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Part 5

INTERACTION KINETICS BETWEEN DISSOLVED INORGANIC MERCURY
AND ESTUARINE SUSPENDED MATTER

W. BAEYENS¹, G. DECADT¹, F. DEHAIRS^{1*}, L. GOEYENS¹,
H. DEDEURWAERDER¹ and G. GILLAIN²

ABSTRACT : The adsorption kinetics (adsorption capacity and adsorption rate) of mercury on natural suspended matter of the Scheldt estuary were studied. The results indicated that up to 2 ppm, the particulate matter adsorbed all the mercury added (24 h. experiments) independently of salinity and redox potential.

At higher mercury concentrations the ratio Hg-adsorbed:Hg-dissolved was inversely proportional to the salinity except at low redox potential ; in that case the salinity showed no influence. Great evidence exists that organic matter is a major mercury scavenger.

Accurate mercury adsorption rates were obtained with a continuous filtration system connected to a mercury auto-analyzer. The adsorption rate increased with increasing temperature, turbidity and dissolved mercury, but decreased with increasing salinity and adsorbed mercury. As a consequence the adsorption rate in the upstream area of the estuary appeared to be about ten times faster than in the downstream area.

1. Laboratorium voor Analytische Scheikunde, Vrije Universiteit Brussel, Pleinlaan, 2, B-1050 BRUSSEL (Belgium).

2. Institut de Chimie, Laboratoire d'Océanologie, Université de Liège, SART TILMAN, B-4000 LIEGE (Belgium).

* Senior Research Assistant at the National Fund for Scientific Research (Belgium).

INTRODUCTION

The fate of a pollutant discharged into the marine environment depends on the hydrodynamical conditions of the area and the possible interactions with other chemical and biological constituents. If the pollutant is a conservative element, its concentration is only influenced by external inputs and outputs. This is, however, not the case for heavy metals. Indeed, calculations based on atmospheric and telluric inputs provide theoretical concentrations of copper, nickel, silver, gold, lead and other metals in the oceans, which are many orders of magnitude higher than the best currently measured values (Turekian, 1977). Mercury concentrations measured in the Southern Bight of the North Sea also appear much lower than those permitted by thermodynamical solid-dissolved equilibrium calculations (Baeyens et al, 1979).

The mean residence time of the dissolved radionuclides ^{210}Pb , ^{210}Po , ^{234}Th , ^{228}Th , relative to particle removal, have all been shown to be between a half-a-year and a year-and-a-half in the open ocean, according to Turekian (1977). As the coastal areas are approached the residence time for these nuclides in the water column drops sharply to tens of days and in coastal mixing basins with a heavy load of resuspended bottom sediments it drops to one day. To the extent that a trace metal follows the pattern of all of these radionuclides, they also can be expected to be effectively sequestered by particles for transport out of the surface layers. This is indeed the case for mercury, since only 0.1 to 0.07 % of the amount of mercury entering into the oceans remains in the water column (Krauskopf, 1956).

Laboratory and field studies suggest that among the various constituents of natural particulate matter, organic matter (Lindberg & Harriss, 1974 ; Reimers & Krenkel, 1974) hydrous manganese oxides (Harriss, 1968 ; Lockwood & Chen, 1973) and clays (Reimers & Krenkel, 1974 ; Frenet-Robin & Ottmann, 1977 and 1978) seem to be the most effective mercury scavengers. Until now most of the adsorption studies concerning mercury aimed only at the determination of (1) the maximum adsorption capacity of this metal on a particular solid and (2) the ratio dissolved mercury : adsorbed mercury at equilibrium.

Few attempts have been made to measure the rates of adsorption. This is probably due to the difficulties encountered in finding an appropriate solid-liquid separation method capable of assessing in a sufficiently accurate way the rapid decrease of the dissolved mercury concentration. In general, it has only been possible to determine the time necessary to reach the equilibrium state (Reimers & Krenkel, 1974 ; Lockwood & Chen, 1973).

Therefore we have developed an automated method allowing the continuous assessment of adsorption rates of mercury on particulate suspended matter (Baeyens et al, 1982).

In this paper, the adsorption capacities of mercury on particulate suspended matter of the Scheldt estuary as well as the ratios dissolved mercury : adsorbed mercury at equilibrium are discussed. In addition adsorption rates including the influence of some important water-quality parameters, such as temperature, salinity and redox potential are presented.

EXPERIMENTAL

Characterisation of the natural samples.

The particle size distribution has been determined with a Coulter Counter (Coulter Electronics Ltd). The redispersion of coagulated particulate matter has been carried out with a Branson Sonifier (Model S-75), until the particle size distribution corresponded again to the original one. The heavy metal content of the suspended matter has been determined as described by Gillain et al (1982), while organic matter has been quantified by the dichromate oxydation method. Determination of the weight loss between 550°C - 1100°C, which is correlated with the carbonate content and the weight loss between 100 - 1100°C, which is anti-correlated with the SiO₂ content, have been carried out on the particulate matter too.

In the solution the pH (Tacussel pH-meter), Eh (Pt and calomel electrodes), chlorinity (by gravimetry) and the organic matter content (by dichromate oxydation) were measured. Particulate and dissolved mercury concentrations were manually determined as described by Gillain et al (1982).

Adsorption capacity determinations.

Twenty four hours after the injection of a known amount of dissolved mercury, particulate and dissolved mercury concentrations were measured manually. To avoid sedimentation of the particulate material, we used flasks with a screw-cap attached to a continuous rotating system (10 rpm).

The mercury auto-analyzer.

The concept of the auto-analyzer (figure 1) is based on the manual method of Hatch & Ott (1968) and on the semi-automatic method as reported by Goulden & Afghan (1970) and Agemian & Chau (1975).

The sample is successively acidified with nitric acid (1 + 2) and sulphuric acid (1 + 1), oxidized at 80°C with potassium permanganate (1 %) and cooled to 20°C. The excess potassium permanganate is eliminated with hydroxylamine (1 %) and mercury (II) is

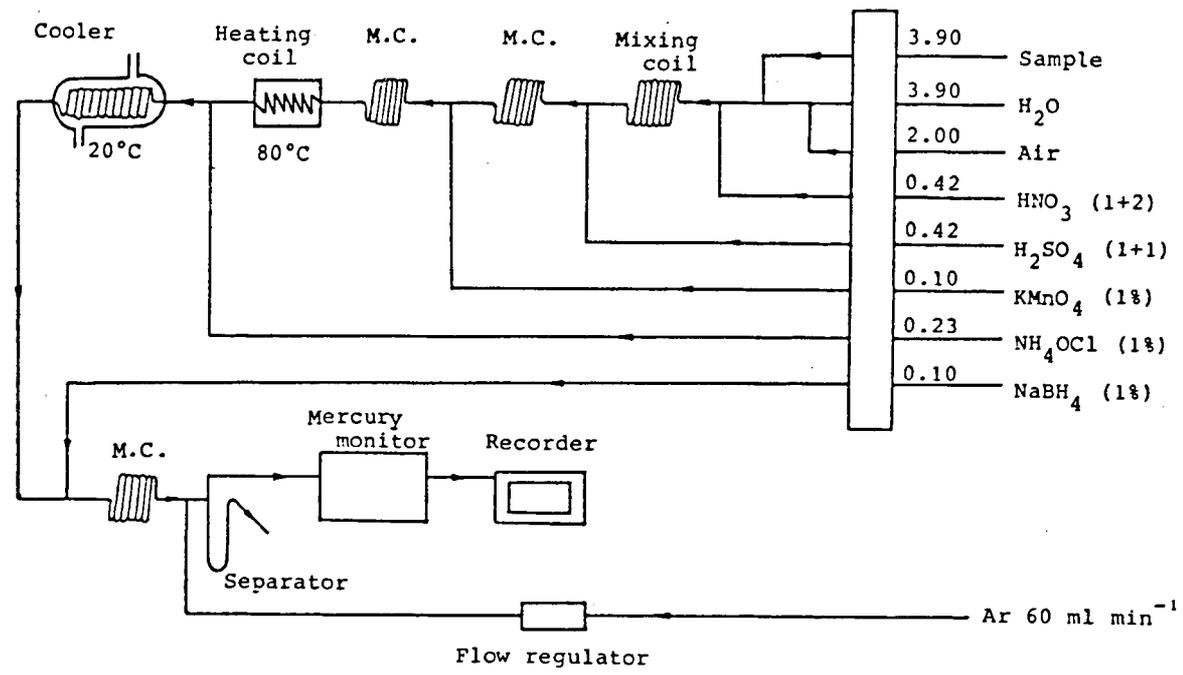


Figure 1 : Mercury Manifold

reduced to metallic mercury with sodium borohydride (1 %). In the gas separator metallic mercury is swept from the solution by a current of argon. The argon gas flow rate is kept as constant as possible with a Brooks gas flow regulator (60 mL min^{-1}). The gasstream was dried over magnesium perchlorate. All mercury detections were made on a Coleman Instruments Hg Analyzer (MAS-50). The sampling tube of the mercury manifold is connected to an automatic switching valve, which conducts sample from the reaction vessel to the mercury manifold and a 2 percent nitric acid wash-solution to the waste or the inverse. For our experimental condition, a wash solution-reactor solution time ratio of 2:1 appeared to be sufficient for a complete return to the baseline.

The reaction vessel.

The adsorption vessel is a double-wall plexiglass (345 mL) or pyrex glass (325 mL) container, fitted with a filtering device, an injection system, a thermometer and Eh-probes.

Two kinds of materials (plexiglass and pyrex glass) have been used, in order to verify if the nature of the wall had any influence on the adsorption kinetics. The double wall, which almost entirely surrounds the inner container, serves as a thermostatic mantle. In this way a constant sample temperature is ensured.

The sample is continuously pumped out of the vessel by a Technicon pump, but is alternatively conducted to the manifold and to the waste, according to the position of the switching valve. A Millipore filter with a pore-size of $0.8 \mu\text{m}$, fitted in an air-tight filter head at the outlet of the vessel, prevents losses of particulate material. Although a partial clogging of the filter could not be avoided, it appeared (1) that the outlet flow rate remained constant during the time of the experiment and (2) that the amount of suspended material in the vessel did not substantially decrease. The solution leaving the reactor is automatically replaced by a filtered sample. Changes in the volume of the reactor sample were avoided by using identical in and outflow rates.

Through the injection system known amounts of mercury were added to the sample. These injections were made with an automatic Hamilton syringe ($5\text{-}20 \mu\text{L}$). Insertion of the thermometer and the Eh-probes into the sample is possible through air-tight silicone joints.

As the whole analyzing device forms a closed system, vaporization or atmospheric contamination of mercury is negligible.

Estuarine samples.

Sample characteristics had to fulfil the following requirements: low salinity and high turbidity. Indeed this allows us to vary salinity or turbidity in an easy way, respectively by adding salt or diluting with filtered water; this procedure, we

believe, does not disturb the initial characteristics of the sample. The samples were collected in the Scheldt estuary at 90 km from the mouth ; at this site typical values of salinity and turbidity are respectively 1‰ NaCl and 300 mg l^{-1} particulate matter.

In each case, thirty litres of natural estuarine water were returned to the laboratory in a polyethylene container, and subdivided in 2.5 l polyethylene bottles. One bottle served for the characterisation of the sample. These characteristics are summarized in table 1. The remaining bottles were rapidly deep frozen and maintained at $-20^{\circ}C$.

Table 1
Sample characteristics

	Unit	Sample 1 2.09.76	Sample 2 22.10.76	Sample 3 18.04.77
pH		7.4	7.5	7.4
Eh	mV	300	300	280
Turbidity	$g. l^{-1}$	320	520	200
Chlorinity	$gCl^{-} l^{-1}$	0.15	0.8	0.3
DOM	$mg CH_2O. l^{-1}$	30.8	36.7	
POM	$mg CH_2O. l^{-1}$	47.3	66.1	
Dissolved Mercury	$\mu g Hg. l^{-1}$	< 0.05	< 0.05	< 0.05
Particulate Mercury	$\mu g Hg. l^{-1}$	0.15	0.26	0.12
Particulate Calcium	% Ca	7.9	3.0	
Particulate Iron	% Fe	3.8	4.2	
Particulate Magnesium	% Mg	0.40	0.31	
Particulate Manganese	% Mn	0.07	0.07	
Weight loss 100-550°C	%	13		
Weight loss 550-1100°C	%	8.7		

Operational procedure for the determination of the adsorption rates.

A differential procedure has been adopted for the determination of the adsorption rates. Such a method has the advantage

that as long as processes other than adsorption on particulate matter (mainly losses of mercury to the reactor wall) are not competitive, their effects are negligible. The first experiment, hereafter called the dilution experiment, is carried out on the filtered sample (pore-size of $0.8 \mu\text{m}$). The same filtered sample is also used as inlet solution. After injection of a known amount of mercury (II) chloride or metallic mercury, the evolution of the mercury concentration in the vessel sample is followed during 30 to 40 minutes ; the dissolved concentration in real time, the particulate concentration from the law of mass conservation as well as from a control measurement at the end of the experiments. As the mercury concentration in the vessel sample was always a few orders of magnitude higher than in the inlet solution, the former one is continuously diluted.

The second experiment, hereafter called the adsorption-dilution experiment, is similar to the dilution experiment except that in this case the reaction vessel contains natural, unfiltered sample. The dissolved mercury concentration decreases much faster in this experiment as a result of the combined effect of dilution by the inlet solution and adsorption on the particulate matter.

Dilution constants.

Injections of dye in distilled water showed that the vessel solution is sufficiently homogeneous to admit that the internal and the outflowing concentrations are equal. Moreover the inflowing mercury concentration was always negligible compared to that in the vessel.

Under such conditions the law of mass conservation reduces to the following equation :

$$\frac{dC}{dt} = -kC \quad \text{or} \quad C = C_s e^{-kt} \quad (1)$$

However, since in the experiments k was of the order of 10^{-2} min^{-1} , the dilution curve equation approximated a linear relation.

The dilution experiments also showed a definite functional relationship between temperature and k , and salinity and k .

Hence, for each set of physicochemical conditions, the adsorption rate has been computed using the mean k -value obtained under the same conditions.

Adsorption rates.

Since the decrease in mercury in the vessel during the adsorption-dilution experiment equals the sum of the decreases due to adsorption and to dilution, one can write at time t :

$$\left(\frac{dC}{dt}\right)_{\text{vessel}} = -kC + \left(\frac{dC}{dt}\right)_{\text{adsorption}} \quad (2)$$

The left handside of equation (2) represents the derivative of the adsorption-dilution curve equation ; it has been determined by a least squares polynomial fitting through the set of data-points.

It appeared that a cubic curve satisfied very well.

RESULTS

Figure 2 shows the dissolved and particulate mercury concentrations measured 24 hours after a mercury injection varying between 0.1 and 50 ppm. The assumption that after one day both mercury forms are at equilibrium is justifiable. Indeed, Reimers and Krenkel (1974) found that illite, montmorillonite, octadecylamine and dodecanethiol adsorbed all of their inorganic mercury in 10 minutes, kaolinite and stearic acid attained maximum capacity in approximately 1 hour, and sand required 3 to 4 hours to reach maximum capacity. Frenet-Robin and Ottmann (1978) on the other hand found that the clays involved in their studies attained maximum capacity in 4 hours.

Our results indicate that up to 2 ppm, almost all mercury injected in samples 1 and 2 is scavenged by the particulate suspended matter, at low as well as at high salinity. For higher mercury level injections, however, different dissolved to particulate ratios are observed, depending on the salinity and the redox potential. At a redox potential of approximately 360-440 mV, 70 percent of a 10 ppm mercury injection disappears on the particulate matter at low salinity, while at a salinity of 20 g NaCl l^{-1} only 30 percent is adsorbed. A high salinity seems to prevent the adsorption of Hg^{2+} ions at certain sites or on a certain fraction of the suspended material. At a low potential, when metallic mercury is the stable species, this salt effect seems not to exist. Indeed, for a redox potential of 100 mV 70 percent of a 20 ppm injection disappears on the particulate matter at low as well as at high salinity. These results suggest that the particle charge is modified by the salt increase, so that the Hg^{2+} ions are more strongly repelled while the neutral metallic mercury compound seems not to be affected. In the study of the adsorption kinetics, the mercury concentrations varied between 10 and 50 $\mu g\ l^{-1}$. It is obvious that in this concentration range, desorption effects have not to be taken into account.

The coefficient of variation for the initial adsorption rates resulting from duplicate dilution and adsorption-dilution experiments ranged, according to the physicochemical conditions, from

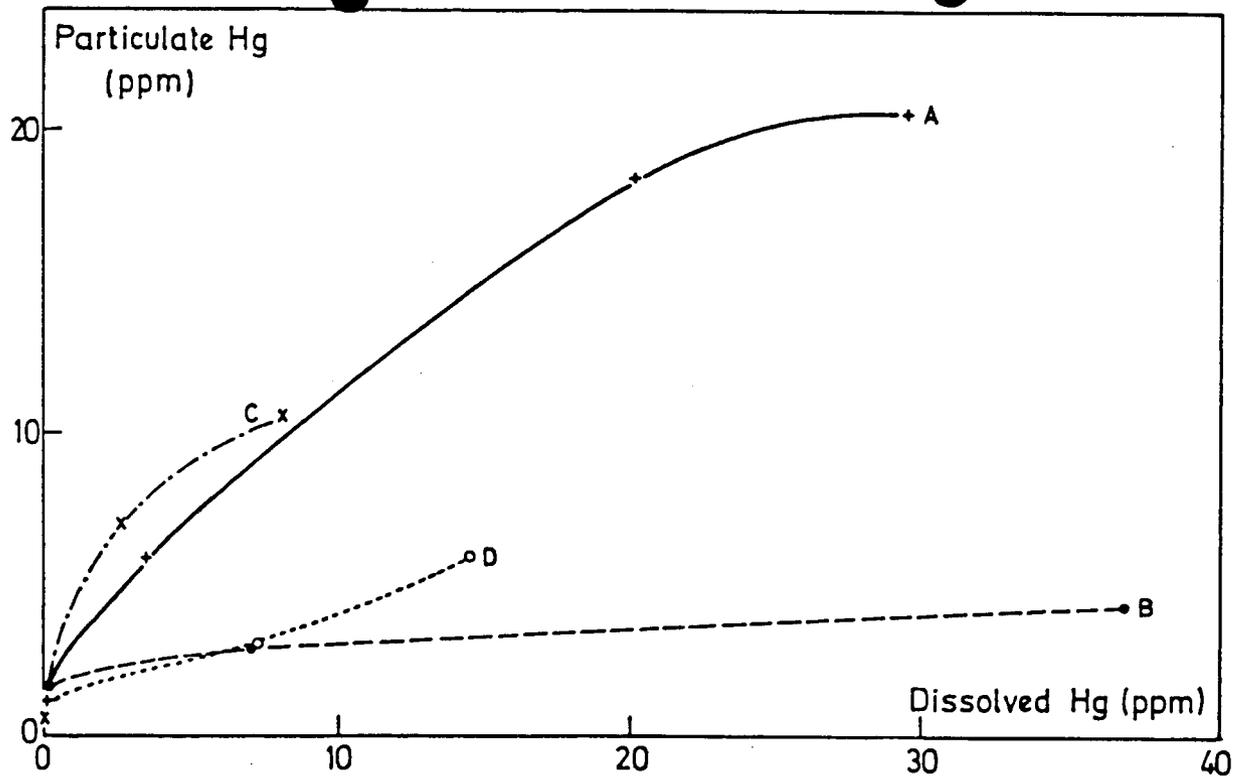


Figure 2 : Equilibrium profiles of dissolved and particulate mercury (A) sample 1, (B) sample 1 + 20 g NaCl l^{-1} , (C) sample 2, (D) sample 2 + 20 g NaCl l^{-1} .

1 to 6 %. The variation on the dilution constant k contributed only slightly to this overall variation. A sensitivity test indicated that a 10 % increase of k , which is beyond the observed range of variation, modified the adsorption rate by no more than 0.3 %.

The applied differential method theoretically eliminates any contribution to the adsorption rate resulting from possible interactions with the vessel wall. In order to prove this, we compared adsorption rate data obtained with a plexiglass and a pyrexglass vessel under similar physicochemical conditions (see table 2). In view of the different nature of the two materials it is unlikely that they react with mercury in an identical way. But this also means that if the mean difference between the two data sets equals zero, the nature of the vessel wall has no influence on the adsorption rate determinations. A paired T-test (Dagnelie, 1970) allowed us to accept the hypothesis of equality of both data sets on the 0.05 level.

The influence of the various parameters on the initial adsorption rate (the initial amount of adsorbed mercury is negligible), which is fairly well illustrated in table 2, can be expressed as follows :

$$V_{t=0} = 1.48 \cdot 10^{-3} (2.63 + 0.17 \text{ Hg}) (\text{SM}) (\text{TE}) (27.01 - 0.43 \text{ SA}) \quad (3)$$

with $V_{t=0}$: initial adsorption rate in $\mu\text{g-Hg l}^{-1} \text{ min}^{-1}$
 Hg : dissolved mercury concentration in $\mu\text{g-Hg l}^{-1}$
 SM : suspended matter concentration in g-solid l^{-1}
 TE : temperature in $^{\circ}\text{C}$
 SA : salinity in g-NaCl l^{-1}

The influence of the redox potential and hence of the mercury speciation on the adsorption rate was not unequivocal. With the pyrexglass vessel the adsorption rate slightly decreased for a decreasing potential, while the inverse occurred with the plexiglass vessel. Therefore this parameter is not included in the equation.

Although the adsorption capacity of the suspended material exceeds by far the amounts of mercury added to the samples, the adsorption rate normalized with respect to the prevailing dissolved mercury concentration decreased initially rather fast. As soon as R , the ratio $\text{Hg-adsorbed} : \text{Hg-dissolved}$, approached however a value of 0.3, the rate became constant (figure 3). Taking into account that in our experiments $V_{R=0}$ equals $V_{t=0}$ in equation (3), the decrease of the adsorption rate in function of R can be expressed as follows :

$$\bar{V} = \bar{V}_{t=0} + (0.017 - 1.477 \bar{V}_{t=0} - 3.949 \bar{V}_{t=0}^2) \times R \quad R < 0.27 \quad (4)$$

$$\bar{V} = \bar{V} \quad (R=0.27) \quad R > 0.27 \quad (5)$$

Table 2

Mercury adsorption rates obtained with a pyrex glass and a plexiglass reaction vessel,
under similar physico-chemical conditions

Parameter conditions ^b	Plexiglass vessel		Pyrex glass vessel		Differences
	Initial adsorption rate ^c ($10^{-2} \text{ l min}^{-1} \text{ g}^{-1}$)	Initial Hg-concentration ($\mu\text{g l}^{-1}$)	Initial adsorption rate ^c ($10^{-2} \text{ l min}^{-1} \text{ g}^{-1}$)	Initial Hg-concentration ($\mu\text{g l}^{-1}$)	
Reference			31	18.0	
Reference	27	20.0	29.8 ^a	20.0 ^a	- 2.8
Reference	26.7 ^a	22.9 ^a	28	22.9	- 1.3
Reference	26.3 ^a	26.2 ^a	28	26.2	- 1.7
Reference	26	28.3	27.4 ^a	28.3 ^a	- 1.4
Reference	25	29.0	27.1 ^a	29.0 ^a	- 2.1
Reference	22	42.9	23	42.3	- 1
T = 40°C	31	29.3	40	24.9	- 9
T = 14°C	13	29.5	12	34.8	1
+ 20g l^{-1} NaCl	15	29.2	15	28.5	0
Eh = 150 mV	29	26.3	24	26.4	5

^a These values are linear interpolated values.

^b Reference : T = 25°C ; Eh > 300 mV ; salinity < 1.3 g - NaCl l^{-1} ; turbidity = 100 mg - solid l^{-1} (sample 3) and 260 mg - solid l^{-1} (sample 2).

^c The adsorption rate is normalized with respect to turbidity and dissolved-Hg concentration.

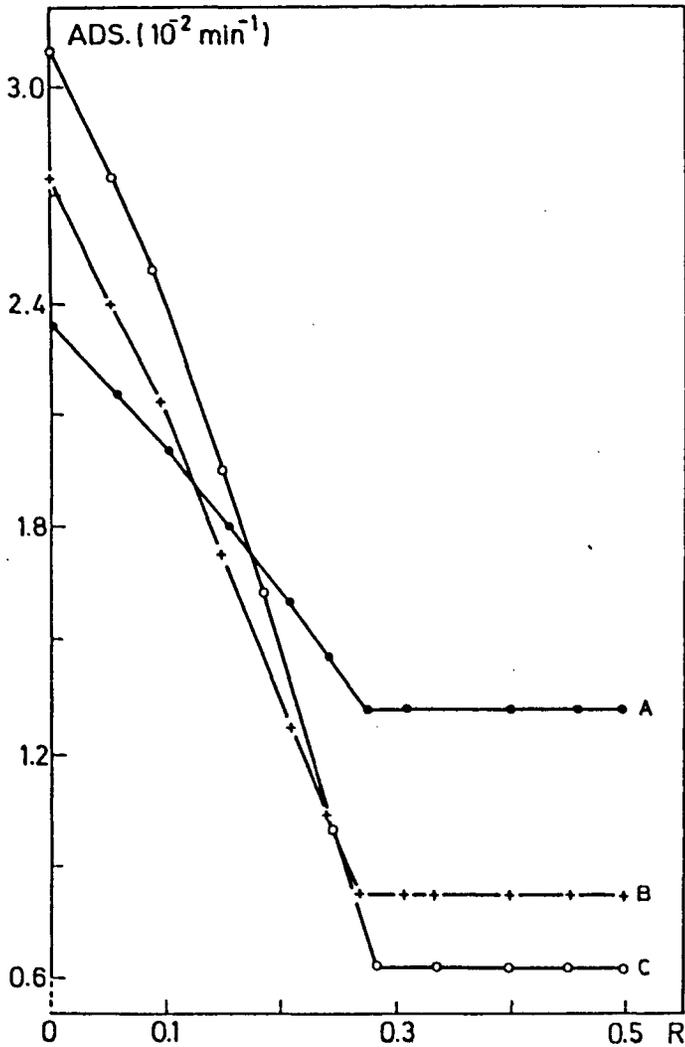


Figure 3 : The decrease of the adsorption rate with respect to the ratio Hg-adsorbed : Hg-dissolved. (A), (B), (C) = initial Hg-dissolved concentration of 42.3, 26.2 and 17.9 $\mu\text{g-Hg l}^{-1}$ respectively. R = ratio Hg-adsorbed : Hg-dissolved. V_{ADS} = adsorption rate normalized with respect to the dissolved Hg-concentration.

with \bar{V} the adsorption rate normalized with respect to turbidity and dissolved mercury concentration.

As an example, the short-term behaviour of dissolved and particulate mercury (initially respectively 10 and 0 $\mu\text{g Hg l}^{-1}$) in the upstream area (2g-NaCl l^{-1} , 160 mg-solid l^{-1} , 15°C) respectively downstream area (25g-NaCl l^{-1} , 20 mg-solid l^{-1} , 15°C) has been calculated by introducing in equations (4) and (5) the right parameter. This computation yields the following results :

UPSTREAM			DOWNSTREAM		
time (min)	Hg-diss. ($\mu\text{g l}^{-1}$)	Hg-ads. ($\mu\text{g l}^{-1}$)	time (min)	Hg-diss. ($\mu\text{g l}^{-1}$)	Hg-ads. ($\mu\text{g l}^{-1}$)
0	10	0	0	10	0
6	8.24	1.76	41	8.92	1.08
28	5.84	4.16	311	5.84	4.16
58	3.68	6.32	641	3.60	6.40
148	0.93	9.07	1391	1.20	8.80

Apparently, the adsorption of mercury in the upper part of the estuary proceeds about ten times faster than in the downstream part. As a consequence only a small fraction of the total amount of mercury discharged into the upstream area of the estuary will reach the sea, due to the adsorption process and an intensive sedimentation of the particulate suspended matter in the area of 1 to 5 ‰ salinity, estimated to $90.6 \text{ kg m}^{-2} \cdot \text{year}^{-1}$ (Baeyens et al, 1981), and corresponding to about $60 \text{ mg-Hg m}^{-2} \cdot \text{year}^{-1}$.

In several studies e.g. Klein (1973), Lindberg and Harris (1974), strong correlations between the mercury and organic matter content of suspended sediments or bottom sediments have been found. Hence, the suggestion has been made, that the particulate organic matter is the most important mercury scavenger in the aquatic environment. In the Scheldt estuary the particulate suspended matter is composed of quartz, clays, carbonates, hydroxydes of iron and manganese and organic matter. Heating this material two or three times up to 550°C yields us a residue free of organic material.

This residue has than been redispersed in filtered estuarine water sample (0.8 μm filter) using ultra-sounds, until the particle size distribution corresponded to the natural one (see table 3). The mercury adsorption capacity of this inorganic suspended matter was however significantly lower than the capacity of the natural material ; in fact it was inferior to 1 ppm for Hg^{2+} and inferior to 2.5 ppm for metallic mercury when an amount of 10 ppm Hg was added.

These results seem to corroborate the important role played

Table 3
Particle size distributions

Diameter		Number of particles		
limits μm	mean μm	Natural sample	Suspension free of organic matter	
			redispersed (ultra-sounds)	not redispersed
22.05 - 27.79	24.92	80	122	84
17.51 - 22.05	19.78	266	454	269
13.89 - 17.51	15.70	570	1250	482
11.03 - 13.89	12.46	952	2475	763
8.75 - 11.03	9.89	1817	4730	1194
6.95 - 8.75	7.85	3665	9193	1789
5.51 - 6.95	6.23	7105	16913	2871
4.37 - 5.51	4.94	12326	26480	3963
3.47 - 4.37	3.92	21133	37187	5334
2.76 - 3.47	3.11	34723	48428	7379
2.19 - 2.76	2.47	54884	60554	11096

by the organic matter. However, there are two facts we do not have verified yet : (1) could the heating of the suspended matter up to 550°C, modify the surface characteristics of the inorganic compounds ? (2) is coprecipitation especially with iron and manganese hydroxydes, an important process of mercury removal in the Scheldt ?

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to the Belgian Ministry for Science Policy for the financial support of their research.

They thank particularly the Management Team of the Model of the North Sea for providing ship time on the R/V Mechelen as well as technical assistance.

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