A study of the distribution of mercury in the various compartments of the North Sea and Scheldt Estuary ecosystems

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ABSTRACT

The distribution of mercury in various compartments of the North Sea and Scheldt ecosystems was investigated. The experimental results showed that: (1), in the North Sea, the ratio of particulate to dissolved mercury in the water column was close to 1 : 1, while in the estuary (particularly in its upper portion) this ratio was much higher; (2), the mercury content of living organisms was higher in phyto- and zoo-plankton than in fish, although detrital matter still contained about five times more mercury than phytoplankton; and (3), the concentration of mercury in marine sediments was situated between those found in zooplankton and fish.

Thermodynamic stability diagrams for aqueous and solid mercury compounds in seawater and brackish water provided valuable information for the interpretation of the observed mercury distribution. Under reducing conditions, mercury-sulphide compounds were predominant, in both water systems. These compounds play a very important role in the accumulation and release of mercury in sediments (the stable solid compound under reducing conditions, cinnabar, determines the mobility of mercury in the interstitial water), and in living organisms (the latter produce metallo-thioneins, which contain a large number of −SH groups and show high affinities for mercury). In combination with electrostatic forces these compounds probably also play a role in the process of adsorption of $Hg\,Cl_3^-$, which is theoretically the predominant mercury compound in the North Sea and the major part of the Scheldt estuary, on suspended matter.

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RÉSUMÉ

Étude de la distribution du mercure dans les divers compartiments des écosystèmes Mer du Nord et Escaut

La distribution du mercure dans les différents compartiments des écosystèmes Mer du Nord et Escaut a été étudiée. Les résultats expérimentaux montrent que : primo, en Mer du Nord le rapport mercure particulaire mercure dissout, dans la colonne d'eau, est voisin de un, tandis que dans l'estuaire (spécialement dans la partie amont) ce rapport est beaucoup plus élevé; secundo, la concentration de mercure dans les organismes vivants est plus élevée dans le phyto- et le zooplancton que dans les poissons, bien que la matière détritique contienne toujours environ cinq fois plus de mercure que le phytoplancton; et tertio, la concentration de mercure dans les sédiments marins est intermédiaire à celles trouvées dans de zooplancton et dans des poissons. Les diagrammes de stabilité thermodynamique pour les composés de mercure dissous et solides en eau de mer et en eau saumâtre, fournissent des informations utiles pour l'interprétation de la distribution de mercure observée. Dans des conditions réductrices les composés de mercure dominants, dans les deux systèmes aqueux, sont des dérivés du sulfure mercurique. Ces composés jouent un rôle important dans

l'accumulation et la libération de mercure, d'une part dans les sédiments; dans des conditions réductrices le composé stable, le cinabre, contrôle la mobilité du mercure dans les eaux interstitielles, et d'autre part dans les organismes; ils produisent des metallothionéines, qui contiennent un grand nombre de groupes −SH et qui font preuve d'une très grande affinité pour le mercure. Combinés aux forces électrostatiques, ces composés peuvent également jouer un rôle plus ou moins important dans le processus d'adsorption sur de la matière en suspension de $HgCl_3^-$, composé de mercure, théoriquement le plus important en eau de mer et dans la plus grande partie de l'estuaire.

INTRODUCTION

As a consequence of the dense population and high degree of industrialization around the Southern Bight of the North Sea, pollution has increased to such a level that it has become necessary to monitor and −where possible−to control the impact of domestic and industrial wastes on the finite and relatively small water mass of the Southern Bight. The impact of pollution in this area on the remainder of the North Sea appears to be relatively unimportant, because the comparatively clean Atlantic water flowing in along the coast of Scotland is responsible for continuous cleansing (Weichart, 1973). On a local scale, however, such high concentrations of pollutants can seriously perturb the normal equilibrium of the ecosystem. Due to its high toxicity, mercury is a pollutant which requires particular attention.

Mercury in different chemical forms enters the environment from a variety of sources. Industrial effluents (chlor-alkali, pigments, waste from electrical installations, catalystic processes and so on) are predominant, but wastes of agricultural origin, fallout from the atmosphere, dumped material, etc. should not be disregarded. The distribution and evolution of mercury in one form or another depend on various factors, including the hydrodynamic characteristics and the physico-chemical conditions of the area, the assimilation of mercury by living organisms (including transfer through food chains) and interactions with other constituents of the marine environment which can modify its form in the water column, in sediments or within the bodies of living organisms. In view of the complexity of these phenomena (mercury is subject to a large number of interactions), a stepwise multidisciplinary approach is the only way to resolve the problem. The second part of this paper describes the mercury content in the main compartments of the ecosystem, as well as some exchanges fluxes between them. This provides the basis for further considerations which lead finally to the construction of a mathematical circulation model for mercury, by means of which its evolution in space and time may be predicted.

Mercury distribution in the marine environment was studied in the Southern Bight of the North Sea (Fig. 1). This area may be described as a well-mixed coastal sea, heavily polluted because of its shallow depth (the mean depth is 15 m), and the large amount of pollutants (ICES, 1977; Weichart 1973). The residual circulation pattern (Ronday, 1977) shows the existence of a gyre −with a radius of a few kilometres−off the Belgian coast (Fig. 1), which increases the residence time of the pollutants in that area and consequently augments the local degree of pollution.

Considerable quantities of waste material reach the North Sea *via* rivers such as the Rhine, Thames, Elbe, Scheldt and others although their contribution varies. Mercury transport in the estuarine environment was studied in the Scheldt, which belongs to the partial mixed type, is strongly tidal (the tidal amplitude reaches 3.8 m at the mouth and increases to 4.9 m at Antwerp, 75 km upstream) and includes a large number of tidal flats. The mean fresh water discharge amounts to 80 m³ per second, resulting in a rather small residual current.

THEORETICAL CONSIDERATIONS OF THE BEHAVIOUR OF MERCURY IN AQUEOUS MEDIA

The form in which mercury will be present in the environment depends principally on the initial released form, the thermodynamic stability of this compound and the transformation rate of the released form to a more stable one. Standard free energies of formation are known for many of the most significant inorganic species of mercury which can be present in water. With the exception of liquid dimethylmercury, data on organomercury compounds are not available. Whereas data on solid mercury (I) carbonate is available in the literature, none would appear to exist on solid mercury (II) carbonate, which, according to Jedwab (personnal communication) does not appear to exist in nature. It was synthesized *in vitro* and showed a very low solubility in water.

Knowledge of the free energy values and activities of the various inorganic compounds and of liquid dime-
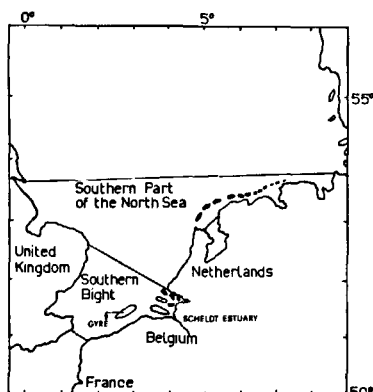

Figure 1
Southern part of the North Sea.

thylmercury, makes it an easy matter to calculate the electrochemical and chemical equilibrium curves between them and, in consequence to obtain the relatively most stable form for various Eh-pH fields. These stability fields for mercury compounds, both dissolved in seawater and in the solid and liquid phases, together with the solubility of the stable compounds, have been calculated by Wollast (1972) for a wide range of pH and redox potential values under conditions of normal temperature and pressure. However, because the water composition chosen is only representative of seawater, the conclusions of Wollast (1972), which are valid for the North Sea, cannot be extended to the brackish water zone we are dealing with in the estuary. We have therefore recalculated the stability diagrams for the same system of elements (Hg-Cl-S-H_2O), at 25°C and 1 atm.

Calculation of the predominant mercury species in the dissolved phase for the system of elements (Hg-Cl-S-H_2O) is done on a stage by stage basis, the same procedure being applied in the case of the solid phase.

We first consider the two element systems (Hg-H_2O), (Cl-H_2O) and (S-H_2O). We write the equilibrium reactions between all the various dissolved species belonging to a particular two-element system, and calculate the standard free energy of formation for each equilibrium, using thermodynamic data from Wagman (1968, 1969) and from Hem (1970). The activities of the various substances involved in the reactions (pH is a variable) are: 10^{-7} moles per litre for mercury species, 10^{-3} moles per litre for sulphur and $8.5 \cdot 10^{-2}$ moles per litre for chloride or $4°/_{00}$ Cl^-. Chloride and sulphur activities are of the same order of magnitude as those naturally occuring in the brackish zone, while mercury activity is that found in industrial effluents. This enables us to calculate the free energy of formation. If the equilibrium depends neither on the Eh, nor on the pH, one of the two species, according to the sign of the free energy, is eliminated. The equilibria between the remaining species are represented in the Eh-pH diagram by straight lines, with one of the species predominating on each side. For each species, it is then possible to determine the stability field(s).

The next step is to determine the predominant mercury species for the element systems (Hg-Cl-H_2O) and (Hg-S-H_2O). Again, in a manner similar to that described for a two-element system, we calculate the free energy of formation for all the equilibrium reactions between the various mercury forms belonging to a particular system. Each equilibrium which is neither Eh-nor pH-dependent leads to the elimination of one of the two mercury species involved, according to the sign of the free energy of formation. Again, the equilibria between the remaining species are represented in the Eh-pH diagram by straight lines with one mercury species predominating on each side of the line. However, two further checks must be performed on each line. If, for a particular equilibrium, one of the two mercury species involved also belongs to the (Hg-H_2O) system (for example Hg$(OH)_2$), its stability field(s) in the (Hg-H_2O) system and its equilibrium line in the three-element system must have a common part. We therefore superimpose the diagrams of the two-element and three-element systems, and maintain only that portion of the equilibrium line which is common to each. A second check must be performed if a non-metal species is also involved in the equilibrium reaction. Again, the diagram of the three-element system and the non-metal-H_2O system are superimposed, only that portion of the equilibrium line which is common being maintained. Proceeding in this way, we obtain all the stable segments for a particular mercury species, and consequently its stability field(s).

The four-element system (Hg-Cl-S-H_2O) is solved in an analogous manner, Finally, the stability of some specific mercury compounds (for example, liquid dimethylmercury and solid mercury (I) carbonate) is checked against those of the obtained predominant mercury species. The resulting Eh-pH diagrams for the solid and liquid species and for the dissolved species are shown in Figures 2 and 3.

The predominant compounds are indicated for every region; the solids are identified by the abbreviation "c", liquids by "l" and the dissolved species by "aq" or their ionic state.
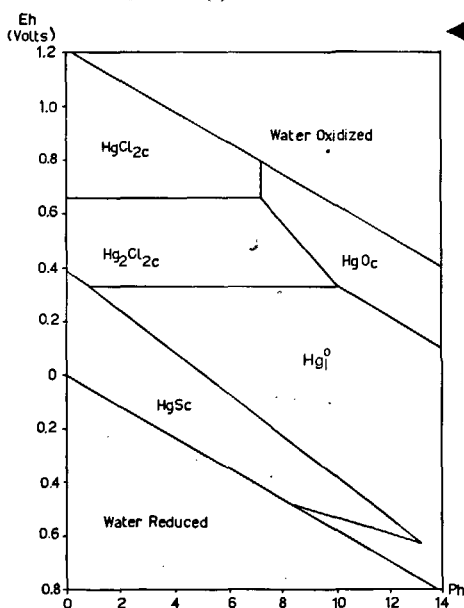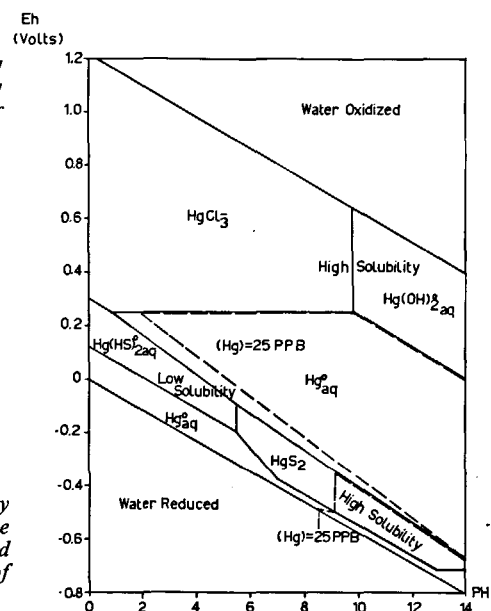

◀ Figure 2

Fields of stability for solid (c) and liquid (l) mercury species at 25°C and 1 atmosphere in brackish water of $4°/_{00}$ Cl^-.

Figure 3 ▶

Fields of stability for aqueous mercury species at 25°C and 1 atmosphere pressure in brackish water of $4°/_{00}$ Cl^-. Dashed line indicates approximate solubility of mercury.

It is then possible to write for any Eh-pH value the equilibrium equation between the stable dissolved and solid mercury compound, care being taken to ensure that only non-metal species which are also stable at the Eh-pH considered are involved in the reaction. As we know the activities of the different non-mercury substances and the thermodynamic data required to calculate the standard electrochemical potential, we are able to determine the solubility of mercury in brackish water over the whole range of Eh and pH (results are shown in Figure 3).

The diagrams clearly indicate the main features of the theoretical behaviour of the inorganic mercury compounds in sea and brackish water under equilibrium conditions. At the pH values likely to occur in surface seawater and brackish water, liquid metallic mercury is theoretically the stable solid compound except at high Eh value (Eh > 350 mV), where mercury (I) chloride (calomel) is more stable. In mildly reducing conditions, such as are likely to occur in the interstitial water of the sediments, HgS (cinnabar) is the predominant solid species. The organometallic compound dimethylmercury is not thermodynamically stable in either of the two systems (seawater and brackish water). It would appear that, in well aerated seawater, the anionic complex $HgCl_3^-$ is the most stable compound over the whole range of pH considered, whereas in brackish water, $Hg(OH)_{2aq}$ becomes predominant at high pH. This is in a good agreement with observations made by Hem (1970) for the fresh water system. The area of dominance of $HgCl_3^-$ ($HgCl_{2aq}$ at low chloride concentrations), becomes smaller as the Cl^- concentration decreases. Mercury (I) compounds are not stable except at very low chloride concentrations (Hem, 1970). The solubility in aerated water of the $HgCl_3^-$ or $Hg(OH)_2$ complex is very high and may reach several grams per litre.

The predominant mercury species in solution over much of the range of moderately oxidizing conditions (pH > 4) is dissolved metallic mercury. Its solubility is nearly constant over the whole range of dominance, but is much lower, namely 25 ppb, than those of $HgCl_3^-$ or $Hg(OH)_2$. This means that if the electrochemical potential is lowered to 200 mV in seawater or 250 mV in brackish water, mercury may precipitate as liquid mercury. Such concentrations, however, are not likely to occur. In reducing conditions such as may occur in the sediments, or in anaerobic water, HgS_2^{--} is the most stable dissolved species for a pH greater than 5, and $Hg(SH)_{2aq}$ at lower pH values. The solubility of these species is very low. Cinnabar, the stable solid compound in this area of Eh-pH, has a solubility of less than a nanogram per litre. However, under very strong reducing conditions and a pH greater than 9, HgS_2^{--} becomes very soluble and cinnabar may redissolve. Lu and Chen (1977) also calculated the equilibrium between cinnabar and various mercury species under reducing conditions and in the pH range 6 to 9. Their results agreed very well with those obtained by Wollast (1972). In the same range of Eh-pH, they also measured the concentrations of various metals, including mercury, in the interstitial water of three types of sediments after long-term incubation, finding the results as far as mercury was concerned to be very close to the theoretical calculations.

We have not discussed organomercury compounds, although methyl mercury is a very important mercury form in fish (Johnels et al., 1967, Herman, Vanderstappen, 1977), in sediments (Jensen, Jernelov, 1969) and possibly in some other compartments of the ecosystem as well. Unfortunately, no free energy value could be found or estimated, and this species could not therefore be considered in constructing the diagrams.

A considerable amount of valuable information concerning aqueous mercury chemistry may be obtained from the Eh-pH diagrams. However, when interpretating in situ measurements, we must bear in mind that the theory applies to a system at equilibrium, which is an idealized situation. In natural waters, it is common to find species that are not in equilibrium, because transformation rates to more stable compounds can be very slow. This is one reason why methylmercury, although it might be thermodynamically less stable than some inorganic species, should not be ignored. Another general remark is that most mercury species are much more soluble in organic solvents than in water (Moser, Voigt, 1957).
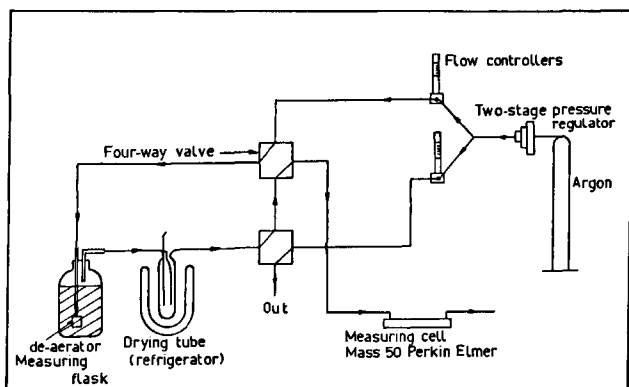
THE NORTH SEA

Measurements and results

Various forms of mercury in different compartments of the ecosystem have been measured as part of the Belgian National Research and Development program on the Environment–Sea Project: Mathematical Model 1970-1976, special attention being paid to sampling and storage procedures and to the avoidance as far as possible of contamination or loss prior to analysis. Determinations of particulate and "dissolved" mercury concentrations have been carried out on seawater samples collected in polyethylene bottles using a centrifugal pump made of Teflon. These samples are rapidly frozen at − 40°C and maintained at − 20°C prior to analysis and filtered through a 0.8 μm pore-size Millipore filter, using a closed pressure filtration system. The filters are pretreated with dilute acid and distilled water.

Analysis is carried out by means of a semi-automatical system based on the method of Hatch and Ott (1968). Analysing and purging times are maintained constant by a series of automatically operating valves; the resulting flow scheme is represented in Figure 4.

As an illustration of the spatial distribution of "dissolved" and particulate mercury in the North Sea, we provide some results in Table 1 and Figures 5 and 6.

Plankton samples were collected with a 100 μm mesh nylon net, rinsed several times with distilled water to remove the seawater salts, and frozen at − 20°C in polyethylene bottles. Because of their great heterogeneity,

Figure 4
Flow scheme of the semi-automatic system of Hg-species analysis.

Table 1
April 1972 Cruise.

Identification (*)	Hg-dissolved (µg/l)	Hg-particulate (µg/l)	Hg-total (µg/l)
M 1486.140472.2020.05	0.05	0.04	0.09
M 1634.170472.1730.05	0.03	0.04	0.07
M 67.180472.0610.05	0.09	0.05	0.14
M 01.040472.1730.05	0.03	0.07	0.10
M 1097.040472.1130.05	0.05	0.04	0.09
M 1693.180472.1030.05	0.04	0.04	0.08
M 59.140472.1700.05	0.05	0.04	0.09
M 72.180472.0130.05	0.07	0.03	0.10
M 67.140472.0820.05	0.04	0.02	0.06
M 01.040472.1730.05	0.04	0.02	0.06
M 1348.130472.1630.05	0.02	0.01	0.03
M 1699.140472.1345.05	0.07	0.01	0.08
M 2552.180472.1550.05	0.04	0.02	0.06
M 1097.040472.1130.05	0.04	0.02	0.06
M 1344.130472.1350.05	0.04	0.03	0.07
M 1352.130472.2010.05	0.05	0.01	0.06
M 2689.180472.1235.05	0.04	0.01	0.05
M 61.140472.2330.05	0.05	0.02	0.07
M 06.050472.1030.04	0.07	0.12	0.19
M 06.050472.1100.06	0.19	0.10	0.29
M 06.050472.1130.08	0.08	0.12	0.20
M 06.050472.1200.10	0.09	0.16	0.25

(*) The code M 1693.180472.1030.05 signifies a sample taken by the ship Mechelen at point 1693, on 18 April 1972, at 10.30 a.m. at a depth of 5 metres.

these samples must be treated in various stages before the final determination of mercury. After rapid thawing, the samples are successively lyophilised for a period of 24 hours in a Leybold-Heraeus GT 2, ground in a mechanical agate mortar to reduce the size of the particles to less than 100 µm, and dried again in the lyophiliser for a period of 12 hours before weighing. The final phase of the analysis comprised the wet digestion of 300 mg subsample, according to the technique described by Janssen (1978); mercury in this residue was determined as described above for seawater samples. Tests on the homogeneity of the subsamples clearly indicate that an amount of 300 mg is representative of the

gross sample. For the amount of exogenous material present in these samples, such as carbon, nitrogen and silica, *see* Elskens (1977 a).

Figure 5
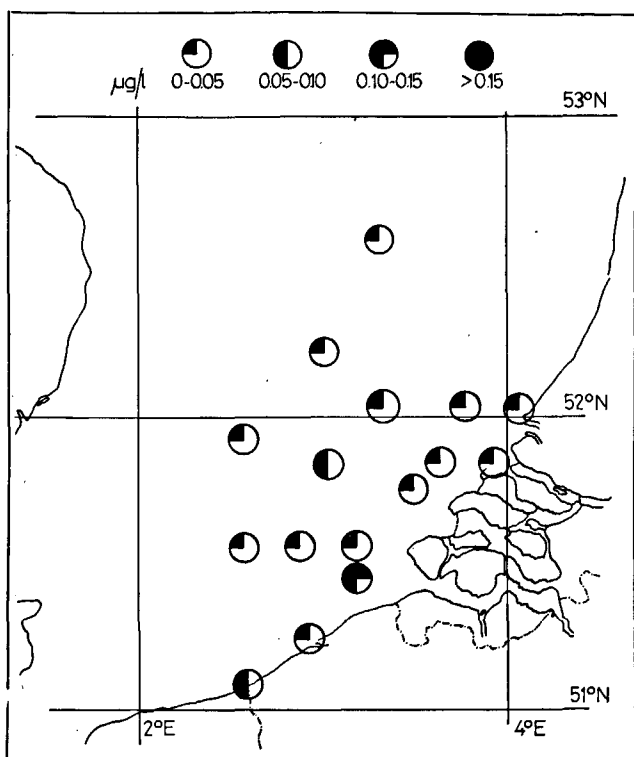*Dissolved mercury concentrations (µg/l) in the North Sea.*

Figure 6
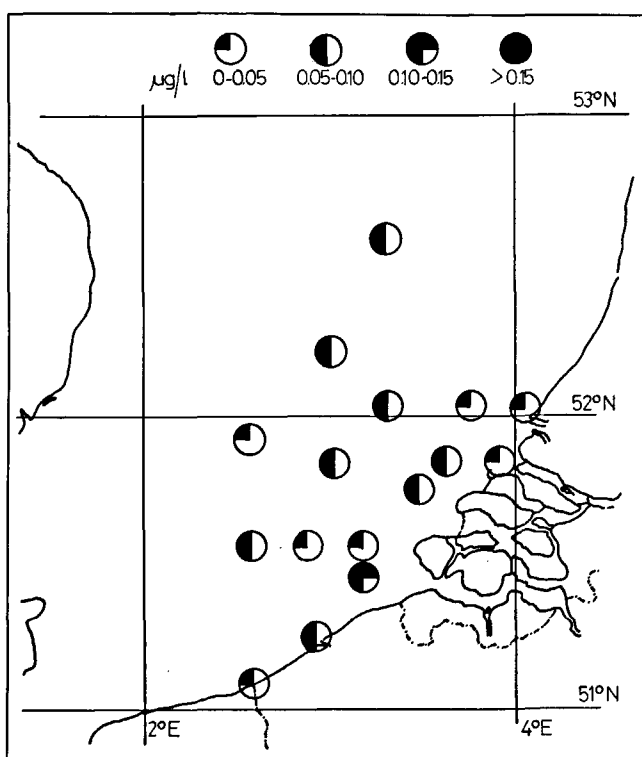*Particulate mercury concentrations (µg/l) in the North Sea.*

Table 2

JONSDAP ([1])-September October 1973 cruise: heavy metal content of plankton.

Identification	Hg (ppm)	Pb (ppm)	Cu (ppm)
M 05.240973.1400.01	2.87	30.2	72.0
M 06.240973.1745.01	3.22	57.5	67.0
M 1343.250973.1100.01	0.75	27.7	48.0
M 1450.250973.1440.01	0.72	23.5	63.0
M 1452.250973.1810.01	3.17	26.5	305.0
M 14.260973.0910.01	8.10	41.0	165.0
M 60.260973.1315.01	1.50	152.0	155.0
M 59.260973.1630.01	1.65	10.7	17.2
M 2689.270973.0740.01	2.10	55.0	59.5
M 1097.021073.0920.01	1.40	33.5	33.5
M 1101.021073.1235.01	1.67	30.5	32.5
M 02.021073.1655.01	1.65	28.5	120.0
M 07.041073.1300.01	1.60	9.2	59.0
M 23.051073.0750.01	1.02	13.7	26.0
M 22.051073.1050.01	0.87	20.0	28.2
M 21.051073.1400.01	1.00	22.0	30.5
M 1989.051073.1730.01	2.50	63.5	40.2
M 1695.061073.0845.01	1.00	37.0	49.5
M 06.111073.1030.01	7.30	39.5	720.0
M 17.111073.1115.01	1.72	19.5	51.0
M 18.081073.2000.01	3.40	1.5	147.0
M 52.121073.0930.01	1.52	20.5	16.0
M 63.081073.1000.01	14.00	275.0	3 275.0
M 65.111073.1330.01	1.90	6.2	26.0
M 1993.111073.1715.01	20.00	36.0	360.0
M 1995.111073.1545.01	2.05	26.5	95.0

N.B.: ppm, milligramme per kilogramme lyophilisated sample.
([1]) JONSDAP, Joint North Sea Data Acquisition Program.

Figure 7

Mercury concentrations in plankton (ppm = mg per kg lyophilised sample) in the North Sea.

Table 2 and Figure 7 show the results of mercury determinations on plankton carried out with samples collected during cruises in 1973.

In addition to the determination of mercury in seawater and plankton, concentrations have also been measured in fish and shellfish (organic and inorganic mercury) by Herman and Vanderstappen (1977), the results being shown in Tables 3, 4 and 5 and in sediments by Wollast (1977), the results of which are shown in Figure 8.

The set of results obtained during the North Sea project provides us with a relatively detailed picture of the mercury distribution in different compartments of the ecosystem (watercolumn, sediments and living organisms). Mean mercury values are summerized in Table 6.

Discussion

Page 450, we calculated the equilibrium concentrations of mercury species, both dissolved in seawater and in the solid and liquid phases, for a wide range of Eh-pH values. The results obtained are very useful for the interpretation of mercury concentrations observed in the different compartments of a natural system. It is obvious, however, that they alone cannot explain the distribution of mercury as found in the North Sea or the Scheldt. The reason is that complex chemical compounds such as the suspended particulate matter or the living organisms are not considered in the simple theoretical system $(Hg\text{-}S\text{-}Cl\text{-}H_2O)$; they will however certainly modify the equilibrium concentrations and the predominant species obtained.

Water column
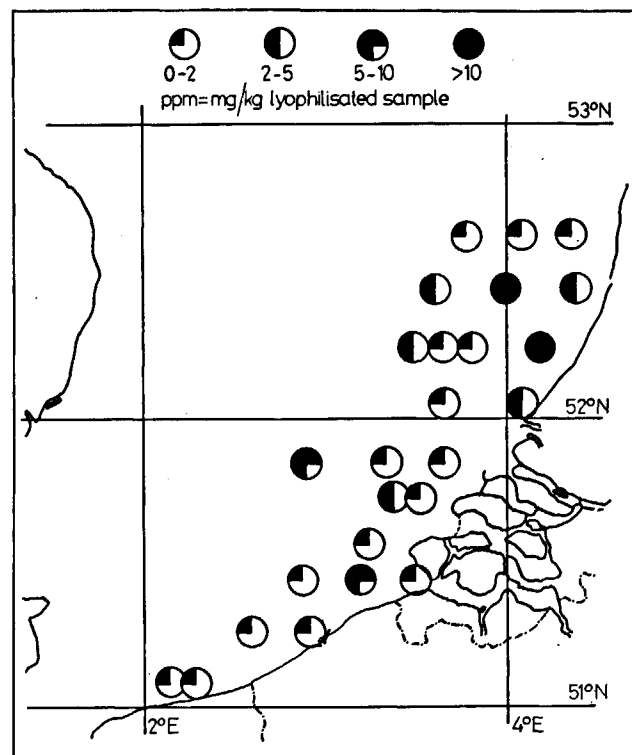
Usual pH values in the North Sea are about 8, Eh values

are at least 350 mV. At these Eh-pH values, Hg_2Cl_2 is the predominant mercury species in the solid phase and $HgCl_3^-$ in the dissolved phase. Moreover, the solubility of $HgCl_3^-$ is so high that only the dissolved form is theoretically present in the North Sea. Due however to interactions with other compartments of the eco-

Table 3

Mean mercury concentrations of drained fillets of 14 fish species, Belgian coastal zone, 1975.

Species	Total Hg (ppm-wet weight)			
	n	x	s	v (%)
Cod, Gadus norhua L.	6	0.16	0.06	37.5
Yellow Gurnard, Gallionymus Lyra L.	10	0.09	0.04	44.5
Sandeel, Ammodytes tobianus L.	10	0.06	0.02	33.3
Flounder, Pleuronectes flesus L.	10	0.41	0.18	43.9
Herring, Clupea harengus.	10	0.07	0.03	42.8
Dab, Pleuronectes limanda L.	10	0.08	0.02	25.0
Horse Mackerel, Trachurus tracharus L.	10	0.87	0.30	34.5
Whiting, Merlangus merlangus L.	50	0.21	0.11	52.3
Rockling, Onos mustela L.	10	0.22	0.08	36.3
Tub Garnard, Trigla lucerna.	10	0.11	0.03	27.3
Plaice, Pleuronectes platessa L.	50	0.11	0.04	36.3
Sole, Solea solea L.	25	0.19	0.09	47.3
Sprat, Clupea sprattus L.	13	0.10	0.02	20.0
Pout, Gadus luscus L.	10	0.16	0.09	56.2

functional groups, such as $-SH$, $-Cl$, $-COOH$, etc; the same is valid for the organic particulate matter. Hence, if $HgCl_3^-$ is attracted by a particle, it can form a stable bound with a ligand present on this solid. As may be seen, both factors contribute to the adsorption capacity of a particle (Baeyens, 1977). Adsorption capacity studies of heavy metals on particulate matter such as clay (Reimers, Krenkel, 1974), hydrous iron and manganese (Gadde, Laitinen, 1974; Decadt, 1977) and organic matter (Baeyens, 1977; Vloebergh, Perpeet, 1977) are well known.

Various processes will determine the particulate mercury concentration. As discussed in the previous paragraph, these include interaction between "dissolved" mercury and particulate matter, especially organic detrital matter, which, according to several authors (Crecelius et al., 1975, Lindberg, Harriss, 1974, Baeyens, 1977), is the most important mercury adsorbent. The processes also include degradation by microorganisms or uptake by zooplankton of this organic detrital matter, and the netto mercury flux between the watercolumn and the sediment. Table 6 indicates that the concentration of particulate mercury constitutes a major part of the total concentration in the water column.

Theoretical calculations cannot provide us with information on the equilibrium between mercury in solution and mercury adsorbed on particulate matter—for a specific case, adsorption isotherms obtained in an empirical manner can describe this equilibrium—because adsorption of mercury on suspended matter is not considered in the theoretical system. Nevertheless, the theoretical results are valuable for interpretation of the adsorption mechanism. On the one hand, $HgCl_3^-$ is subjected to the electrostatic forces exerted by the particles; on the other hand, according to the potential of the water and the solute concentrations in the vicinity of these particles, which can differ quite considerably from those of the bulk of the water, mercury is able to form a more stable bond with certain ligands present on the particle.

Living organisms

In analysing the concentrations of mercury in living organisms, a distinction must be made between the different trophic levels. Direct adsorption on phytoplankton, which is the main cause of contamination, has been studied by Vloebergh and Perpeet (1977), who moreover compared the adsorption capacity of phytoplankton and detrital matter. Despite the lower adsorption capacity of phytoplankton, its mercury content was still considerable, and amounted to 15-20 per cent of that found in detrital matter. For zooplankton and shellfish, as for fish, two main routes of transfer within the marine food chains must be considered: direct uptake from the water, and indirect uptake through ingestion of phytoplankton, zooplankton, organic matter, etc. This latter pathway is common to the three groups of living organisms just mentioned. Rates of indirect uptake have been studied by Elskens (1977 b) the values found for zooplankton and pelagic and demersal fish in the Southern Bight being respectively 3.42 mg Hg, 0.41 mg Hg and 0.019 mg Hg

per square metre in 15 m column. Accumulation rates are significantly lower, however, due to the excretion of 80-90 per cent of the amount ingested.

Mytilus edulis (mussels) are often selected for the assessment of the existing level of marine pollution, because their particular characteristic of filtering large amounts of seawater renders them very sensitive to water-quality changes. The direct uptake of Hg^{++} by *Mytilus edulis* has been studied by Vloebergh et al. (1975), using a radioactive tracer technique. The results show that the target organs, where accumulation is highest, are the gills and the digestive tract. In the case of fish, the gills appear to be the most likely site of intake (Bouquegneau et al., 1977). Direct accumulation through this organ appears to be the major route, leading to the conclusion that the toxic effect of the two possible pathways will cumulate. While mercury concentrations in seawater will affect membrane permeability and enzyme activity in peripheral metabolic systems directly exposed to seawater, the body burden of toxic substances will disturb internal metabolic systems.

Independent of the pathway, the accumulation of mercury can reach a very high level in these organisms, because they produce proteins of low molecular weight which contain a large number of $-SH$ groups, which have high affinities for heavy metals like mercury and cadmium. The release into uncontaminated water should be a comparatively slow process, because of the formation of these metallothioneins, and will rather involve a redistribution of mercury within the body.

The methylmercury: total mercury ratio varies between 32 and 94 per cent in fish, and between 14 and 100 per cent in shellfish, with a value of 61 per cent for shrimps (Herman, Vanderstappen, 1977), but although this study is based on a great number of analyses, no definitive conclusions may be drawn for the moment. As a general trend, according to Johnels et al. (1967), the inorganic: organic mercury ratio decreases with the age of the fish.

Sediments

Sedimentation rate, together with the mercury content of particulate matter will mainly determine the mercury input-flux to the sediments. Elskens (1977 b) calculated for the Belgian Coastal Zone the mean annual sedimentation rate of mercury, and found it to amount to 4.5 mg Hg per square metre. The accuracy of this value relies upon the carbon fluxes in the Southern Bight, as given by Billen (1977), the mean carbon content of the particulate matter (Elskens, 1977 b) and the particulate mercury concentration (see Table 6) in the same area. External forces acting on the sediment and internal chemical and biological interactions will, on the other hand, cause a partial release of the sedimentated mercury.

Resuspension is a physical process which occurs at a certain stage of the tide, when shear stress exceeds a certain threshold. However, according to Lindberg and Harriss (1977), the temporary release of mercury into the surrounding water is followed by a decrease to levels close to those predicted by ideal dilution calculations of the interstitial water. Degradation of
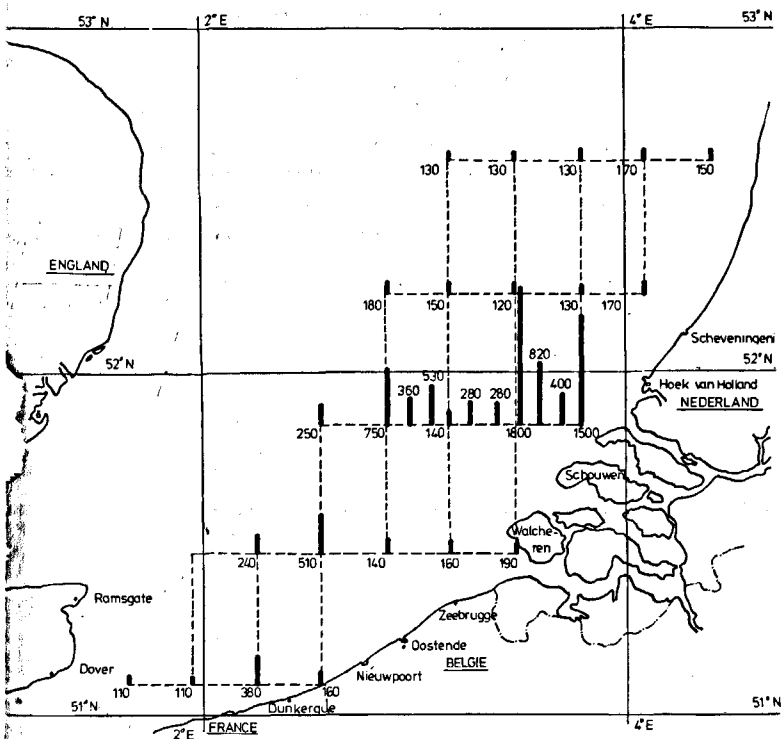
Table 5

Mean methylmercury concentration (MeHg) and (%) MeHg (R) of fish fillets. Belgian coastal zone.

Fishing year	Cod MeHg (ppm)	Cod R (%)	Whiting MeHg (ppm)	Whiting R (%)	Plaice MeHg (ppm)	Plaice R (%)	Sprat MeHg (ppm)	Sprat R (%)
1972	–	–	0.19	70	0.06	32	0.08	53
1973	0.11	73	–	–	–	–	–	–
1974	0.13	54	0.12	50	0.09	53	0.05	55
1975	0.16	94	0.17	85	0.12	100	0.08	80

Table 6

Mean mercury content of various compartments of the ecosystem.

Compartment		Hg-concentration
Water column	"dissolved"	50×10^{-3} μg/l
	particular	33×10^{-3} μg/l or 5.5 μg/g dry matter
Total		83×10^{-3} μg/l
Sediments		400 ppb (fresh material)
Fish		150 ppb (fresh material)
Shellfish		50 ppb (fresh material)
Zooplankton		1 550 ppb (fresh material)

◄ Figure 8

Numerical and graphical representations of mercury concentrations (ppb-dry weight) in the sediments of the North Sea.

system, mainly particulate matter and living organisms (*cf.* point B), the concentration of dissolved mercury is reduced.

The adsorption mechanism of mercury on solid matter may be explained in terms of chemical binding in combination with electrostatic forces of attraction. The interface between the particles and the water is characterized by a potential difference. Depending on the sign and magnitude of the electrokinetic potential of the solids, mercury may be adsorbed strongly on the fixed part

of the double layer, or less strongly on the outer side of this layer, where it acts as a counterion. In addition to the part played by the potential in the adsorption process, it is apparent that the number of specific reactive sites on a particle must also be taken into account for example, tensioactive substances adhere to a particle in such a way that they must be considered as a part of the latter, and may contain a large number of

Table 4

Heavy metal content of benthic invertebrata, Belgian coastal zone, 1975.

Species	n	H₂O (%)	ppm (dry weight) Hg total	Cu	Pb	Zn	Cd
Crustacea:							
Crangon crangon 1972	50	71	0.28	50.3	10.4	91.4	0.17
Crangon crangon 1974	50	71	0.22	44.0	3.0	87	0.16
Pagarus bernhardus	6	60	0.13	87	2.1	95	0.22
Pagarus bernhardus	3	56	0.29	121	1.0	104	0.45
Carcinus maenas	2	66	0.15	28	2.4	84	0.07
Portunus puber	2	65	0.12	26	2.8	108	0.16
Portunus puber	1	62	0.11	93	1.3	115	0.37
	7	64	0.19	32	2.6	98	0.14
Macropipus holsatus	5	66	0.17	216	6.3	115	0.25
Échinodermata:							
Asterias rubens	7	65	0.34	7.6	8.1	163	0.24
Asterias rubens	3	67	0.51	8.4	3.7	195	0.38
Ophiura species	3	45	0.10	2.7	4.1	117	0.17
Ophiura species	1	42	0.14	3.0	3.2	149	0.28
Echinocardium cordatum	1	28	0.08	3.3	128 (?)	28	0.40
Bryozoa:							
Calcyonidium digitatum	3	84	0.19	8.6	6.6	107	0.63
Flustra foliacea	1	71	0.14	9.8	15.2	336	0.68
Mollusca:							
Buccinum undatum	5	61	0.32	107	0.64	47	0.18
Annelida:							
Lanice conchilega	3	33	0.03	2.6	9.8	45	0.16
Pisces:							
Gobius minutus	2	71	0.19	3.2	1.3	73	0.09
Coelenterata:							
Metridium senile	1	74	0.15	–	–	–	–

Table 7
Scheldt estuary. February 1975 cruise

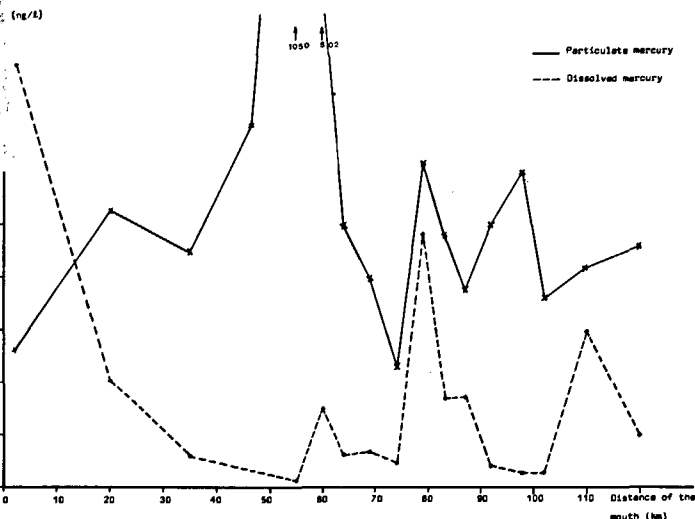| Point	KM	Hg-particulate µg/l	Hg-dissolved µg/l	pH	Eh mV	Salinity gr Cl⁻/l
1	2	0.13	0.40	7.75	385	13.00
4	20	0.26	0.10	7.35	325	10.20
7	35	0.22	0.03	7.05	315	6.30
10	46.5	0.34	0.02	7.05	320	4.00
12	54.5	1.05	0.01	7.30	320	1.60
14	59.5	0.50	0.08	7.25	320	0.90
16	64.5	0.25	0.03	7.15	312	0.50
18	68.5	0.20	0.03	7.15	318	0.40
20	73.5	0.11	0.03	7.10	275	0.30
22	78.8	0.31	0.24	7.00	320	0.30
24	82.8	0.24	0.09	6.97	280	0.30
26	87.5	0.19	0.09	7.00	280	0.30
28	92	0.25	0.02	7.10	290	0.30
30	97.5	0.30	0.02	7.15	300	0.30
32	103.5	0.18	0.02	7.25	340	0.30
34	113.5	0.21	0.13	7.30	345	0.35
36	121.6	0.23	0.05	7.30	350	0.35

organic particulate matter by bacterial activity can lead to the release of mercury. In addition, the form of the mercury compounds can be changed by mineralization (Billen, 1973) or methylation (Jensen, Jernelov, 1969). Also, as pointed out in section I, chemical processes can play a role. Under very strong reducing conditions and high pH, such as those likely to occur in the sediments of the sea floor (Wollast, 1972), mercury sulphide anions become very soluble, which results in an increased mobility of mercury in the interstitial water and in alteration of the mercury content in the sediments.

THE SCHELDT ESTUARY

Measurements and results

Attention was concentrated on the transport mechanisms of mercury, in order to explain the observed longitudinal patterns. The high degree of pollution reduces the number of living organisms, especially in the upper part of the estuary, almost to zero, but further downstream the situation improves. With the exception of micro-organisms, which constitute a part of the particulate suspended matter, no living organisms have been considered.

Longitudinal concentration profiles of particulate and "dissolved" mercury concentrations have been drawn from measurements on estuarine samples. The latter were collected with a centrifugal pump made of Teflon, and immediately filtered on board the vessel through a 0.8 µm poresize Millipore filter, using a closed pressure filtration system. The filtrate was acidified to pH 1 with pure nitric acid and, stored for a maximum of three days in a BOD (glass) bottle. Filters were rapidly deep frozen and stored in plastic holders. Hoenig (1977) had previously measured the particulate mercury concentration in a different manner. To obtain a more representative sample, he collected the suspended matter using a centrifugal system (Alpha-Laval centrifuge), over a period of half an hour, and stored it in a polyethylene bottle.

Sample analysis was carried out in the manner described above for the seawater samples. The results and the longitudinal profile of "dissolved" and particulate mercury (ng/l) are shown in Table 7 and Figures 9. Figure 10 represents the longitudinal profile of particulate mercury (µg/g solid) obtained by Hoenig.

Sediment samples were collected at only one point, 60 km upstream from the mouth (Bouquiaux, Herman, 1977), and the mercury level detected was 1.8 ppm. Wollast (1977) has estimated the mean annual quantity of mercury sedimentating in the Rupelmonde-Doel sector (km 92-km 61) at 1.2 ton, and in the Doel-Hansweert sector (km 60-km 35) at 0.1 ton.

Discussion

While longitudinal variations in pH are small — the result in Table 7 indicates that with the exception of point 1,

Figure 9
Longitudinal concentration profiles of dissolved and total particulate mercury (ng Hg/l) in the Scheldt estuary.

Figure 10
Longitudinal concentration profile of particulate mercury and copper (µg-metal/g solid) in the Scheldt estuary.
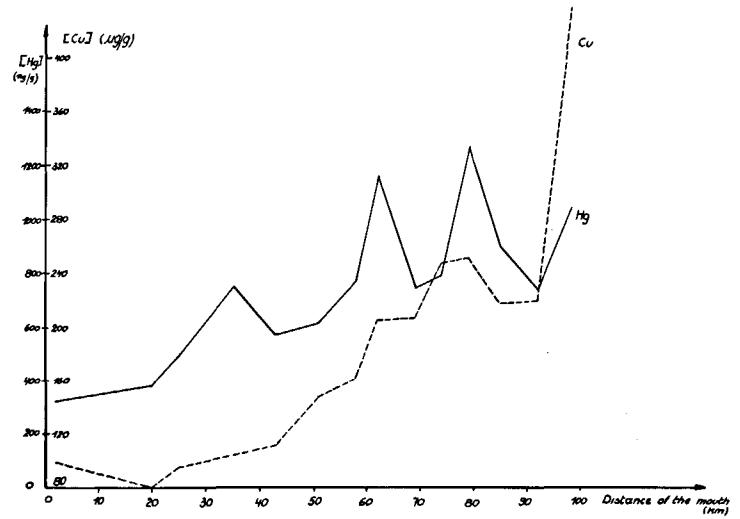
pH values lie between 6.95 and 7.35 — the redox potential shows considerable longitudinal and seasonal variations. Figure 11 shows some longitudinal Eh profiles for different periods of the year. Two specific zones in the estuary may be distinguished, one aerobic and the other more or less anaerobic. Downstream, from km 55 to the mouth, redox potential has the normal value of aerated water, so that dissolved $HgCl_3^-$ is the most stable mercury species. In the upper region, however, the potential fluctuates between -50 and $300\,mV$ depending on the season and the locality, so that either $HgCl_3^-$ or Hg_{aq}^0 will be stable compounds. In the estuary, mercury concentrations are never high enough to provoke chemical precipitation.

Comparison of the concentration of total particulate mercury, expressed in terms of ng Hg-particulate per litre, with "dissolved" mercury leaves no doubt that adsorption mechanisms play a still more important role in the estuary than in the North Sea. Because the absolute mercury concentration (defined as µg Hg per g dry matter) varies very little from point to point, the total particulate mercury profile shown in Figure 9 must be due to the turbidity profile, which has maxima generally situated between km 40 and km 90, depending on the fresh water discharge.

The total particulate: "dissolved" mercury ratio is high, especially in the upper part of the estuary but is progressively reduced in a downstream direction, as a result of three factors: (a), due to sedimentation, only a small proportion of the particulate mercury reaches the sea; the main part will accumulate in the upstream sediments; (b), mercury originating in the industrial zone around Ghent is discharged into the Scheldt at 20 km from the mouth; (c), the absolute mercury concentration decreases from km 50 to the mouth, as may be seen on Figure 10. While points (a) and (b) require no further comment, point (c) is attributed by Muller and Forstner (1975) to dilution of the highly polluted upstream suspension, by suspended matter of marine origin, which is much less contaminated. Analogous observations have been made for other particulate heavy metals, as well as particulate carbon concentrations (Wollast, 1977).

As far as sediments are concerned no conclusions on the relation between theory and measurements may as yet be drawn, in view of the small number of results obtained so far. An extensive study on sediment concentrations and related processes is necessary for a better understanding of the mercury transport in the estuary.

Acknowledgement

Figure 11

Longitudinal profiles of redox potential in the Scheldt estuary.
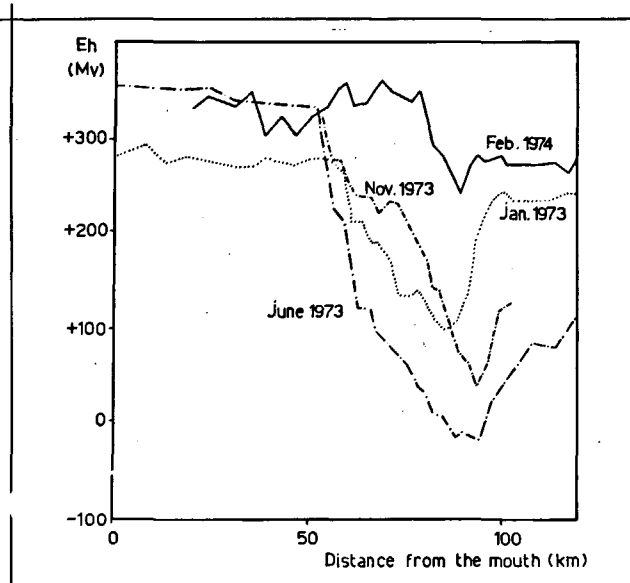
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