

ANNA BRZEZIŃSKA
Institute of Meteorology
and Water Management, Gdynia

THE OCCURRENCE OF MERCURY IN THE SOUTHERN BALTIC SEA

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Abstract

The results of systematic investigations on the occurrence of the mercury in the Southern Baltic, the part constituting Polish economic zone, are presented. Unfiltered seawater, sampled in 1978 - 1981 from 10 stations selected for international and national pollution monitoring in the Baltic has been analyzed. Total mercury concentration was determined by a flameless AAS technique, after mineralization of organic mercury compounds.

1. INTRODUCTION

There has been a continuing interest of the marine chemists and ecologists in the problem of distribution and interaction of mercury compounds in the marine environment owing to high toxicity of its compounds, in particular methylmercury. A variety of chemical forms together with low levels of mercury in the sea provide some difficulties in assaying the metal in sea water. In spite of the fact that there have been many efforts to introduce new analytical methods for assaying mercury, such as chemiluminescence or atomic emission, the most widespread is the cold vapour technique of the flameless atomic absorption spectrometry with its various modifications [7, 8, 11, 15].

In the Department of Physics and Chemistry of the Sea, Institute of Meteorology and Water Management, Gdynia, investigations have been carried out into application of this technique to the determination of mercury and its compounds in the Baltic water. The purpose of this paper is to verify earlier reports on the level of pollution with mercurials of the Polish economic zone of the Baltic Sea [2, 4].

2. MATERIALS

The occurrence of mercury was investigated in the southern region of the Baltic Sea within Polish economic zone. Three regions differing in hydrological and meteorological conditions were distinguished in this zone, namely the Gulf of Gdańsk, a deep-water zone of the open sea with the depth exceeding 30 m, and a shallow zone of the open sea including off-shore waters with the depth down to 30 m, extending from Rozewie to Świnoujście.

Samples were taken in 1978 - 1981 during ten cruises to 7 stations selected for

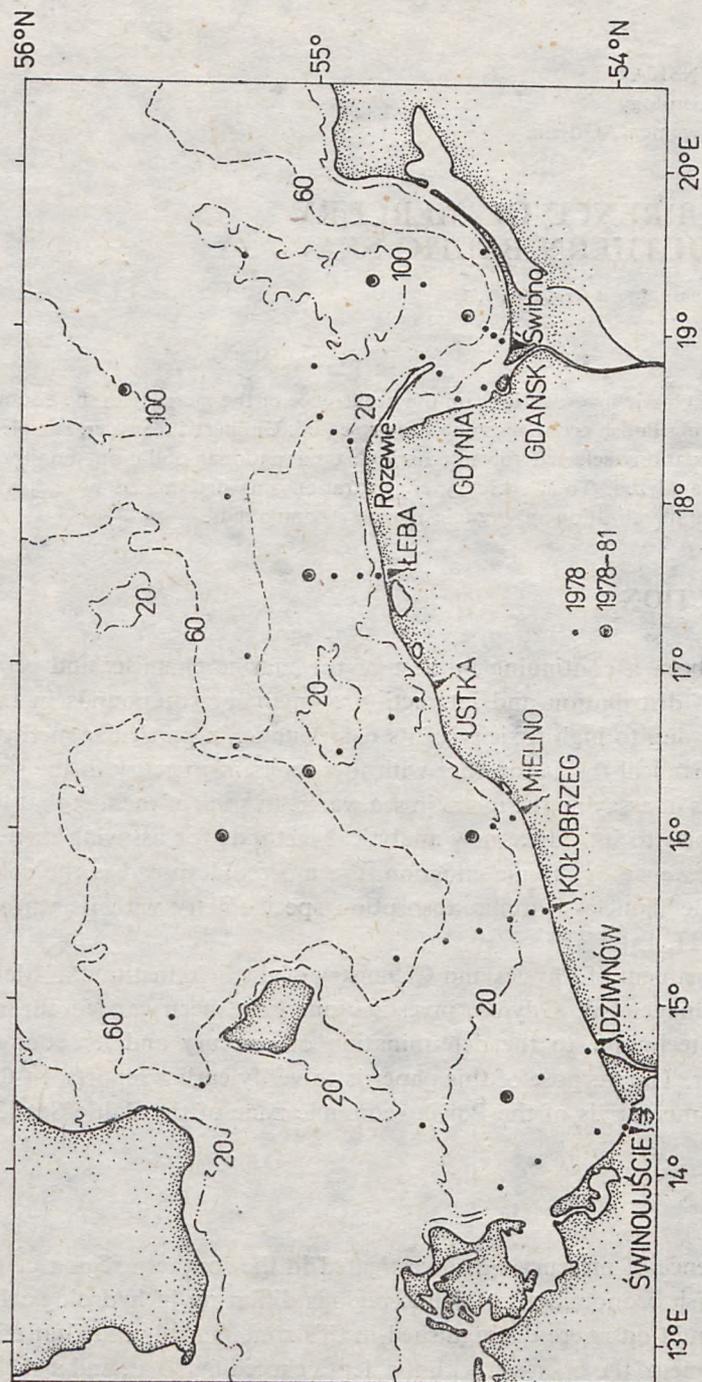


Fig. 1. Net of sampling stations in Polish economical zone of the Baltic Sea.

monitoring of the pollution of the Baltic Sea. In 1978, the number of stations was higher, but water was sampled from the surficial layer only (Fig. 1). According to the methodological agreement among Baltic countries, unfiltered water taken from the sea surface and from levels of 10 and 2 to 5 m above the bottom was analyzed.

3. METHODS

3.1. SAMPLING AND STORAGE OF SAMPLES

Sea water was sampled with a 5-litre Go-Flow type bathometer, manufactured by General Oceanics, U.S.A., specially constructed for sampling sea water for assaying trace metals. Samples were kept in vessels made of a white heavy polyethylene, at -20°C . The vessels were washed by extraction with a 1 : 1 nitric acid followed by repeated rinsing with a three times distilled water. The vessels were then selected for sampling by assaying mercury levels in the three times distilled water kept in them (Table 1).

Table 1. The scheme of the analytical procedure during the determination of total mercury in sea water (All volumes in millilitres)

Reagents	Tube No.			
	1	2	3	4
Sea water	40	40	40	40
HNO ₃ conc.	1	1	1	1
H ₂ SO ₄ conc.	1	1	1	1
KMnO ₄ 5%	0,5	0,5	0,5	0,5
K ₂ S ₂ O ₈ 5%	1	1	1	1
Standard Hg, 100 $\mu\text{g}\cdot\text{dm}^{-3}$	—	0,1	0,2	0,3
(Additions)	—	(10 ng Hg)	(20 ng Hg)	(30 ng Hg)
Mineralization in closed tubes for 2 hours				
Hydroxylamine				
hydrochloride 12%	0,2	0,2	0,2	0,2
SnCl ₂ 20%	1	1	1	1
The measurement of absorption on Hg monitor				

3.2. STANDARDS AND REAGENTS

— The stock solution of mercury ($1000\text{ mg}\cdot\text{dm}^{-3}$), manufactured by MERCK, was stabilized with 5 cm^3 of concentrated sulphuric acid per 100 cm^3 of the stock solution and with a small quantity (ca 1 mg) of potassium bichromate.

— The standard solution of mercury ($100\text{ }\mu\text{g}\cdot\text{dm}^{-3}$) was prepared on the day of carrying out the analyses by suitable dilution of the stock solution.

— Mercury-free sulphuric acid ($d=1.84\text{ g}\cdot\text{cm}^{-3}$) (MERCK).

— Mercury-free 5% potassium permanganate solution (MERCK).

- Mercury-free nitric acid ($d = 1.40 \text{ g} \cdot \text{cm}^{-3}$) (MERCK).
- Mercury-free 5% potassium persulphate solution (MERCK).
- Mercury-free 12% solution of hydroxylamine hydrochloride (MERCK).
- Mercury-free 20% SnCl_2 solution (MERCK) in a 1 : 1 hydrochloric acid (spectrograde reagent).
- Distilled water - distilled once in a laboratory still and doubly distilled in a quartz still - was used for the preparation of reagents and for rinsing the vessels.

3.3. DETERMINATIONS

Mercury was assayed by the method of standard addition. To determine total mercury level, organomercurials occurring in sea water were digested with a mixture of concentrated nitric and sulphuric acids as well as with potassium permanganate and persulphate, in glass vessels adaptable to a mercury monitor. The mercury level in the blank, calculated as the difference between a single and double quantities of the reagents used for wet oxidation, ranged between 0.5 and 1.5 ng of Hg, depending on the purity of water used for their preparation.

3.4. EQUIPMENT

Absorbance of mercury generated by reduction with stannous chloride was measured in a mercury monitor (Laboratory Data Control, U.S.A.) equipped with a 100-kW mercury lamp and two quartz cuvettes, 300 mm long and 5 mm in diameter. Signals were recorded by a Radiometer (Copenhagen) recorder. A peak height corresponding to the signal of 10 ng of Hg was 50 ± 2 mm. A linear dependence between signal intensity and mercury content in sample extended up to 200 ng of Hg. The flow rate of air entraining mercury vapours into the instrument was $600 \text{ cm}^3 \cdot \text{min}^{-1}$. Before introducing into the measuring cuvette, mercury vapours were dried with magnesium perchlorate.

3.5. STATISTICAL EVALUATION OF RESULTS

The detection limit, calculated as double standard deviation from ten runs in a blank, was 0.3 ng of Hg, corresponding to the concentration of 8 ng of Hg per dm^3 . The precision of determinations, expressed in terms of the coefficient of variation calculated at a confidence level of 0.95, was 50% on average for the concentration range 10 - 30 $\text{ng} \cdot \text{dm}^{-3}$, 30% for the range 30 - 60 $\text{ng} \cdot \text{dm}^{-3}$ and it dropped to 15% for higher concentrations. This corresponds to the reproducibility of mercury assays obtained during several international interlaboratory workshops [1, 10, 12, 17].

In 1981, a dust-free chamber manufactured by POLON, Poznań, was installed in the laboratory, in which the samples were digested. A comparative series of ten or so assays carried out in this chamber and under a typical laboratory hood, did not reveal any differences in the concentration of mercury. The reproducibility, ho-

wever, was improved in the chamber, and amounted to 30% for the concentration of 30 ng of Hg per dm^3 .

To evaluate the effect of storage on the results, comparative determinations were run on board of the research ship and after delivering the frozen water to the laboratory on shore. Also in this case there was no significant difference in concentrations in a series of ten or so samples of mean concentration of $50 \text{ ng} \cdot \text{cm}^{-3}$. Mercury in sea water can be assayed on board provided that current feeding the instrument has stable voltage.

4. RESULTS AND DISCUSSION

The mean mercury level in the Polish economic zone of the Baltic Sea, calculated from 177 determinations carried out in 1978 - 1981, was $89 \text{ ng} \cdot \text{dm}^{-3}$ (Table 2). The lowest mercury level corresponds to the detection limit ($8 \text{ ng} \cdot \text{dm}^{-3}$) and the highest reached the value of $300 \text{ ng} \cdot \text{dm}^{-3}$ (Fig. 2).

The positively skewed distribution of the concentrations causes that the mean value is more than twice as high as the predominant one.

Differences between mean values for selected regions of the area under study, evaluated by using Student t-test, were statistically insignificant for all cases with the exception of the difference between the mean values in the shallow and deep zones of the open sea which was significant with the probability of 0.7. The distribution of mercury concentrations in the Gulf of Gdańsk approximates to the normal distribution (Fig. 3). The predominating value is comparable with the mean one. Both of them were, however, twice as high as the most frequent range of concentrations in the open sea. Hence, it can be concluded that the mercury level in waters of the Gulf of Gdańsk is roughly twice as high as that in the Southern Baltic.

Table 2. Statistic evaluation of mercury concentration ($\text{ng} \cdot \text{dm}^{-3}$) in the Polish economic zone of the Baltic

Region or water layer	No. of samples	Arithmetic mean and standard deviation	Weighted mean and standard deviation	Mode
Regional division				
Gulf of Gdańsk	38	86 ± 58	89 ± 60	84
Open sea area				
- coastal waters	69	99 ± 74	97 ± 43	41
- deep waters	70	82 ± 58	80 ± 39	38
Vertical division				
Surface (0-1 m)	76	85 ± 61	85 ± 43	39
Depth 10 m	47	85 ± 61	82 ± 56	50
Near-bottom layer (70-105 m)	54	98 ± 71	99 ± 46	44
Polish economic zone of the Baltic Sea				
All samples	177	89 ± 65	87 ± 28	40

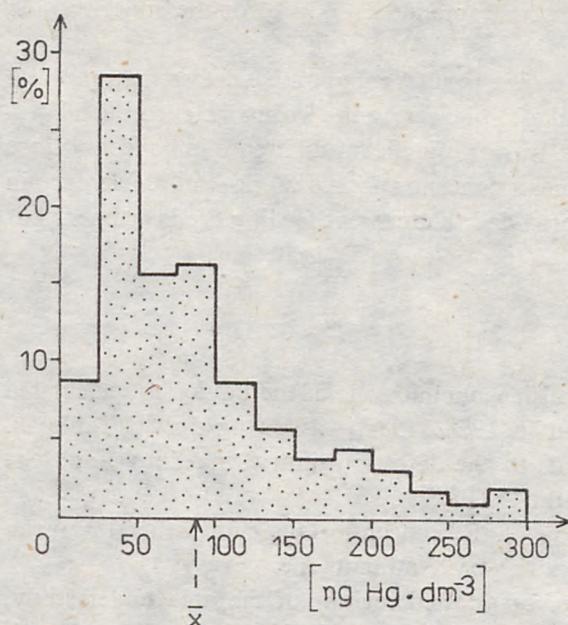


Fig. 2. Histogram of total mercury concentration in unfiltered sea water from the Polish economic zone of the Baltic Sea.

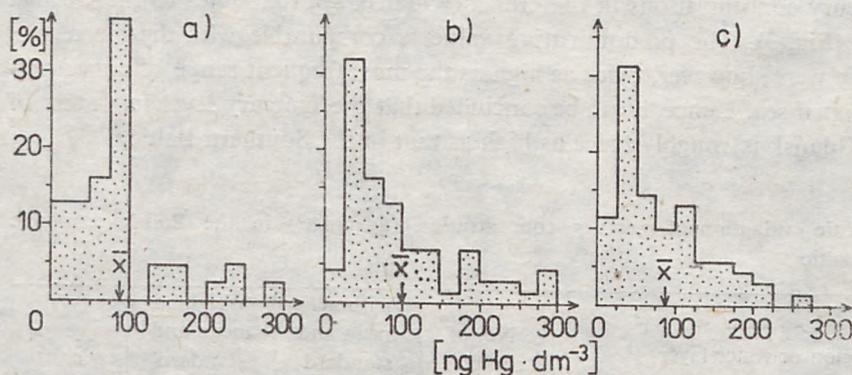


Fig. 3. Histogram of total mercury concentration in different regions of the Polish economic zone of the Baltic Sea: *a* – Gulf of Gdańsk, *b* – deep water zone of the open sea (depth > 30 m), *c* – shallow water zone of the open sea (depth < 30 m).

When considering the variations of mercury concentrations in the water column (Table 2, Fig. 4) it is seen that the metal concentrates usually at the bottom. The differences between the mean values for the deep waters and other layers were statistically non-significant, however.

Concentrations predominating in particular water layers are comparable with modal values for the whole basin considered. The highest modal value ($50 \text{ ng} \cdot \text{dm}^{-3}$) was obtained for the 10-m layer. This was caused by high mercury concentrations (ca $200 \text{ ng} \cdot \text{dm}^{-3}$) observed in the early spring of 1979 in the off-shore zone. This

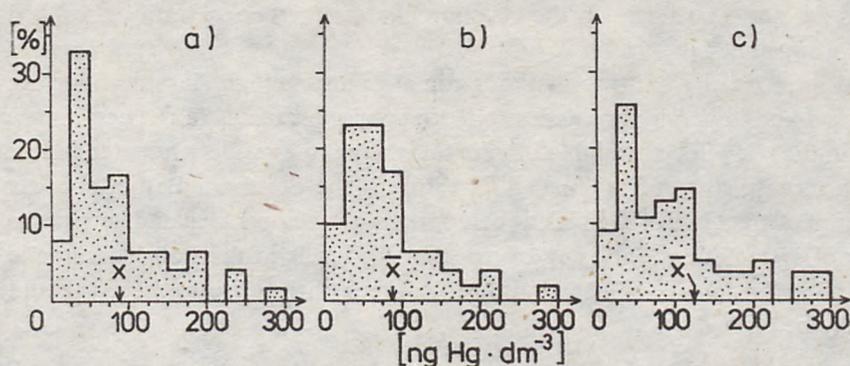


Fig. 4. Histogram of total mercury concentration in the surface (a), 10 m depth (b) and near-bottom layer (c) of the Polish economic zone of the Baltic Sea.

finding was subsequently confirmed by high mercury contents in plankton taken from these waters during that time.

In 1979 high mercury levels were also found occasionally at the surface and at the bottom. For the whole area, the mean mercury concentration in 1979 was $135 \text{ ng} \cdot \text{dm}^{-3}$, whereas during other periods of investigations it was $58 \text{ ng} \cdot \text{dm}^{-3}$. An analysis of the entire period of investigations in respect of the mercury level in the Baltic water showed that there was an irregular tendency of increase in the concentrations during 1978 - 1979 and a distinct decline by the end of 1979 which persisted in 1980. An attempt to relate this decreasing tendency with a diversified in time influx from the continent was confirmed by a considerable reduction of the Vistula run-off and the decrease of the mercury level in the atmosphere (unpublished data).

A comparison of the mercury content in the Polish economic zone with those in other Baltic regions reveals similar concentration ranges [6, 16]. In 1978, Brüggmann [5] found total mercury levels in open Baltic waters to fall within the range $4 - 250 \text{ ng} \cdot \text{dm}^{-3}$. The frequency distribution of the concentrations exhibited two peaks of 10 and $40 \text{ ng} \cdot \text{dm}^{-3}$. A little lower concentration range, $2 - 60 \text{ ng} \cdot \text{dm}^{-3}$, was found in the Danish Straits [13]. Mercury was assayed by the neutron-activation analysis which has not been satisfactorily intercalibrated with the widely used atomic absorption spectrometry.

In ocean waters mercury occurs at lower concentrations than in the Baltic Sea. Jones [9] collected available data on the occurrence of mercury in the North and Middle Atlantic, published up to 1975. From this compilation it follows that in many marine and oceanic regions high mercury levels, attaining $1 \mu\text{g} \cdot \text{dm}^{-3}$, can be found. These high figures should now be critically evaluated owing to imperfect analytical and sampling techniques.

Piuzé and Tremblay [14] studied the occurrence of mercury in the Saint Lawrence Bay, situated at the Atlantic coast of Canada, and found the mercury concentration to vary between 3 and $30 \text{ ng} \cdot \text{dm}^{-3}$. On the basis of inspection of many reports published in 1975 - 1979, they suggest the typical mercury level in clean ocean waters

to be several $\text{ng} \cdot \text{dm}^{-3}$, whereas in the off-shore waters the concentrations reached several tens of $\text{ng} \cdot \text{dm}^{-3}$.

Efforts to improve the existing methods for assaying mercury in sea water are being continued and hopefully in the future more precise estimates of the occurrence of the metal in the sea will be available. At the time being, the results presented in this paper offer a clear picture of regional differences in the Southern Baltic, confirm higher pollution of the Gulf of Gdańsk as compared with the open sea, and emphasize the necessity of systematic monitoring of trace metals levels in the Polish economic zone of the Baltic Sea. Studies on the output of sources of metals into the sea should simultaneously be carried on.

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