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in the watercolumn of the Southern Bight of the North Sea,
with adapted analytical procedures

W. BAEYENS , G. DECADT and I. ELSKENS



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Introduction

Mercury is in the marine environment a constituent which asks for special attention because of its high toxicity. In the international Commissions - especially those of the Oslo, London and Paris Conventions - for the protection of the marine environment and for the reduction of the pollution, it was decided to give the first priority to the problems caused by mercury pollution. The final aim, namely the establishment of discharging norms, however, can only be realized if the coherence between the monitoring results of various origin is considerably improved. This implies that the different methodologies of sampling, storage and analysis, are examined and compared with the utmost attention. It is not very probable that a chain of manipulations, where different instruments and working methods are used, would give the same final result.

Intercalibration programs allow to compare statistically the accuracy of methods and instruments under the condition that the mercury component(s) and compartment(s) of the eco-system to be analysed, were unambiguously defined.

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Previous examinations (Baeyens et al., 1978 - Wollast, internal report, personal communication 1977 - Iparcom, 1977) lead to the conclusion that *dissolved* mercury concentrations in the marine environment are mostly very low and approach the sensibility of the analytical instrument. The reason of these low concentrations is a direct consequence of the adsorption kinetics and the large adsorption capacity of particulate suspended matter for several mercury components (Baeyens, 1977 - Decadt, personal communication 1977). In this view the determination of dissolved mercury requires a certain number of treatments - to avoid for example the adsorption on the wall of the container or loss to the atmosphere - from the moment of sampling to the final analysis, so that the result obtained would still be representative for the real *in situ* value.

If the determination of dissolved mercury caused problems in connection with sampling, filtration and storage aspects, the direct determination of the *total mercury content* in the water column is even more difficult because the particulate mercury fraction is linked to, possibly incorporated in, the suspended solid matters. Depending on the digestion technic used, the total quantity of mercury present can be released or not and possibly even a part of the volatile components can be lost.

The applied digestion method plays also a very important part in analysing mercury in the sediments or centrifuged suspended matter. In order to release metals, not only a series of acid media ranging from ammonia-acetate till mixtures of concentrated hydrogen fluoride, nitric acid, perchloric acid (CNEXO, 1978) are available, but also a choice of the oxydator, temperature and the digestion time will influence the result.

This study concerns the establishment of a "tentative" relationship between the obtained results for total and particulate mercury in the water column and the applied analytical procedure. It is tried to find an explanation of the spatial mercury distribution in the water column of our coastal zone for some of the 1978 cruises. Finally it is examined whether or not a correlation could be derived from the observed values of mercury and some interacting parameters such as turbidity.

1.- Sampling problems

1.1.- DETERMINATION OF TOTAL MERCURY CONCENTRATION

During each consecutive treatment phase - sampling, storage and analysis - it is potentially possible to perturb the mercury concentration in the sample. This system can be improved considerably by excluding the storage phase and carrying out the analysis on board of the ship immediately after sampling. Since, because of practical reasons, this is very difficult to realize at present time, the finalizing of such a storage procedure becomes one of the main requirements in order to maintain the "original" distribution of the mercury in solution. Adsorption or desorption on the wall of the container, the loss to the atmosphere as a consequence of the volatility of various mercury compounds and the chemical transformations to forms of mercury with a larger adsorption - desorption capacity or volatility, are factors that can influence the reliability of the method. Several storage technics, in combination or not, can be used, such as : acidification, oxydation, storage at low temperature (in refrigerator or freezer), preconcentration, complexing, ...

For the cruises of the actual routine program organized in the North Sea by the "Unité de gestion du Modèle Mer et Estuaire, Belgium", it appears difficult to apply the extremely appropriate storage technics in use for the Scheldt-cruises, because of the very low levels to be determined, the heterogeneity of the samples and on the other hand, longer storage time needed. Different alternatives were available, but in view of a later speciation in the laboratory itself (determination of dissolved, particulate and total mercury in one and the same sample), a freezing method at -20°C was chosen, in analogy with the method used by Duyckaerts et al. (1977) for other heavy metals. The polyethylenecontainer was pretreated with dilute acid and was several times rinsed with deionized water. The results of the first cruises (Dec.77 - Feb.78) in respect of the examination of mercury were all situated at the detection limit (tables 1 and 2). After repeated treatment of the container with an acidified solution of $\text{pH} = 1$ or an unique treatment with a permanganate - acid solution¹, measurable quantities were released as a consequence of a

1. both mercury free solutions.

Table 1
Cruise December 1977

<p>a) <u>Working method</u></p> <ul style="list-style-type: none"> - Treatment prior to cleaning polyethylenebottles : Rinse with deionized water - Precautions to assure the stability of the solution : Freeze at -40°C - Treatment of the polyethylenebottles after sampling and prior to measurement : (1°) Thawing of samples → measurement; (2°) - add 20 ml/l KMnO_4 (2%) in H_2SO_4 (50%); - leave 24 hours → measurement. - Measuring method : (1°) - $\text{KMnO}_4/\text{HNO}_3/\text{H}_2\text{SO}_4$; (2°) - idem <p>b) <u>Results</u> :</p>		
Identification	Direct measurement $\mu\text{g}/\text{l}$ Hg	20 ml/l KMnO_4 in H_2SO_4 $\mu\text{g}/\text{l}$ Hg
12.03.151277.1200	N.D.	0.43
42.03.151277.1400	N.D.	0.39
32.03.151277.1450	N.D.	0.08
13.03.121277.1055	N.D.	0.46
43.03.121277.1255	N.D.	0.40
33.03.121277.1350	N.D.	0.13
15.03.131377.1115	N.D.	0.29
45.03.131277.1345	N.D.	0.25
35.03.131277.1445	N.D.	0.85
11.03.141277.1045	N.D.	0.51
41.03.141277.1340	N.D.	0.27
31.03.141277.1445	N.D.	0.07

desorption of the metal from the wall. This indicates that a storage method which is completely efficient for certain metals, appears to be insufficient for others. After treatment of the samples in this way, we found for the first cruises 0.3 μg Hg/l (total mercury) as mean concentration for the points located under the influence of the Scheldt plume (fig. 1; points 14, 15, 25 and 35). This value, however, is much too high, since concentrations in the Scheldtmouth itself, probably the main input of heavy metals in our coastal waters, fluctuate between 0.4 and 0.1 μg Hg/l (Baeyens et al., 1978 - Wollast, 1977, personal communication - Iparcom, 1977).

Table 2
Cruise February 1978

a) <u>Working method</u>			
- Treatment prior to cleaning polyethylenebottles : Rinse with deionized water			
- Precautions to assure the stability of the solution : Freeze at -40°C			
- Treatment of the polyethylenebottles after sampling and prior to measurement : (1°) Thawing of samples → measurement; (2°) add HNO ₃ (1 : 2) until pH sample = 1; leave 24 hours → measurement; (3°) measurement of desorption of the wall of the polyethylenebottle.			
- Measuring method : KMnO ₄ /HNO ₃ /H ₂ SO ₄ .			
b) <u>Results :</u>			
Identification	Direct measurement µg/l Hg	pH=1 Hg µg/l	Desorption Hg µg/l
12.03.200278	0.05	0.30	0.16
11.03.200278	N.D.	0.14	0.01
13.03.200278	0.01	0.18	0.13
14.03.240278	0.40	0.56	0.01
15.03.240278	0.01	0.07	0.09
25.03.240278	0.03	0.10	0.01
32.03.210278	N.D.	0.28	N.D.
45.03.240278	N.D.	0.31	0.17
22.03.210278	N.D.	0.09	0.02
35.03.240278	N.D.	0.05	N.D.
21.03.210278	N.D.	0.05	N.D.

Thus after these first cruises it was decided to improve the pre-treatment of the polyethylene bottles on one hand and the storage procedure on the other. Some specific tests showed that a pretreatment of the container with a solution of KMnO₄ (2%) in H₂SO₄ (50%) during 24 hours made the polyethylene bottle completely mercury-free¹. As has been discussed above, a storage procedure can be efficient for one element and totally insufficient for another; furthermore the efficiency of mostly used storage procedure for mercury is not subject to an unanimous judgement. Topping et

¹. excluding a possible influence on aging of the containers.

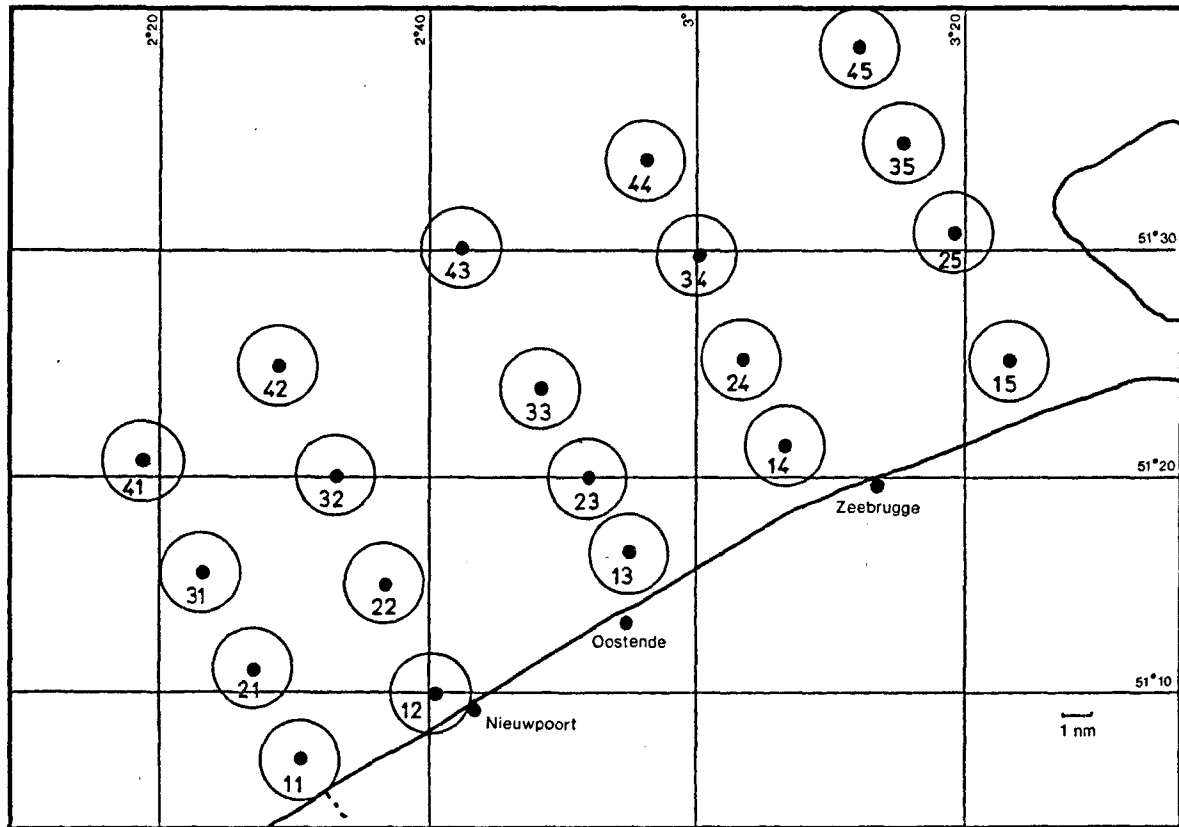


fig. 1.

Map of the Belgian coastal zone

al. (1972) and Carr et al. (1978) assert that adding 20 ml/l of a KMnO_4 (2%)-solution in H_2SO_4 (50%) or the acidification with HNO_3 to pH = 1, stabilized the sample completely, while Feldman (1974) considers this working method to be insufficient. Feldman (1974) and Fitzgerald (1974) came to the conclusion that storage in pyrex- or teflonbottles instead of polyethylene containers, results in a notable improvement.

Finally we opted for a sample storage at -20°C in a polyethylene bottle after acidification to pH = 1 of the samples (determination of total mercury). The cruise of September 1978 was used, however, to compare the storage efficiency of pyrex- and polyethylene bottles. Because mercury concentrations in the North Sea often approach the detection limit, it is impossible to draw a conclusion already now. Supplementary experiments will be carried out for that purpose, with more sophisticated instruments in order to improve the detection limit.

1.2.- SUSPENDED MERCURY

The sample is immediately filtered on board of the vessel through a $0.45\ \mu\text{m}$ poresize Milliporefilter for the determination of the particulate mercury concentration. The filtration system is shown schematically in figure 2. During 8 days the filters were submerged in a 0.01 M DTPA-solution (pH = 6), (Duyckaerts et al., 1977) to minimize the content of heavy metals, and subsequently rinsed several times with double deionized water. Immediately after filtration, the filters are freeze-d at -40°C and stored at -20°C .

2.- Analytical methods

Although these methods must be considered as classical at this time, (Vanderstappen et al., 1975, personal communication), it will be helpful to recall *some aspects* of the procedures, taking into account that each

1. The next step in the improvement will be the use of a continual centrifugal separator, with teflon container (Kocken, Instituut voor Bodemvruchtbaarheid, The Netherlands, 1979, personal communication).

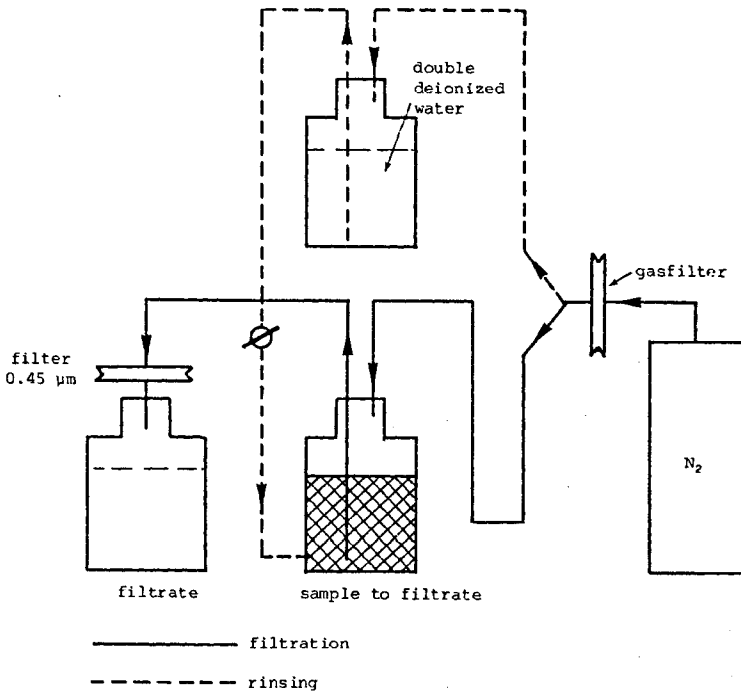


fig. 2.

Scheme of the filtration system

step in the determination is a possible source of misunderstanding in the interpretation of the results.

2.1.- TOTAL MERCURY CONTENT

The method is based on the complete conversion of all mercury components present to Hg(II) , subsequently reduction of this form to Hg(0) and spectrophotometric determination after aeration of the solution. An important part of the mercury components is associated with the particulate matter and exists in the form of metallic or organic mercury, or is complexed with certain organic constituents. It is therefore important to choose an appropriate digestion method for the complete oxydation to Hg(II) .

2.1.1.- $\text{KMnO}_4/\text{HNO}_3/\text{H}_2\text{SO}_4$ - method

Subsequently 5 ml HNO_3 (1:2), 5 ml H_2SO_4 (1:1) and 5 ml KMnO_4 (5 %) is added to 150 ml sample. The digestion carried out lasts 16 hours at 60 °C .

The excess KMnO_4 is reduced with 1 ml hydroxylamine (5 %). The volume in the BOD-bottle is brought to 180 ml . After adding 1 ml NaBH_4 (1 %), measuring with a MAS-50 is carried out.

Blanco : 150 ml double deionized water to which the same quantities of reagents are added.

2.1.2.- $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ - method

5 ml concentrated H_2SO_4 and 3 ml H_2O_2 (30%) are added to 100 ml sample. The sample is heated to 80°C under reflux during 24 hours. After refrigeration to roomtemperature the sample is quantitatively transferred into a BOD-bottle. KMnO_4 is added until a light pink colour appears. This slight excess is reduced with hydroxylamine (5%).

The volume in the BOD-bottle is brought to 180 ml and after addition of 1 ml NaBH_4 (1%) the measurement with the MAS-50 is carried out.

Blanco : 100 ml double deionized water to which the same reagents are added.

2.2.- PARTICULATE MERCURY CONTENT

Subsequently 5 ml concentrated H_2SO_4 and 15 ml KMnO_4 (5%) are added to the filter. The sample is heated to 60°C during 24 hours. The excess of KMnO_4 is reduced with hydroxylamine (5%). The volume in the BOD-bottle is brought to 180 ml. After addition of 1 ml NaBH_4 (1%), the measurement with the MAS-50 is carried out.

Blanco : the same quantities reagents are added to a blanco filter.

3.- Results and discussion

The results of the first cruises in respect of mercury examination were already discussed in paragraph 1.1. Consequently only measurements with *the improved analysis* procedure are here taken into account. The total

Table 3
Cruise September 1978

Identification	polyethylene bottles		pyrex bottles	Turbidity mg/l
	KMnO ₄ - method µg/l	H ₂ O ₂ - method µg/l	KMnO ₄ - method µg/l	
41.03.180978.1141	0.03	-	0.01	21.6
31.03.180978.1245	0.01	N.D.	0.03	7.9
21.03.180978.1340	0.02	N.D.	0.01	6.1
11.03.180978.1430	N.D.	-	N.D.	14.2
12.03.180978.1535	0.01	N.D.	0.02	16.7
22.03.180978.1640	N.D.	0.01	0.03	14
13.03.190978.0845	0.01	0.02	0.02	23.8
23.03.190978.0940	0.10	0.06	0.02	10
33.03.190978.1035	0.07	0.04	N.D.	18
43.03.190978.1200	N.D.	N.D.	N.D.	15.2
42.03.190978.1320	0.05	0.02	N.D.	18
32.03.190978.1425	0.03	N.D.	N.D.	19.8
24.03.200978.1010	0.06	-	0.05	73
34.03.200978.1055	0.02	-	N.D.	21.6
44.03.200978.1150	0.04	-	N.D.	21.2
45.03.200978.1350	0.03	0.02	N.D.	12.6
35.03.200978.1430	0.06	0.04	N.D.	47.6
25.03.200978.1515	0.09	0.06	0.08	127.4
15.03.200978.1620	0.14	0.12	0.14	165
14.03.200978.1805	0.10	0.08	0.13	124.2

and particulate mercury concentrations determined in our coastal zone during several representative cruises (September, October and November 1978) are shown in the tables 3, 4 and 5, while the spatial distribution is represented

Table 4
Cruise October 1978

a) <u>Working method</u>		
- Treatment prior to cleaning bottles : Fill with a soap solution (extran, 50°C); rinse with deionized water; fill with solution of 20 ml/l KMnO ₄ (2%) in H ₂ SO ₄ (50%); leave 24 hours; rinse with deionized water		
- Precautions to assure the stability of the solution : add 20 ml/l HNO ₃ (1 : 2) (pH sample = 1 ± 2); freeze at -40°C.		
- Treatment of the bottles after sampling and prior to measurement : thawing of samples → measurement.		
- Measuring method : KMnO ₄ /HNO ₃ /H ₂ SO ₄		
b) <u>Results</u> :		
Identification	Hg µg/l	Turbidity mg/l
11.03.161078.1120	0.02	40.2
31.03.161078.1320	0.03	22.2
32.03.161078.1600	0.02	14.4
15.03.191078.1140	0.04	45
35.03.191078.1330	0.01	29
41.03.161078.1415	N.D.	17.2
22.03.161078.1645	N.D.	32.2
12.03.161078.1030	0.02	33.4
42.03.161078.1515	N.D.	21.4
25.03.191078.1245	0.07	82
21.03.161078.1225	N.D.	18.4
45.03.191078.1405	0.01	23.6
13.03.201078.0940	0.03	-
43.03.201078.1215	0.02	12.6
24.03.191078.1610	0.02	51.4
34.03.191078.1530	0.02	21.4
23.03.201078.1015	0.02	41.4
14.03.191078.1035	0.12	168
33.03.201078.1035	0.01	-

graphically by the figures 3 to 6. Although an unambiguous determination of the iso-concentration curves is impossible, - given the too limited number of points in the zones where relatively important concentration gradients are distinguished -, the following general characteristics, for the total

Table 5
Cruise November 1978

a) Working method

1) Hg total :

- Treatment prior to cleaning bottles : Fill with a soap solution (extran, 50 °C); rinse with deionized water; fill with solution of 20 ml/l KMnO₄ (2 %) in H₂SO₄ (50 %); leave 24 hours; rinse with deionized water.
- Precautions to assure the stability of the solution : add 20 ml/l HNO₃ (1 : 2) (pH sample = 1 à 2); freeze at - 40 °C .
- Treatment of the bottles after sampling and prior to measurement : thawing of samples → measurement.
- Measuring method : KMnO₄/HNO₃/H₂SO₄ .

2) Hg suspension :

- Treatment prior to cleaning the filters : wash in a 0.01 M DTPA - solution; rinse with tridistilled H₂O .
- Precautions to assure the stability : freeze at - 40 °C .
- Treatment of the filters after sampling and prior to measurement : wait until room temperature is reached; dissolve in 5 ml H₂SO₄ (conc.) + 30 ml H₂O + 15 ml KMnO₄ (5 %); let digest at 60 °C during 16 hours; measurement at total or at an aliquot.

b) Results

Identification	Hg-total µg/l	Hg-suspension µg/l	Turbidity mg/l
11.03.221178.1550	N.D.	0.03	10.8
21.03.221178.1410	0.01	0.04	8.2
31.03.221178.1300	0.02	0.05	8.8
41.03.221178.1140	N.D.	0.03	8.6
12.03.221178.1700	N.D.	0.02	12.6
13.03.241178.0905	0.04	0.10	24.6
23.03.241178.0940	0.03	0.08	20.4
33.03.241178.1040	0.02	0.05	-
43.03.241178.1145	N.D.	0.03	10.6
14.03.231178.1750	0.06	0.12	58.2
24.03.231178.1635	0.04	0.08	27.4
34.03.231178.1610	0.01	0.05	17.6
44.03.231178.1515	0.03	0.06	11
15.03.231178.1015	0.05	0.10	52.8
25.03.231178.1130	0.08	0.15	105.6
35.03.231178.1220	0.04	0.08	22.2
45.03.231178.1335	0.03	0.06	19

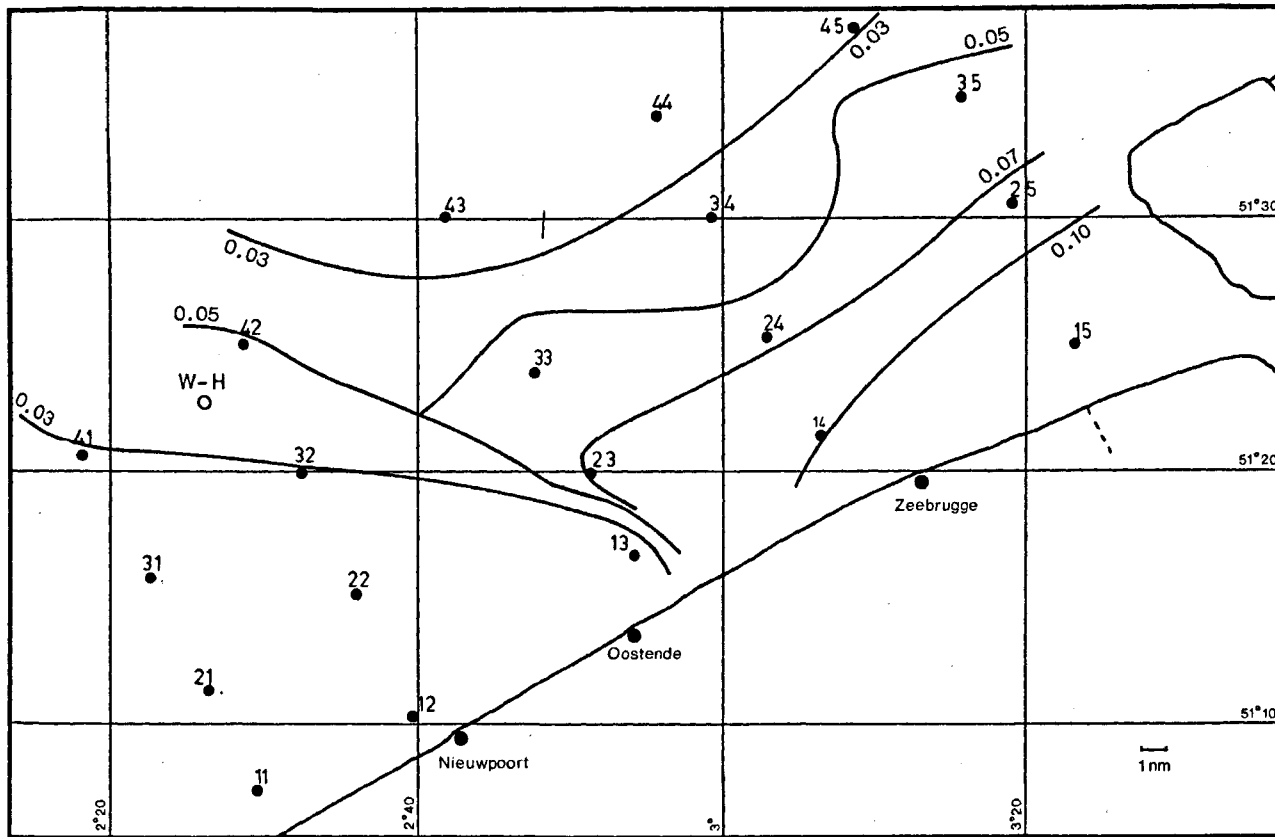


fig. 3.
 Spatial distribution of total mercury ($\mu\text{g Hg/l}$)
 September 1978

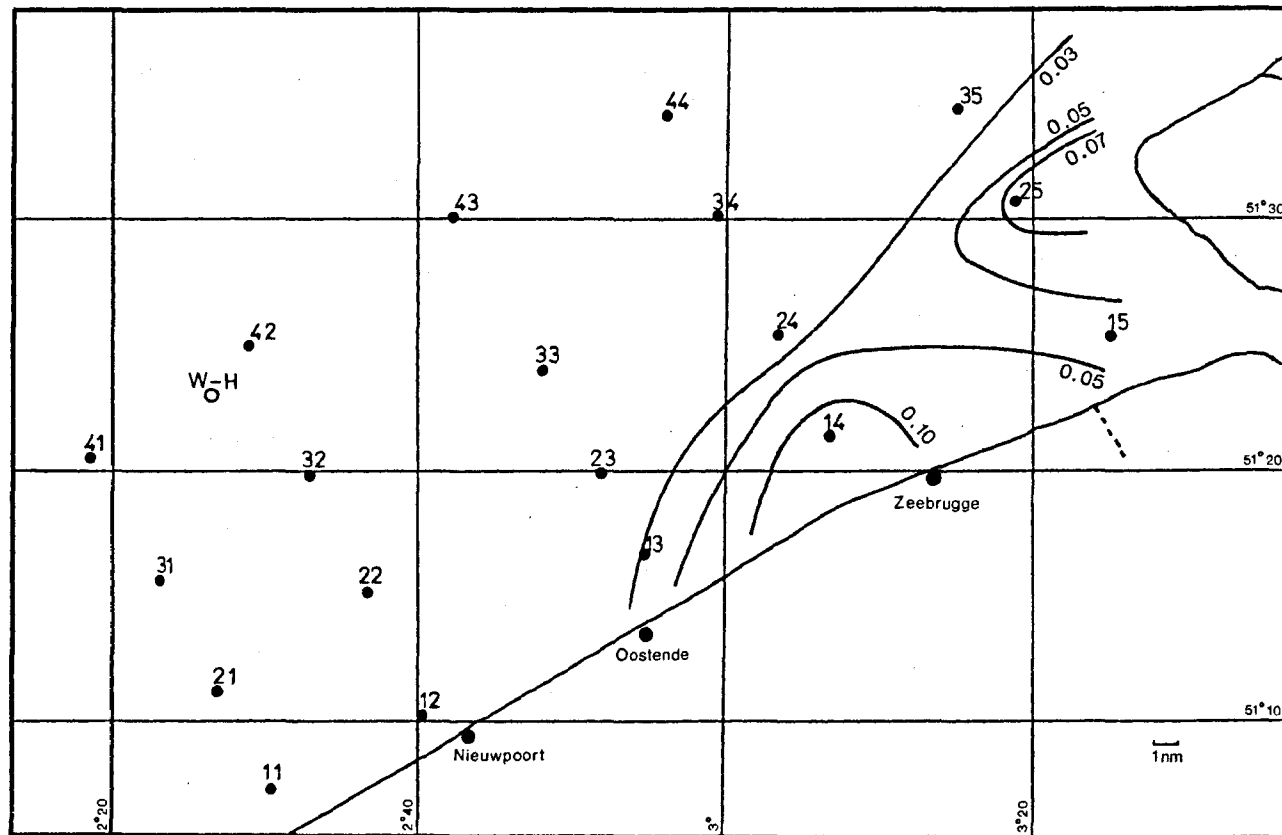


fig. 4.
 Spatial distribution of total mercury ($\mu\text{g Hg/l}$)
 October 1978

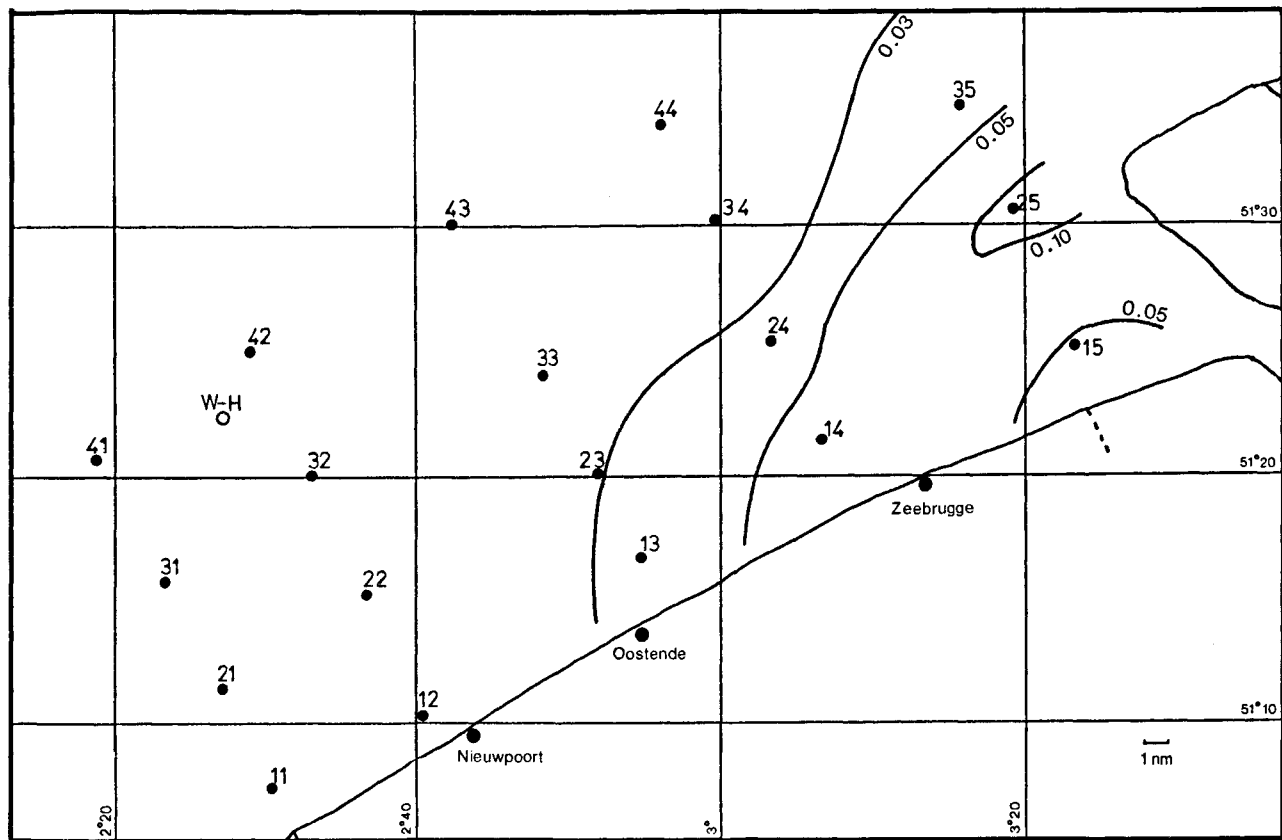


fig. 5.
 Spatial distribution of total mercury ($\mu\text{g Hg/l}$)
 November 1978

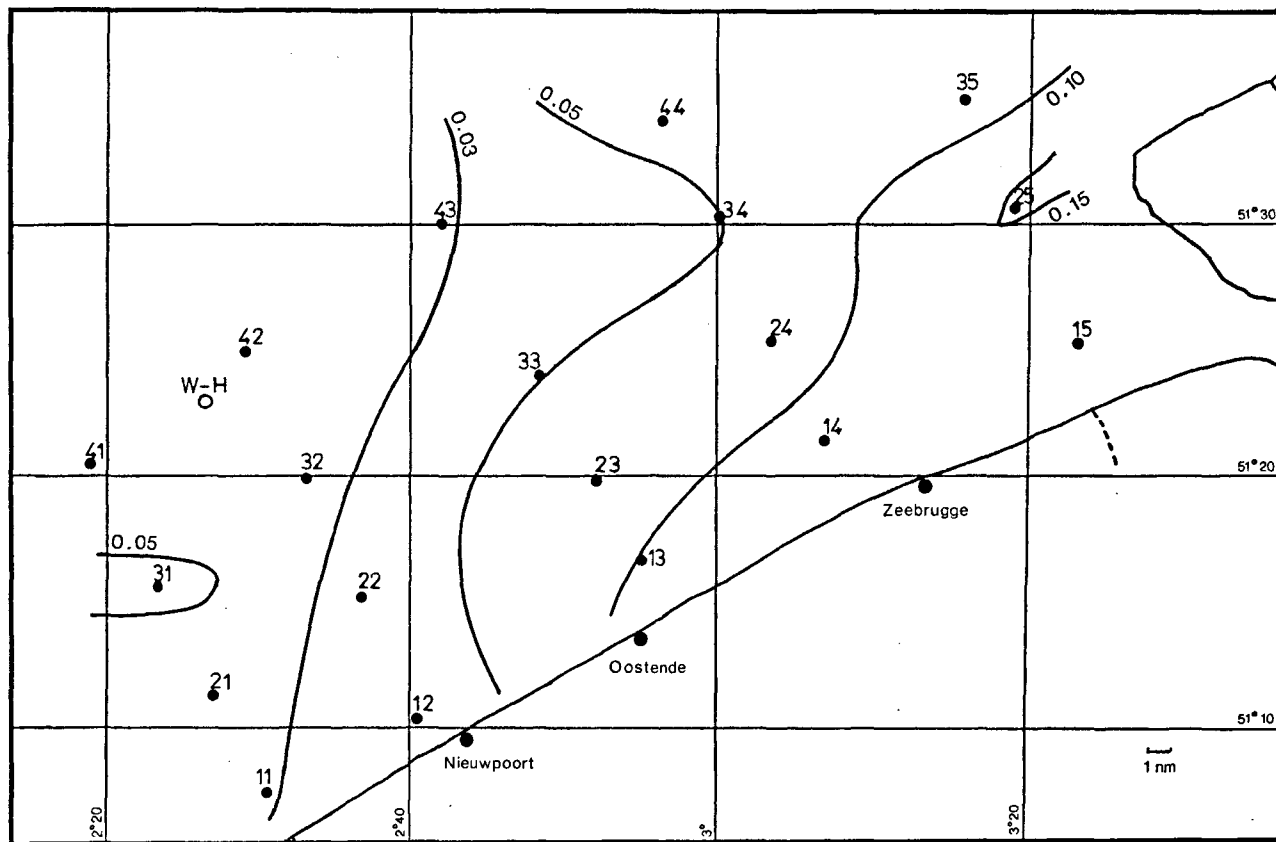


fig. 6.

Spatial distribution of particulate mercury ($\mu\text{g Hg/l}$)
November 1978

as well for the particulate mercury content, may be drawn out :

- 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 ocean water, namely $0.03 \mu\text{g Hg}/\text{l}$, according to the distance from the Scheldtmouth.

As previous studies (Baeyens et al., 1978 - Baeyens, 1977) show a strong interaction between several mercury components and the suspended matter, it was tried to derive *graphically* a relation between turbidity and mercury content. When more data would be available, more sophisticated statistical methods will be used.

For a first approach, both curves, total and particulate mercury content versus turbidity, are shown in figure 7.

- A first important fact that clearly appears from this figure is a difference in accuracy of the analytical procedures for the determination of particulate and total mercury. This is probably due to the fact that in the actual state of the sampling procedure, *the absolute quantities* involved in the case of the determination of the particulate mercury are more or less 6 times higher than in the case of the determination of the total mercury.
- *In general* the concentrations of total and particulate mercury are practically identical, since the dissolved mercury concentrations are mostly located on the detection limit. An adapted method (extraction and preconcentration on an exchange-column) for the determination of dissolved mercury is checked at present time, in order to obtain a more exact value of these "dissolved" concentrations.
- For the measurements at high turbidity, a constant factor is observed between the particulate Hg concentration and the total Hg concentration measured at the same turbidity and, both expressed in $\mu\text{g}/\text{l}$. The constant difference can be due to incomplete release of the mercury from the suspended matter during the determination of the total mercury content, while when determining *directly* the particulate mercury after filtration, the release does take place completely, according the use of a highly

1. Although rather limited in number but still significant.

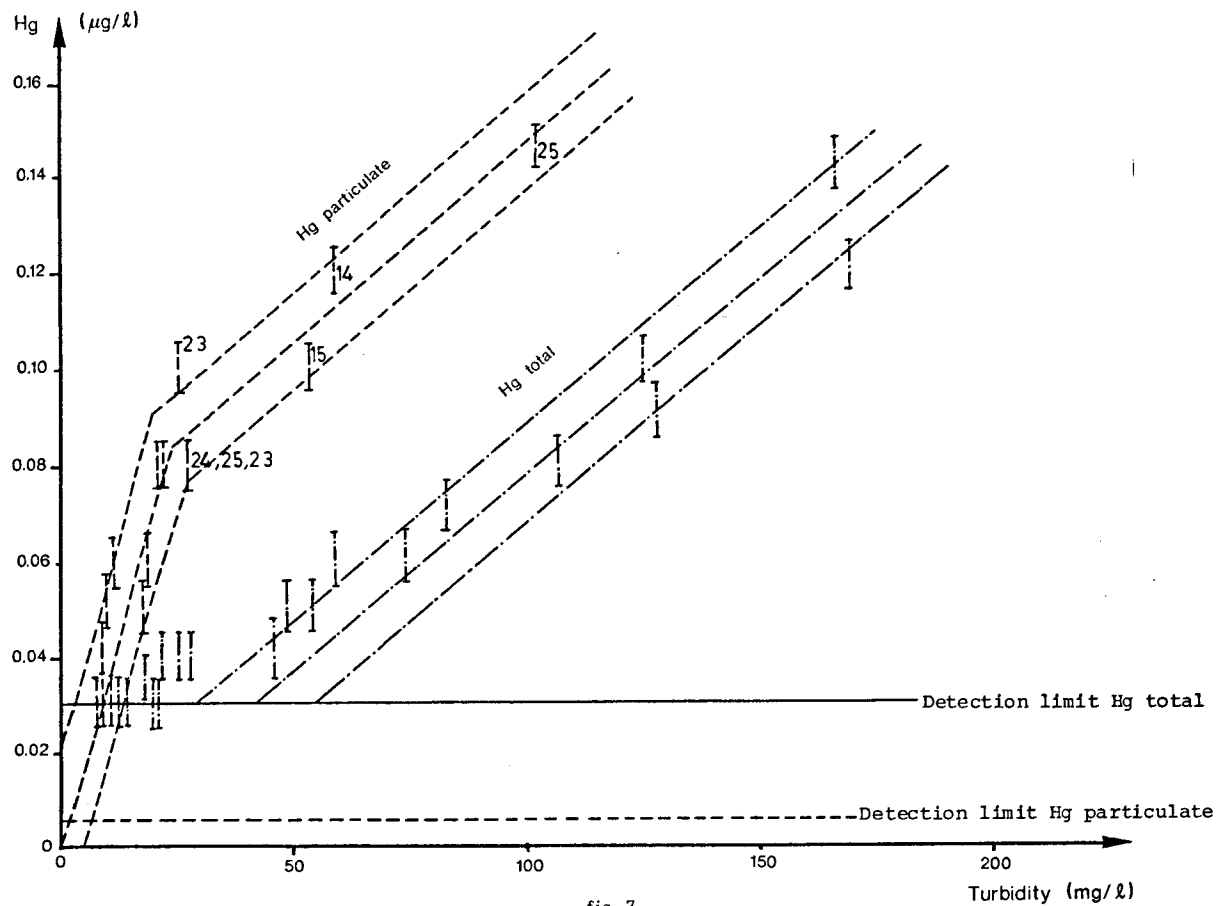


fig. 7.

Total and particulate mercury content versus turbidity

concentrated acid combined with a strong oxydator. Tests were carried out to check whether one of these methods : $\text{KMnO}_4/\text{acid}$ or $\text{H}_2\text{O}_2/\text{acid}$ would give the best results for the determination of the total mercury content. During the cruise of September 1978 (table 3) both methods were compared, but no systematic difference could be shown. On the other hand, the acidification to $\text{pH} = 1$, prior to the storage of the sample for the determination of total mercury, can perturb its original concentration. With such a pH , a desorption of particulate mercury takes place with forming of HgCl_3^- and/or $\text{Hg}(0)$. Simultaneously CO_2 is evolved, through which a fraction of the present mercury can diffuse to the atmosphere.

The curve (fig. 7) indicating the relation between the particulate mercury concentration and the turbidity, shows two discrete parts. More mercury is adsorbed per weight-unit of suspended matter at low than at high turbidity. The points of low turbidity are open-sea points and no mercury is discharged in this zone. Its origin must be sought in one or more of the following hypothesis :

- the fine matter transported by the Scheldt plume and containing most mercury, precipitates relatively slowly, while the more coarse material, containing little mercury, does not reach the open sea.
- there is a continuous remobilisation of dissolved mercury (through the decomposition of organic matter, through the Eh-pH circumstances in the sediments, etc.) with a reasonable rapid re-adsorption on smaller quantities of suspended matter.
- the Scheldt transports particulate as well as dissolved mercury. If the suspended marine matter has a higher adsorption capacity and/or follows another reaction kinetic scheme than for the particulate Scheldt-matter, it can contain more mercury per weight-unit of suspended matter.

4.- Conclusion

In the present approach, the storage and the analysis steps were *before all* studied thoroughly and improved, but the *sampling procedure* also will be examined in more details in the future. Direct determination of the total mercury content, however, still causes problems. The dissolved mercury

concentrations will therefore also be measured, after an extraction or a preconcentration procedure. The particulate mercury concentrations obtained after filtration and centrifugation will be compared with each other. Finally, a certain number of supplementary studies will be carried out to explain the higher mercury content per weight unit of solid matter in the open sea zone. The kinetics of the adsorption of mercury on the particulate matter in the Scheldtmouth, the Scheldt plume and in the open sea zone will be established for that purpose. Parallel to this program, valuable information concerning the fate of the particulate matter transported by the Scheldt can be supplied by studies on sediment transport.

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