

C.M. 1980/E:37

Determinations of mercury in various compartments
of a coastal marine ecosystem

G. DECADT, M. BOGAERT, L. GOEYENS and W. BAEYENS

Laboratorium voor Analytische Scheikunde
Vrije Universiteit Brussel, Belgium

Determinations of mercury in various compartments
of a coastal marine ecosystem

G. DECAET, M. BOGAERT, L. GOEYENS and W. BAEYENS

Laboratorium voor Analytische Scheikunde
Vrije Universiteit Brussel, Belgium

Abstract

Accurate determinations of mercury in the different compartments of the ecosystem are a basic requirement for the study of its circulation. Sampling and analyzing techniques have been examined for the watercolumn, analyzing techniques for the sediments and the biological compartment. Two seawater sampling techniques (Niskin bottle and peristaltic pump) are compared; they give statistically no different results. For the preconcentration of dissolved mercury a self-synthesized resin seems to satisfy very well. In three different sediment samples mercury has been assessed after total, strong and weak attacks. The most reproducible results are obtained with HF/HNO₃ (total attack) and HNO₃/KMnO₄ (strong attack). Several mineralisation-digestion techniques for the analysis of mercury in plants have been tested. HF/HNO₃, KMnO₄/H₂SO₄/HNO₃ and H₂SO₄/HNO₃/V₂O₅, KMnO₄ provided the best results.

The spatial patterns of total and particulate mercury in the Belgian coastal zone confirm the earlier observed concentration gradients. In addition the adsorption capacity studies on particulate matter of the Scheldt estuary suggest that for mercury the particulate, solid phase is more important than the dissolved phase.

Introduction

The first step towards a better understanding and eventual modelisation of the mercury circulation in the Southern Bight of the North Sea requires the knowledge of its distribution among the different compartments of the ecosystem and its spatial-temporal fluctuations in each of these compartments. The distribution of mercury among the various compartments of the North Sea

and Scheldt ecosystems has been described in a previous paper (Baeyens et al., 1979a). For the study of spatial-temporal patterns, we focused our attention on the watercolumn, owing to the dynamical features of this system. But from an analytical point of view, the watercolumn is also the compartment where the risks for contamination or losses are greatest and the detection limit is lowest. Therefore special attention was paid to storage and measuring methods — different procedures for the determination of total and particulate mercury in the watercolumn have been compared (Baeyens et al., 1979b) — but other analytical aspects remained untouched.

This paper deals with some of these untouched analytical problems related to the watercolumn :

- to which extent are the results affected by the applied sampling procedure;
- which is the ratio of dissolved : particulate mercury

and with mercury determinations in the sediments and living matter. Concerning the sediments, one of the major problems is the interpretation of the results. For example, total, strong and moderate attacks of the sample provide different results. These are not necessarily correlated to environmental factors such as the anthropogenic fraction, bioavailability, ... Concerning the biological compartment, we investigated the possibilities for including plants and seabirds. Therefore reliable measuring methods have been developed.

This paper also includes some results of the second phase of our program, where we intend to study the dynamical aspects of the mercury circulation. In this regard, the interaction between dissolved mercury and particulate suspended matter is one of the most important processes. Thereat adsorption capacity and adsorption rate studies will bring more insight.

Sampling methodology for seawater

During each consecutive treatment phase — sampling, storage and analysis — it is possible to perturb the mercury concentration in the sample. Such a perturbation is usually not due to the analytical techniques, but is in the methods used to obtain a representative sample which is free from errors, introduced during sampling and storage (Paulsen et al., 1974).

Until now, the practice was to take a sample by means of a Niskin bottle at a depth of 5 m. To verify if sampling with Niskin bottles could be a source of contamination, we made a comparison with samples taken by a sampling system devised by Gillain (Gillain *et al.*, 1979). Figure 1 shows a schematic representation of this sampling device. The principle is to collect continuously subsamples (0.5 l/min) from a much larger flow (5 l/min), screened from atmospheric pollution.

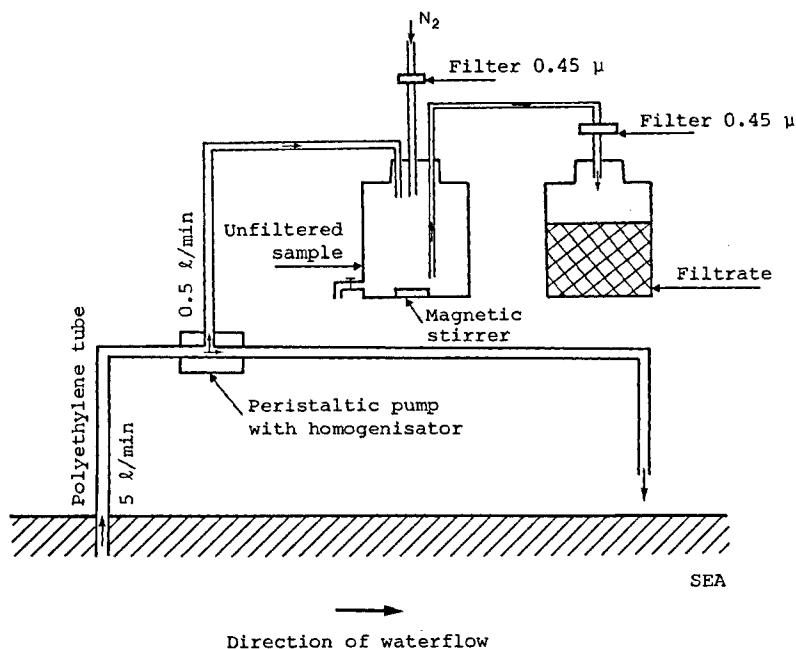


fig. 1.

Sampling system devised by Gillain (Gillain *et al.*, 1979)

In table 1 we compare the results of total as well as particulate mercury obtained with both sampling techniques. The samples were collected during the cruise of October 1979 in our Belgian coastal zone. If the sampling technique has no effect on the results, the mean difference between the two data sets (on the one hand obtained with the Niskin bottle; on the

Table 1

Comparison sampling Niskin bottle—peristaltic pump

Cruise October 1979
 Storage in polyethylene bottles at - 20 °C
 (Acidification to pH = 1)

| Identification | Niskin bottle | | Peristaltic pump | |
|----------------|------------------|------------------|------------------|------------------|
| | Hg total µg/l | Hg part. µg/l | Hg total µg/l | Hg part. µg/l |
| 11 | 0.199 - 0.200 | 0.014 | 0.203 - 0.208 | 0.010 |
| 22 | 0.057 | 0.007 | 0.036 - 0.038 | 0.009 |
| 13 | 0.164 - 0.178 | 0.102 | 0.119 - 0.123 | - |
| 33 | 0.121 | 0.011 | 0.102 - 0.106 | 0.014 |
| 24 | 0.137 - 0.150 | 0.057 | 0.152 - 0.158 | 0.072 |
| 44 | 0.077 | 0.015 | 0.084 - 0.094 | 0.010 |
| 15 | 0.063 - 0.065 | 0.030 | 0.065 - 0.073 | 0.045 |
| 35 | 0.067 | 0.009 | 0.075 - 0.076 | 0.013 |

Paired T-test hypothesis :

No systematic greater or lower values

- 1) Hg_{total} : $t_{obs} = 0.65$; $t_{0.975} = 2.365$
 $t_{obs} < t_{0.975}$.
- 2) Hg_{part.} : $t_{obs} = 1.44$; $t_{0.975} = 2.447$
 $t_{obs} < t_{0.975}$.

⇒ hypothesis acceptable at the 0.05 level.

other hand with the peristaltic pump) has to be zero. This hypothesis is tested by means of the paired T-test. The t-values for total as well as particulate mercury were lower than the theoretical values at the 0.05 level. This means that the results of total as well as particulate mercury obtained with a Niskin bottle give statistically no systematic greater or lower values than those obtained with a peristaltic pump. However, for other metals such as Zn, Pb, Cu, ... sampling with a peristaltic pump seemed to cause less contamination (Gillain et al., 1979).

The determination of dissolved mercury in seawater

The concentration of dissolved mercury in seawater is usually very low, often close to the detection limit of the commercially available instruments (Minagawa *et al.*, 1980). After modification of the single-beam standard apparatus type MAS-50 into a double-beam, we are now able to determine concentrations of 5 ng Hg/l with a 5% accuracy. In order to value our method, we participated in an intercalibration exercise of mercury in seawater, organized by Olafsson (ICES, 1979). The main purpose of this intercalibration was to find out which laboratories were able to measure natural mercury concentrations in seawater and to follow the concentration changes due to anthropogenic inputs. Therefore we investigated

- with which precision these low levels can be measured ;
- which is the recovery capacity of added quantities of mercury.

Table 2

Intercalibration : determination of mercury in seawater
Results of laboratories, reporting less than 10 ng Hg/l in seawater
(ICES Sub-Group on Contaminant Levels in Seawater)

| Lab n° | Sea-water ng/l | Sea-water + spike I | | Sea-water + spike II | |
|--------|-------------------|---------------------|----------|----------------------|---------|
| | | ng/l | % rec. | ng/l | % rec. |
| 1 | 5.3 ± 0.8 | 21 ± 0 | 102 | 108 ± 4 | 72 |
| 4 | 7.2 ± 1.5 | 20.7 ± 0.6 | 87 | 133 ± 1.5 | 88 |
| 11 | 2.9 ± 0.7 | 17.9 ± 3.3 | 97 | 146 ± 7 | 102 |
| 12 | 7.1 ± 1.9 | 26.5 ± 2.5 | 126 | 110 ± 5 | 72 |
| 18 | 2.2 ± 0 | 17.5 ± 0.6 | 100 | 130 ± 2 | 89 |
| 20 | 2.4 ± 0.4 | 17.2 ± 2.9 | 96 | 145 ± 5 | 100 |
| 24 | 2.5 ± 0.4 | 18.1 ± 0.8 | 102 | 143 ± 4 | 98 |
| 26 | 3 ± 0 | 17.5 ± 1.9 | 94 | 153 ± 11 | 105 |
| 27 | 7.2 ± 2.5 | 25.3 ± 1.5 | 118 | 181 ± 19 | 121 |
| 28 | 7.5 ± 0.9 | 25.2 ± 3.2 | 115 | 137 ± 11 | 91 |
| 29 | 2.9 ± 1.1 | 16.9 ± 1.6 | 91 | 141 ± 7 | 96 |
| 30 | 2.4 ± 0.3 | 19.6 ± 1.0 | 112 | 143 ± 3 | 98 |
| 32 | 3.8 ± 0.5 | 19.0 ± 0.5 | 98 | 138 ± 8 | 94 |
| 34 | 2.1 ± 0.2 | 19.4 ± 0.9 | 112 | 150 ± 3 | 104 |
| 35 | 3.9 ± 0.4 | 24.5 ± 0.9 | 134 | 176 ± 5 | 121 |
| 36 | 8.2 ± 1.3 | 26.2 ± 1.2 | 117 | 164 ± 8 | 109 |
| N : 16 | 4.4 ± 2.3 | 20.8 ± 3.5 | 106 ± 13 | 144 ± 20 | 98 ± 14 |

In table 2 our results correspond with Lab n° 1. From these results we deduce that :

- the precision of our method for the measurement of very low mercury levels is very good (compared with the mean value of 16 laboratories, which give concentrations below 10 ng/l) ;
- the recovery of the added quantities of mercury is relatively good.

Preconcentration of dissolved mercury

In spite of the good accuracy we can achieve with our apparatus, it is still very difficult to measure fluctuations of the mercury concentration in the dissolved phase. Furthermore the efficiency of most storage procedures used for mercury determinations is not subject to an unanimous judgement (Topping *et al.*, 1972 ; Fitzgerald, 1974 ; Feldman, 1974 ; Carr *et al.*, 1978 ; Baeyens *et al.*, 1979b). In order to avoid these alterations one could use concentration methods such as extraction (Chester *et al.*, 1973 ; Gardner *et al.*, 1974), amalgamation (Carr *et al.* 1972 ; Olafsson, 1974 ; Baker, 1977 ; Fitzgerald *et al.*, 1979) or resins (Minagawa *et al.*, 1980). However, amalgamation seems to be a technique which is rather laborious to use on board a ship, extraction rather unreliable. A more suitable concentration technique to use on board a ship is probably fixation on a resin. The chelating resin synthesized and tested in our laboratory is a styrene-divinylbenzene copolymer containing sulfonamide groups. The eluting reagent is cysteine hydrochloride. Preliminary results suggest that : (1) the exchange capacity is high ($\pm 10^{-4}$ equivalents Hg/g resin) (2) the retention of Hg(II) and Hg(II)- complexes is complete (3) the elution of fixed mercury is complete (4) the flow rate is very high (± 20 ml/min) which makes it possible to obtain a high concentration rendement. We intend now to test this preconcentration method during one of the next surveys.

Total and particulate mercury concentrations in the Belgian coastal zone

Table 3 shows total and particulate mercury concentrations observed during the cruises of January and October 1979. Figures 2, 3, 4 and 5 represent graphically the spatial distribution. These figures show the same characteristics as those observed in 1978 (Baeyens *et al.*, 1979b), for total as well as for particulate mercury :

- a zone with relatively high concentrations, situated near the Scheldt estuary ;
- a progressive transfer to an open-sea zone where concentrations become comparable with those of relatively unpolluted seawater.

Table 3

Total and particulate mercury concentrations in the Belgian coastal zone
(January and October 1979)

| Identification | January 1979 | | October 1979 | |
|----------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| | Hg tot. ($\mu\text{g}/\text{L}$) | Hg part. ($\mu\text{g}/\text{L}$) | Hg tot. ($\mu\text{g}/\text{L}$) | Hg part. ($\mu\text{g}/\text{L}$) |
| 11 | 0.051 | 0.040 | 0.197 | 0.014 |
| 21 | 0.051 | 0.050 | 0.040 | 0.009 |
| 31 | 0.017 | 0.009 | 0.023 | 0.012 |
| 41 | 0.050 | 0.054 | 0.025 | 0.010 |
| 12 | 0.056 | 0.045 | 0.108 | 0.015 |
| 22 | 0.068 | 0.035 | 0.057 | 0.015 |
| 32 | 0.062 | 0.040 | 0.065 | 0.010 |
| 42 | 0.073 | 0.052 | 0.082 | 0.003 |
| 13 | 0.162 | 0.120 | 0.171 | 0.102 |
| 23 | 0.107 | 0.107 | 0.086 | 0.087 |
| 33 | 0.056 | 0.035 | 0.121 | 0.007 |
| 43 | 0.025 | 0.015 | 0.034 | 0.011 |
| 14 | 0.787 | 0.570 | 0.363 | 0.284 |
| 24 | 0.239 | 0.250 | 0.144 | 0.115 |
| 34 | 0.037 | 0.030 | 0.030 | 0.010 |
| 44 | 0.059 | 0.040 | 0.077 | 0.015 |
| 15 | 0.125 | 0.108 | 0.064 | 0.029 |
| 25 | 0.150 | 0.133 | 0.090 | 0.045 |
| 35 | 0.076 | 0.058 | 0.067 | 0.009 |
| 45 | - | - | 0.047 | 0.010 |

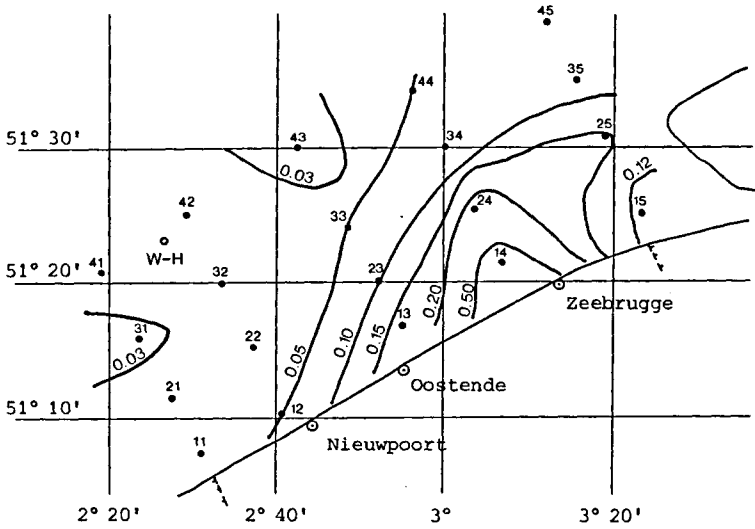


fig. 2.

Spatial distribution of total mercury ($\mu\text{g}/\text{l}$)
January 1979

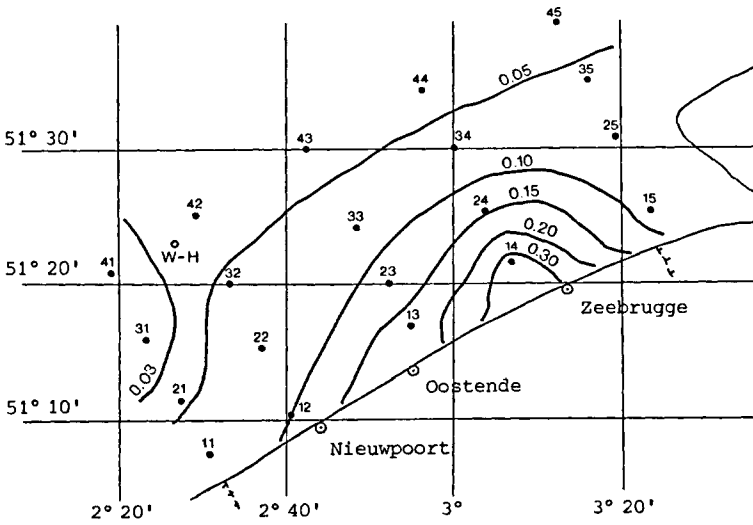


fig. 3.

Spatial distribution of total mercury ($\mu\text{g}/\text{l}$)
October 1979

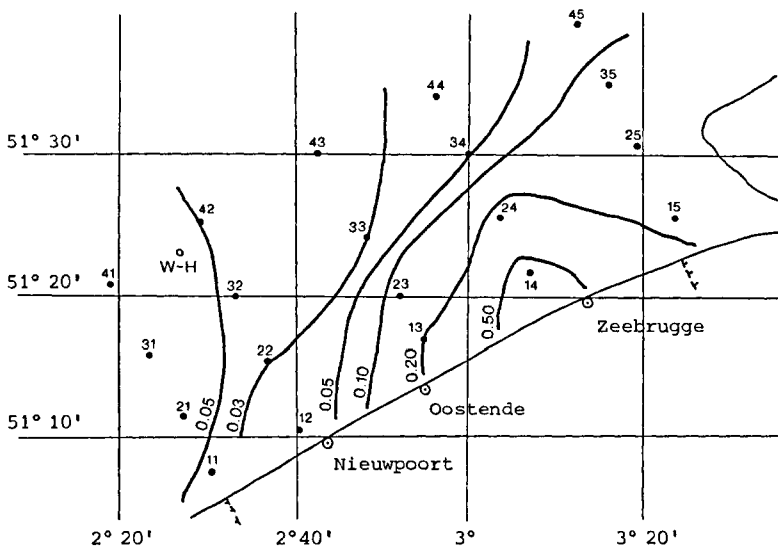


fig. 4.

Spatial distribution of particulate mercury ($\mu\text{g}/\text{l}$)
January 1979

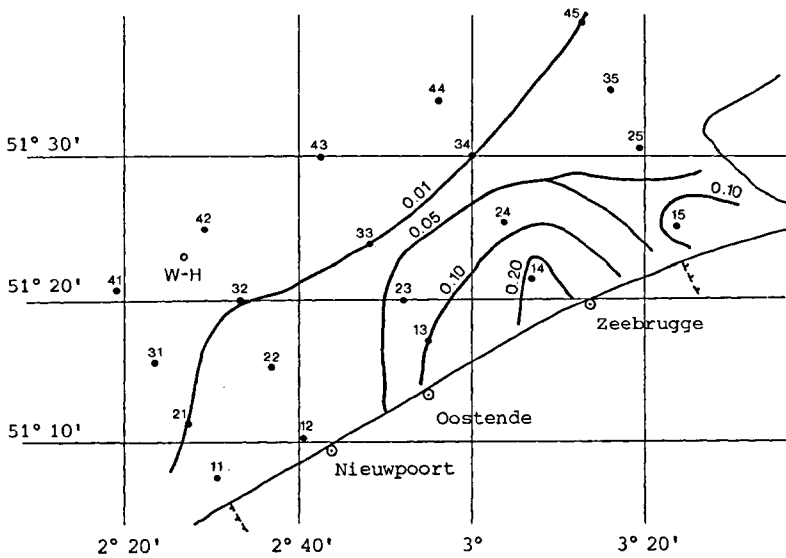


fig. 5.

Spatial distribution of particulate mercury ($\mu\text{g}/\text{l}$)
October 1979

Concerning the particulate mercury concentrations, we notice that they are expressed in $\mu\text{g}/\ell$. As previous studies (Lockwood et al., 1973 ; Reimers et al., 1974 ; Baeyens, 1977) show, there exists a strong interaction between mercury and suspended matter. As a consequence, we find normally a higher mercury content (expressed in $\mu\text{g}/\ell$) at sample points with high turbidity. This does not mean that there is more mercury adsorbed per weight-unit of suspended matter. From the results obtained in 1978, we could derive a relation between the particulate mercury concentration and the turbidity. This curve (Figure 6) shows two discrete parts. More mercury is adsorbed per weight-unit of suspended matter at low than at high turbidity. The points with low turbidity are open-sea points while these with high turbidity are close to the mouth of the Scheldt estuary. Suspended

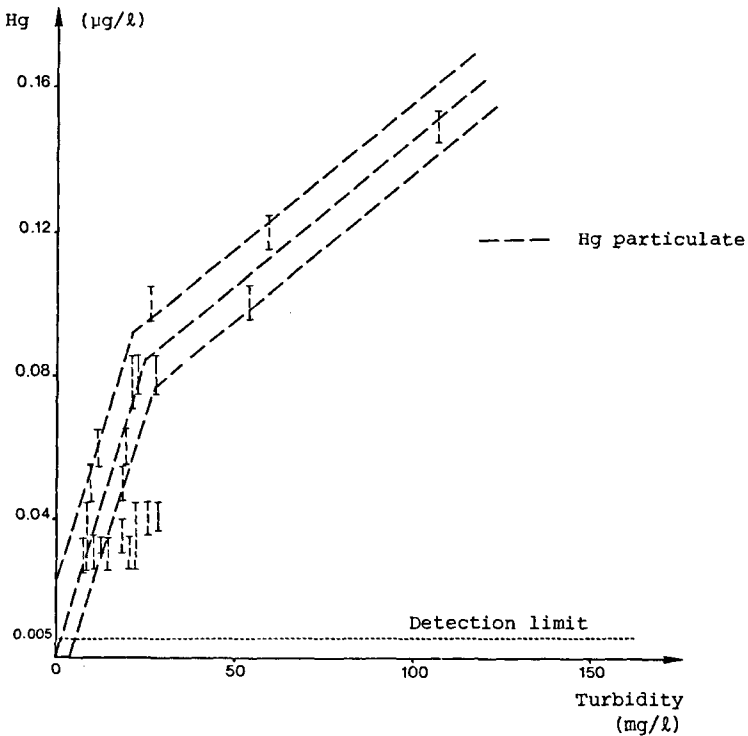


fig. 6.

Particulate mercury content versus turbidity

matter originating from the Scheldt estuary has probably a different chemical composition and/or granulometry than the suspended matter from marine origin and thus a different adsorption behaviour. To investigate this, we intend to carry out adsorption experiments on suspended matter from estuarine and marine origin.

Adsorption experiments

Until now, only adsorption experiments are carried out on suspended matter from the Scheldt estuary (Baeyens, 1977 ; Decadt, 1977). The results, obtained by adsorption capacity experiments, are represented graphically in Figure 7. Up to a concentration of 2 ppm, practically all the mercury is adsorbed on the suspended matter, in fresh as well as salt water

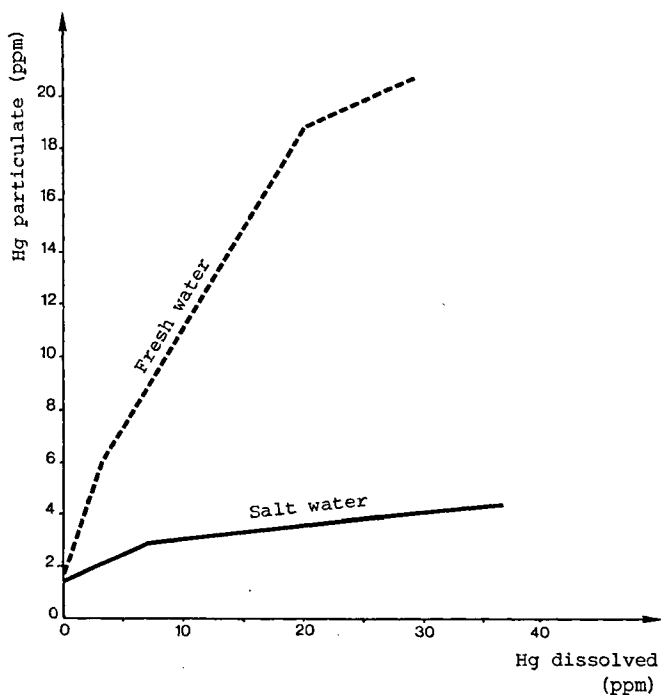


fig. 7.
Adsorption capacity of suspended matter
from the Scheldt estuary

conditions. As natural mercury concentrations in the estuary are a few orders of magnitude lower than the adsorption capacity of the suspended matter, this suggests that on a long term the particulate phase will be enriched in mercury which will be in turn transported to areas where sedimentation occurs. Consequently, monitoring of sediments could give important information about the influence of mercury from anthropogenic origin on the aquatic environment.

Determination of mercury in sediments

To determine the anthropogenic fraction in the sediments, one can use two procedures : (1) a comparison between the mercury concentrations in recent sediments and in sediments anterior to industrialization or (2) analyzing sediment cores which show a clear age profile versus depth. It is clear that this approach must be completed with a study of the chemical and mineralogical composition of the samples.

The standardization of the analysis of heavy metals in sediments deals subsequently with the sampling procedure, the conservation and preparation of the sample prior to analysis, the chemical analysis and finally the presentation of the analytical results. The measuring technique was tested in an intercalibration exercise including three types of samples : a river sediment with high metal concentrations (MS1), an estuarine muddy sediment (MS2) and an estuarine sandy sediment (MS3). Our results are summarized in table 4.

Table 4
Determination of mercury in sediment samples

| | Total attack | Strong attack | | Weak attack |
|------|-----------------------------------|---|---|----------------------------|
| | HF / HNO ₃ (Hg-ppm) | HNO ₃ /KMnO ₄ (Hg-ppm) | H ₂ O ₂ /HNO ₃ /H ₂ SO ₄ (Hg-ppm) | HAc-extraction (Hg-ppm) |
| MS 1 | 1.102 - 1.142 | 0.996 - 1.016 | 1.002 - 1.353 | Not detectable |
| MS 2 | 1.898 | 1.825 | 1.644 - 1.666 | 0.069 - 0.069 |
| MS 3 | 0.042 - 0.058 | 0.016 - 0.016 | 0.005 - 0.005 | Not detectable |

The variation coefficients, calculated on the ensemble of results obtained by the different laboratories, show that : the spread is small for the total attack and the $\text{HNO}_3/\text{KMnO}_4$ strong attack ; the spread is much greater in the case of a $\text{H}_2\text{O}_2/\text{HNO}_3/\text{H}_2\text{SO}_4$ strong attack ; and the spread is unacceptable with a HAC-extraction. Since most chemists do not like the use of HF, and since the results obtained with a $\text{HNO}_3/\text{KMnO}_4$ attack approach very good those obtained with HF/ HNO_3 , the total mercury content in sediments can be estimated quite well with a $\text{HNO}_3/\text{KMnO}_4$ digestion. However a study of the correlation between the results obtained with a weak or moderate attack and the bioavailable fraction seems not yet feasible.

Determination of mercury in biological materials

The analyzing method of mercury in biological material (entirely organic matter) differs somewhat from these used for sediments (mainly inorganic matter) due to their different composition. The basic principle in this case is to oxidize as complete as possible the organic matrix. A detailed study has been carried out on different materials such as milk-powder (MP), two aquatic plants (LM and PR) and one terrestrial plant (OE) to test our methods. The main results of this study are summarized in table 5.

Table 5

Determination of mercury in biological materials

| MINERALISATION | HF/ HNO_3 (teflon bomb) | $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{V}_2\text{O}_5$ (under reflux) | |
|----------------|--|--|------------------------|
| | | KMnO_4 | H_2O_2 |
| Digestion | $\text{KMnO}_4/\text{H}_2\text{SO}_4/\text{HNO}_3$ | KMnO_4 | H_2O_2 |
| Identification | Mercury (ppm) | Mercury (ppm) | Mercury (ppm) |
| OE-62-169 | 0.19 | 0.21 | 0.11 |
| MP-63-161 | 0.005 | < 0.01 | 0.002 |
| LM-60-170 | 0.24 | 0.25 | 0.25 |
| PR-61-170 | - | 0.13 | 0.12 |
| PR-61-168 | 0.12 | - | 0.12 |

The three mineralisation-digestion methods gave all reliable results except in one case (OE). Moreover, it was proved that the biological matrix (after mineralisation and digestion) did not interfere with the measurements and that both organic and inorganic mercury compounds (as far as they were extracted from the biological material) were oxidized to ionic mercury. The same mineralisation-digestion methods were also evaluated for the determination of mercury in muscle tissues of seabirds. All methods provided similar results, but the results obtained with the H_2O_2 -method showed a greater spread.

Conclusion

The development or adaptation of sampling and analyzing techniques will provide us more reliable data of mercury in most of the compartments of the marine ecosystem. An important compartment which has not been considered yet is the atmosphere. However, a method for measuring mercury in the gasphase is available and will be published very soon. In the future we will also try (1) to distinguish between inorganic (free or chelated) and organic mercury compounds and (2) to assess the interaction kinetics between the most important mercury species and natural suspended matter.

References

- BAEYENS, W. (1977). *Bijdrage tot de studie van adsorptiemechanismen van kwik in een estuarium. Ontwikkeling van een bidimensionaal getijafhankelijk dispersiemodel*, Doctoraatsthesis, Vrije Universiteit Brussel.
- BAEYENS, W., DECADT, G. and ELSKENS, I. (1979a). A study of the distribution of mercury in the various compartments of the North Sea and Scheldt estuary ecosystems. *Oceanologica Acta*, vol. 2, n° 4, 447-457.
- BAEYENS, W., DECADT, G. and ELSKENS, I. (1979b). Determination of dissolved, particulate and total mercury in the watercolumn of the Southern Bight of the North Sea, with adapted analytical procedures. International Council for the Exploration of the Sea, CM 1979/E : 61.
- BAKER, C.W. (1977). Mercury in surface waters of seas around the United Kingdom. *Nature* (London), 270, 230-232.
- CARR, R.A., HOOVER, J.B. and WILKNISS, P.W. (1972). Cold vapour atomic absorption for Hg in the Greenland Sea. *Deep Sea Research*, 19, 747-752.

- CARR, R.A. and WILKNISS, P.E. (1978). Mercury short-term storage of natural waters. *Envir. Sc. Techn.*, 7, 62-63.
- CHESTER, R., GARDNER, F., RILEY, J.P. and STONER, J. (1973). Mercury in some surface waters of the world ocean. *Mar. Pollut. Bull.*, 4, 28-29.
- DECADT, G. (1977). *Studie van de adsorptiefenomenen van kwik met gesuspendeerd materiaal uit het Schelde-estuarium*, Licentiaatsthesis, Vrije Universiteit Brussel.
- FELDMAN, C. (1974). Preservation of dilute mercury solutions. *Anal. Chem.*, 46, 1, 98-102.
- FITZGERALD, W.F., LYONS, W.B. and HUNT, C.D. (1974). Cold trap preconcentration method for the determination of mercury in sea water and other natural materials. *Anal. Chem.*, 46, 13, 1882-1885.
- FITZGERALD, W.F. and GILL, G.A. (1979). Subnanogram determination of mercury by two-stage gold amalgamation and gas phase detection applied to atmospheric analysis. *Anal. Chem.*, 51, 1714-1720.
- GARDNER, D. and RILEY, J.P. (1974). Mercury in the Atlantic around Iceland. *Journal du Conseil, Conseil International pour l'Exploration de la Mer*, 35 (2), 202-204.
- GILLAIN, G., DUYSKAERTS, G. and DISTECHE, A. (1979). The determination of trace metals in seawater and suspended matter by classical anodic stripping (Zn, Cd, Pb, Cu) or differential pulse anodic stripping voltammetry with a hanging mercury drop electrode (Zn, Cd, Pb, Cu, Sb, Bi) - An approach to speciation, in *Actions de Recherches Concertées, Rapport des Journées d'Etudes, Programmation de la Politique Scientifique* (Editor), Bruxelles, 123-132.
- LOCKWOOD, R.A. and CHEN, K.Y. (1973). Adsorption of Hg(II) by hydrous manganese oxides. *Envir. Sc. Techn.*, 7, 11, 1028-1034.
- MINAGAWA, K., TAKIZAWA, Y. and KIFUNE, I. (1980). Determination of very low levels of inorganic and organic mercury in natural waters by cold-vapour atomic absorption spectrometry after preconcentration on a chelating resin. *Anal. Chim. Acta*, 115, 103-110.
- OLAFFSON, J. (1974). Determination of nanogram quantities of mercury in seawater. *Anal. Chim. Acta*, 68, 207-211.
- OLAFFSON, J. (1980). Report on the ICES intercalibration of mercury in seawater for the Joint Monitoring Group of the Oslo and Paris Commissions, p. 29.
- PAULSEN, K.E., SMITH, E.F. and MARK, H.B. (1975). Considerations in the design of *in situ* sampling techniques for trace elements in seawater. *Advan. Chem. Ser.*, 147, 22-29.
- REIMERS, R.S. and KRENKEL, P.A. (1974). Kinetics of mercury adsorption and desorption in sediments. *J. Wat. Poll. Contr. Fed.*, 46, 352-365.
- TOPPING, G. and PIRIE, J.M. (1972). Determination of inorganic mercury in natural waters. *Anal. Chim. Acta*, 62, 200-203.