes at the hydrodynamical front are calculated similarly to those of the dissolved metals. The diffusion fluxes amount to 0.45 (Cd), 31 (Zn), 20 (Pb) and 1.3 (Hg) in tons.y^{-1} . These diffusion fluxes represent between 130 and 140% of the particulate metal supply by the river Scheldt except for Cd where the diffusion flux is balanced by the (high) river output. The resulting increases in streamtube I are: 0.0053 (Cd), 0.087 (Cu), 0.37 (Zn), 0.24 (Pb) and 0.015 (Hg), in $\mu\text{g.l}^{-1}$.

Mixing

The increases in streamtube I due to mixing with the coastal-estuarine watermass ($4.4 \text{ km}^3.\text{y}^{-1}$ and concentration observed at $S=31.46$) yield: 0.0035 (Cd), 0.064 (Cu), 0.28 (Zn), 0.17 (Pb) and 0.0083 (Hg), in $\mu\text{g.l}^{-1}$. The mixing fluxes represent between 69 and 103% of the Scheldt supply.

When we compare the concentrations observed at station 13 ($S=31.72$), increased by the contribution from diffusion and mixing as calculated above, with the concentrations at station 26 ($S=31.5$), we find for most metals a good, but not as excellent agreement as that for dissolved metals (*see* Tab. 3). The metal supply (diffusion and mixing) from the coastal-estuarine watermass to streamtube I is, although too low, not supported by the Scheldt input (between 41 and 58%).

Table 3

Comparison of observed and calculated particulate metal concentrations in streamtube I.

	Observed concentrations at $S=31.5$ (station 26) $\mu\text{g.l}^{-1}$	Calculated concentrations after diffusion and mixing at $S=31.5$ $\mu\text{g.l}^{-1}$	Ratio of Scheldt flux/diffusion + mixing flux %
Cd	0.035	0.035	58
Cu	0.78	0.65	41
Zn	3.0	2.7	44
Pb	2.1	1.7	45
Hg	0.15	0.13	45

Exchange of material between streamtube I ($85 \text{ km}^3.\text{y}^{-1}$) and streamtube II ($230 \text{ km}^3.\text{y}^{-1}$) is only possible through diffusion. Upstream of station 13, metal concentration gradients are very small and diffusion is negligible. The diffusion fluxes downstream of station 13 amount to 0.20 (Cd), 14 (Zn), 17 (Pb), 3.3 (Cu) and 1.9 (Hg), in tons.y^{-1} . They are calculated analogous to the diffusion fluxes of dissolved metals from streamtube I to streamtube II. The resulting increases in streamtube II are then: 0.0009 (Cd), 0.06 (Zn), 0.07 (Pb), 0.01 (Cu) and 0.008 (Hg), in $\mu\text{g.l}^{-1}$, and represent a concentration increase in streamtube II of 4 to 5% for Cd, Cu and Zn, of 13% for Pb and of 26% for Hg. These increases fall in the range of observed increases. The coastal values of Pb and Hg are increased more drastically over the marine watermass levels than Cu, Zn and Cd and result in much larger diffusion fluxes and concentration increases. When we compare the particulate metals input of the river Scheldt to the diffusion flux to streamtube II, we find the Scheldt input larger than the diffusion flux for Cd, Zn and Cu (between 1.6 and 2.2 times), but smaller for Pb and Hg (between 0.5 and 0.9 times). Diffusion to the outer streamtubes (III, IV,...) is insignificant, due to the negligible concentration gradients. In any case, if particulates move like the bulk of the fluid, our calculations of mixing and diffusion processes require an additional source (atmosphere, bottom,...) to balance these flows. The deficit expressed in terms of Scheldt input flux varies from one time this flux for Cd, over two times for Zn, Cu and Pb to three times for Hg.

Transport parallel to the coast

The cumulative particulate metal flow through streamtubes I to V equals 1400 (Zn), 520 (Pb), 340 (Cu), 21 (Cd) and 27 (Hg), in tons.y^{-1} , considering particulate metals as conservative substances. The contribution of the Scheldt to these flows is somewhat higher than in the case of dissolved metals and ranges from 1.6 to 3.3%.

The particulate metal flows through the English Channel and the northern North Sea have been calculated in a similar manner to those of dissolved metals. Both particulate metal flows are of the same magnitude, but are about three times lower than the particulate metal flows through the Belgian coastal zone (Tab. 4). Either

Table 4

Particulate metal flows parallel to the coast (tons.y^{-1}) for a water flow of $1260 \text{ km}^3.\text{y}^{-1}$.

	Scheldt	Belgian coast	English Channel	Northern North Sea
Zn	24	1400		
Pb	15	520	190	140
Cu	5.3	340	120	78
Cd	0.44	21	6.0	5.4
Hg	0.88	27		

additional sources or a non-conservative behaviour of the particulate metals (e.g. erosion-sedimentation cycles) must explain this result.

CONCLUSION

The impact of the metal discharge by the river Scheldt is limited to a fairly small watermass (streamtubes I and II in Fig. 3, together corresponding to $315 \text{ km}^3.\text{y}^{-1}$), and does not reach zones further offshore. Transport (diffusion and mixing) from the coastal-estuarine watermass (bound by the hydrodynamical front and streamtube I, see Fig. 3) to streamtube I and thence to streamtube II can explain the observed increases in metal concentration in the latter streamtubes, but these offshore transport fluxes are not completely balanced by the river input. For the dissolved species, the deficit is of the same magnitude as the river input, but for the particulates is it a few times this input.

REFERENCES

- Adam Y., Baeyens W., Mommaerts J. P., Pichot G., 1981. Mathematical modelling of recent sedimentology in the shallow waters along the Belgian coast, in: *Ecohydrodynamics*, edited by J. C. J. Nihoul, Elsevier, Amsterdam, 333-349.
- Baeyens W., Gillain G., Decadt G., Elskens I., 1987. Trace metals in the eastern part of the North Sea. I. Analyses and short term distributions, *Oceanol. Acta*, 10, 169-179.
- Djenidi S., Ronday F., 1985. Tidal and residual circulation on the North-European continental shelf, in: *Progress in Belgian oceanographic research*, edited by R. Van Grieken and R. Wollast, The Belgian Academy of Sciences, Committee of Oceanology, 46-59.
- Duinker J. C., Nolting R. F., 1982. Dissolved copper, zinc and cadmium in the Southern Bight of the North Sea, *Mar. Pollut. Bull.*, 13, 93-96.
- Mommaerts J. P., Pichot G., Ozer J., Adam Y., Baeyens W., 1984. Nitrogen cycling and budget in Belgian coastal waters: North Sea areas with and without river inputs, *Rapp. PV Réun. Cons. Int. Explor. Mer*, 183, 57-69.
- Nihoul J. C. J., 1980. Residual circulation, long waves and mesoscale eddies in the North Sea, *Oceanol. Acta*, 3, 309-316.
- Nihoul J. C. J., Ronday F., 1976. Hydrodynamic models of the North Sea, *Mem. Soc. Sci. Lg.*, 10, 61-96.
- Ronday F., 1976. Modèles hydrodynamiques, *Projet Mer, Rapport Final*, édité par J. C. J. Nihoul, Programmation de la Politique Scientifique, Bruxelles, Vol. 3, 270 p.
- Topping G., Bowers J. M., Jones P. G. W., 1980. A review of the past and present measurements of selected trace metals in sea water in the Oslo Commission and ICNAF (NAFO) areas, *Coop. Res. Rep., Cons. Int. Explor. Mer*, 97, 43 p.
- Wollast R., 1976. Propriétés physico-chimiques des sédiments et des suspensions de la Mer du Nord, in: *Sédimentologie, Projet Mer, Rapport Final*, édité par J. C. C. Nihoul et F. Gullentops, Programmation de la Politique Scientifique, Bruxelles, Vol. 4, 123-143.

Additional sources such as atmosphere, bottom, dumping, are possible explanations and should be considered in future. On the other hand, if—in the Belgian coastal area—flows of particulate metals are only one fourth of those we have calculated (their advective and diffusive velocity is thus four times smaller than the fluid in which they are suspended), then: 1) the flows of particulate metals parallel to the coast are of the same order as those observed in the English Channel and the northern North Sea; and 2) the river input will now show a small excess compared to the offshore flux, excess which satisfies the small deficit of the dissolved metals offshore flux.

Testing the assumption concerning the transport velocity of particulate metals requires information about the size distribution and density of the particles, their settling rates and the size distribution of the particulate metals, while testing the assumption concerning the transfer of metals from the particulate to the dissolved phase requires information about adsorption-desorption processes in the watercolumn and mobilization processes in the sediments.

Acknowledgements

This research was supported by the Ministry of Scientific Policy (Geconcerteerde Acties Oceanologie). We thank the Management Unit of the Mathematical Model of the North Sea for providing ship time.