

ANNA BRZEZIŃSKA, ANNA TRZOSIŃSKA

Institute of Meteorology
and Water Management, Gdynia

WANDA ŻMIJEWSKA, LUDMIŁA WÓDKIEWICZ

Institute of Nuclear Research, Warsaw

TRACE METALS IN SUSPENDED MATTER AND SURFICIAL BOTTOM SEDIMENTS FROM THE SOUTHERN BALTIC

(Received Sept. 2, 1981; in final form Dec. 9, 1981)

Abstract

Surficial bottom sediments and suspensions from the Polish economic zone of the Baltic as well as suspensions collected in the sedimentation traps placed on the bottom of the Gulf of Gdańsk have been analyzed. The metals in the suspended matter were determined by the flameless AAS technique (Cd, Hg, Pb, Cu, Zn) and by NAA technique (Hg, Zn, Co, Cr, Cs, Ag, Se, Sb, Fe), in the sediments by both the flameless and the flame AAS (Cd, Hg, Pb, Cu, Zn, Cr, Co, Ni, V, Mn, Fe).

Statistical evaluation of the data indicates significant spatial differences with respect to the concentrations of the majority of trace metals in suspensions and bottom sediments. They are mainly due to the action of various biogeochemical and hydrological factors, as well as to the strong but irregular emission from antropogenic sources. The approximate amounts of Pb, Zn, Hg, Cr, Cu and Cd deposited on the bottom of the Gulf of Gdańsk, the character of their redistribution in the sea and chemical transformation of deposits with respect to trace metals have been estimated.

1. INTRODUCTION

Studies on the chemical composition of suspended matter and bottom sediments become increasingly important in the sea science both in respect of their cognitive and practical (environmental) implications. As compared with water, the great advantage of the sediments is the fact that they reflect the course of biogeochemical processes occurring in the water body and afford their precise, historically fixed, records in the structure of the sea floor. The composition of suspended matter and surficial bottom sediments has a significant influence on the living conditions of zoobenthos, both filter feeders and deposit feeders, and through them, on many fish species. Such studies are particularly useful for the knowledge of processes occurring in estuaries and off-shore zones of the seas where segregation of the material takes place and its chemical composition undergoes changes in a complicated, dynamic sedimentational system of authigenic suspensions and those brought from the continent.

Trace metals, including heavy metals, are natural constituents of suspensions and bottom sediments of the seas. Both their distribution and balance have always depended on the intensity of rock decay and transportation of the decay products

to the sea as well as on the physico-chemical equilibrium setting up between the solution and the solid phase. At present, however, the metals are supplied from anthropogenic sources in quantities frequently exceeding those of natural resources. The influence of this additional influx was noted at first in the bottom sediments of lakes and estuaries and in the inhabitant organisms. At the same time it became also evident in the seas, in particular the land-locked ones, such as the Baltic Sea [15, 29, 31].

Technical difficulties due to correct sampling provide serious obstacle in studies of marine suspensions and sediments. The problem of taking cores of the sediments with unaffected structure has not yet been solved satisfactorily. Also the sampling of suspended matter poses methodological problems, mostly owing to its high dispersivity in the sea and a variety of their physical and chemical forms. One of the commonly used solutions are suspension traps, which can be either immersed in the water body or placed on the bottom. They enable to collect the material in much larger amounts than that obtained by filtration of water. The interpretation of results is, however, difficult for various reasons. The main reason is the variable trapping efficiency determined by the trap design and the dynamics of the aquatic environment, the changes in chemical composition of the suspensions after trapping, and the small number of the traps limited by technical reasons and their costs.

Owing to the much higher level of trace constituents, suspended matter and bottom sediments provide more convenient objects than sea water, the analyses of which are still accomplished within the detection limits of the contemporary instrumental techniques. Methods enabling to determine total metal concentrations in bottom sediments usually require complete dissolution of samples, thus cause frequent interferences [6]. Hence, non-destructive technique are convenient. Their sensitivity, however, is not satisfactory. In ecogocical investigations, where the estimation of the mobile fraction, which is often identified with anthropogenic fraction, is essential, acid extraction is usually employed combined with oxidation, by analogy with methods utilized in the soil science. In this procedure, that portion of a metal passes into solution which is not built in the crystal lattice of aluminosilicate minerals. This portion may be hazardous to the aquatic environment owing to the ease of leaching and assimilability in metabolic processes. Evaluations of the extent of such extraction are different, being more favourable for sediments rich in organic matter. As reported by Carmody *et al.* [11], hot nitric acid extracted 83 - 100 per cent of the total Cr, Cu, Pb and Zn. The results of the world-wide intercalibration of the methods used for trace metal determination in bottom sediments, carried out in 32 laboratories, confirmed good (80 - 100 per cent) efficiency of various extraction methods of those metals, as well as of Hg, Cd, Fe, Mn, Ni and Co, when the silica content did not exceed 60 per cent [21]. These results are encouraging for employing the methods for the monitoring [30] under standardized extraction conditions of the sediments.

The results presented in this paper provide one of the stages of the study of the system water-suspended matter — bottom sediments-organisms in the Southern Baltic, in the Polish economical zone of the sea. The results of investigations into trace metal levels in organisms are published separately [10].

2. SAMPLING AND PREPARATION OF THE MATERIALS

Suspended matter and bottom sediments for assaying trace metals were sampled from board of r.v. "Hydromet" at stations located within the Polish economical zone of the Baltic (Fig. 1) from July 1977 to September 1980. Suspension traps were shot three times, from June to September 1978, in the Gulf of Gdańsk only (southern region of the Gdańsk Deep), at a station located 10 Nm from the mouth of the Vistula River. The exposition time at a depth of 71 m, i.e. beneath the base of waves, was 3 to 10 weeks.

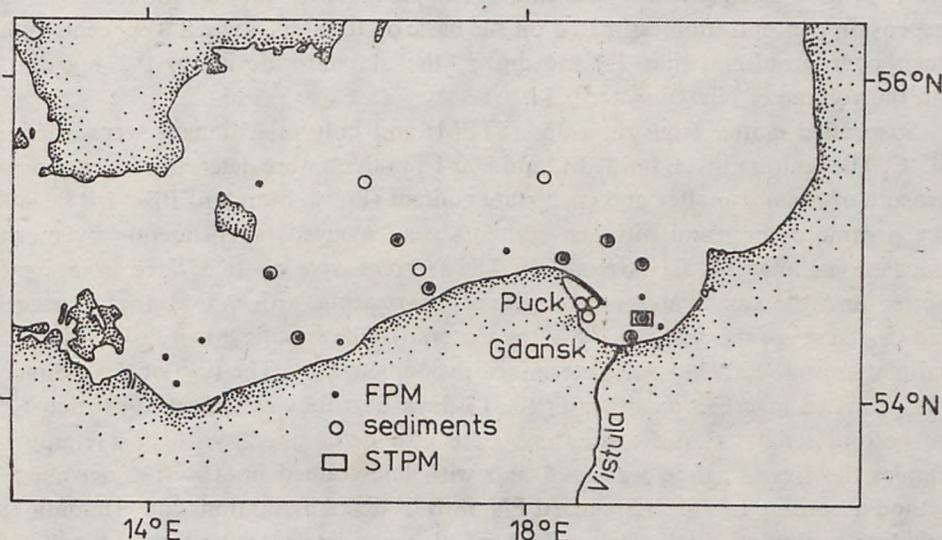


Fig. 1. Locations of sampling stations of suspended matter and bottom sediments in the Southern Baltic.

Two kinds of suspended matter were analyzed:

- a) FPM — suspended matter filtered from various water layers (seston). From 0.5 to 10 l of water were taken with a "Go-Flow" bathometer made exclusively from plastic (General Oceanics, USA), filtered immediately through 0.40 μm pore size Nuclepore membrane filters (Shandon, FRG). The filters were placed in glass microbiological funnels with a teflon net (Milipore, USA). Samples were filtered under reduced pressure using an oil-free pump (Sartorius, FRG).
- b) STPM — suspended matter freely falling into the sedimentation traps placed on the bottom. During shooting and hauling of the trap [28], its grid area (1 m^2) consisting of 100 polystyrene cells, was mechanically closed with a polyvinyl foil. The frame of the trap was made of aluminium alloy. During the exposition the cells were fixed 1 m above the bottom. Divers supervised the placing of the traps on the bottom, so as to reduce disturbance of the bottom sediments to minimum. After

hauling the traps aboard, the cells were tightly closed and delivered to the laboratory on shore, where the collected material was centrifuged or filtered as above. Metals were determined in the material collected in 5 - 8 cells, randomly chosen from each trap. The remaining cells served for other analyses.

Surficial bottom sediments were taken with a Van Veen sampler under supervision of divers, to reduce losses of subtle particles rising in the form of cloud when the sampler struck the bottom too violently. A semiliquid, about 1 cm thick surficial layer of the sediment was taken for analysis using a plastic spatula.

The suspended matter, the filtrate and bottom sediments were kept at -20°C in glass or plastic containers.

Filters were dried at 60°C for 1 h before and after sampling the suspensions (FPM) and kept over silica gel in a desiccator. The precision of the determination of the suspension concentration estimated on the basis of 10 samples was 8.3 per cent, at the mean concentration being $2.4 \text{ mg}\cdot\text{dm}^{-3}$, the standard deviation $0.2 \text{ mg}\cdot\text{dm}^{-3}$ and the volume of filtered water 0.5 l.

Suspended matter from the traps (STPM) and bottom sediments were dried at 105°C . The ignition losses (at 500°C and 800°C) in them were determined as a general measure of organic matter and carbonate content (Polish Standard PN-54/B-02480). The organic carbon and nitrogen contents were assayed independently by means of a Perkin-Elmer 240 CHN analyzer. The samples were disintegrated in an agate mortar and the carbonates were removed by treating with 0.3 M trichloroacetic acid (5 - 8 cm^3 of the acid per 1 g of the material). The specific gravity of the suspended matter and sediments was determined pycnometrically. The type of the sediment was estimated macroscopically after the Lisitsyn-Bezrubov classification. In most of the bottom sediments, sieve fractions were also determined. With coarse-grained samples the sieve method was used and with fine-grained ones - the aerometric method according to Polish Standard PN-58/B-04483. All additional determinations, including geological, biological and chemical, were carried out using the material taken from 4 - 6 cells, randomly chosen from each trap.

3. GENERAL CHARACTERISTICS OF THE MATERIALS

The evaluation of the concentration of suspended matter (FPM) was based on the measurements carried out in March, June and July. It cannot thus be regarded as a representative for all seasons. The concentration of suspended matter (Table 1) varied over a wide range of 0.2 to $14.4 \text{ mg}\cdot\text{dm}^{-3}$. The values greater than $3.5 \text{ mg}\cdot\text{dm}^{-3}$ appeared very rarely, however, only in estuaries in periods of large continental run-off. The concentration $0.8 \text{ mg}\cdot\text{dm}^{-3}$ prevailed (Fig. 2). The statistically significant difference existed between the concentrations of suspended matter in the Gulf of Gdańsk and open sea area. The contents of suspensions in the upper layer of the Gulf was about twice higher than in the waters below the halocline. Filtered suspensions in the Gulf of Gdańsk contained much more nitrogen (1.05 - 3.85 per cent) and phosphorus (0.06 - 0.23 per cent) than those taken in other regions (0.67 - 1.04 and 0.09 - 0.14 per cent of nitrogen and phosphorus respectively). The mean

Table 1. Concentration of suspended matter ($\text{mg}\cdot\text{dm}^{-3}$) in the Southern Baltic

Area	No of samples	Mean	Standard deviation	Range	Mode
Whole area (Fig. 1)	88	1.47	0.48	0.10 - 14.4 ^a	0.79
Open sea area	33	1.27	0.60	0.50 - 7.5 ^a	0.81
Gulf of Gdańsk	55	1.60	0.60	0.10 - 14.4 ^a	0.80
— above the halocline	37	1.88	0.67	0.10 - 14.4 ^a	2.33
— below the halocline	18	1.00	0.56	0.30 - 2.75	0.72

a — Excluded from statistic calculations.

weight/weight ratio of these elements was 19.3 and 7.3 respectively. The latter value is typical of the Baltic plankton and detritus [17].

Remarkable amounts of suspended matter collected in the bottom traps (STPM) enabled more comprehensive determination of their properties (Table 2). The microscopic analysis revealed large amounts of plankton detritus (mostly phytoplankton), coated or filled with saprophytic bacteria. From time to time, completely undecomposed specimens of *Chlorophyceae*, *Cyanophyceae* and *Diatomae* were found; however, complete and broken diatom skeletons, recent pollen from herbaceous plants and trees ($1.2\cdot 10^5\cdot\text{cm}^{-2}$) and grains of sand were most frequent. The suspended matter was still richer in organic matter than silt collected from the bottom under the trap.

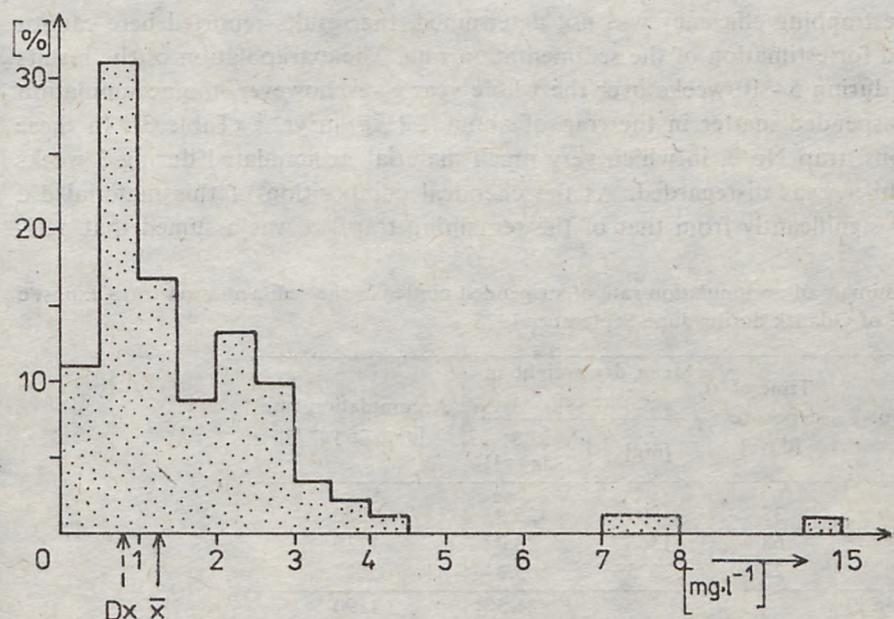


Fig. 2. Histogram of suspended matter concentrations in the Southern Baltic. (\bar{x} — weighted mean, D_x — mode).

Table 2. Properties of suspended matter collected in the sediment traps (STPM) and of surficial bottom sediments from the Southern Baltic

Material and area	Loss on ignition [%]		Specific gravity [g·cm ⁻³]	Percentage			Mass ratio	
	500°C	800°C		Corg.	N	P	C : N	N : P
STPM (1) } Gulf of	18.7	25.4	2.67	5.98	0.91	0.17	6.6	5.3
STPM (2) } Gdańsk	19.9	22.8	2.67	5.87	1.09	0.23	5.4	4.7
STPM (3)	20.7	23.3	2.67	6.37	1.07	0.12	6.0	8.8
Clay silt, Gulf of Gdańsk, area of trap exposure	11.1	14.6	2.59	3.60	0.32	0.04	11.3	9.1
Silt:								
– gulfs	11.0	15.0	2.59	3.96	0.57	0.06	6.9	9.5
– open sea	10.1	14.1	2.59	3.33	0.59	0.04	5.6	14.8
Sand:								
– gulfs	1.6	2.4	2.63	0.58	0.17	0.02	3.4	8.5
– open sea	0.3	0.4	2.65	0.03	0.00	0.01	–	–

(Table 2). The N : P ratio in them was, however, lower than in suspensions collected on filters from upper water layers. Similar low C : N ratios may be due either to advanced degradation of authogenic suspensions [17] remaining in traps for 3 - 10 weeks or to contribution of organic matter brought in by the Vistula River [26]. Analysis of the mineralogical composition of suspended matter from the traps, carried out by X-ray diffractometry, showed strong reflections due to quartz, halite dolomite, and weak ones due to chlorite, illite and plagioclases.

As the trapping efficiency was not determined, the results reported here cannot be utilized for estimation of the sedimentation rate. The extrapolation of the results obtained during 5 - 10 weeks over the whole year gives, however, the accumulation rate of suspended matter in the trap of about 1.2 kg·m²yr⁻¹ (Table 3). In these calculations, trap No 3, in which very much material accumulated during 3 weeks in September, was disregarded. As the chemical composition of this material did not differ significantly from that of the remaining traps, it was assumed that acci-

Table 3. Estimate of accumulation rate of suspended matter in the sedimentation traps exposed in the Gulf of Gdańsk during June-September 1978

Trap No.	Time of exposure [days]	Mean dry weight in one cell		Accumulation rate [g·m ⁻² yr ⁻¹]
		[mg]	[mg·day ⁻¹]	
1	35	907	25.9	1260
2	68	1566	23.0	1119
3 ^a	23	2375	103.3	5027
Mean (1 and 2)			24.5	1190

a – Not included in calculations of the mean.

dental uprising from the bottom took place and trapping of the finest fraction of surficial sediments. Taking into account the specific gravity of STPM (Table 2), such quantity of suspended matter ($1.2 \text{ kg} \cdot \text{m}^{-2}$) will form a 0.45 mm thick layer during the year. If one assumes that the presence of water will double this layer, the value of about 1 mm yr^{-1} will be obtained, the figure being in accord with a number of estimations of sedimentation rates in such Baltic basins as the Gotland Deep or the Bornholm Deep [3, 31].

Samples of the bottom sediments contained sands of different grain size, clay and aleurite-silty loams (Table 2). The majority of the sediments was well classified and had properties characteristic for a particular kind of marine bottom sediments. Only sandy samples taken in the Puck Bay and the Gulf of Gdańsk in the foreground of the mouth of the Vistula contained considerable contribution of organic matter. The richest in C_{org} (more than 4 per cent) were silts from the Gdańsk Deep and the Gotland Deep, i.e. from typical Baltic sedimentational basins, in which mineralization of sinking suspensions was hampered by unfavourable oxygen conditions.

4. ANALYTICAL METHODS

Metal in suspensions (FPM and STPM) were assayed by two methods: (i) the flameless atomic absorption spectrometry (AAS): Hg — by the cold vapour technique, Cd, Cu, Pb and Zn — by electrothermal atomization using a graphite furnace (ii) by the neutron activation analyses (NAA): Hg — with the separation of $^{197\text{m}}\text{Hg}$ after irradiation of samples, whereas Co, Cr, Cs, Ag, Se, Sb, Fe and Zn by non-destructive technique. In bottom sediments the metals (Hg, Cd, Cu, Pb and Zn, Co, Cr, Ni, Mn, V and Fe) were assayed using both the flameless and the flame techniques of AAS.

By the AAS method, the nitric acid extractable fraction of the metals was assayed. This fraction has commonly been recognized as assimilable for aquatic animals. The NAA method was employed for determining total concentrations of all metals, with the exception of mercury, for which the nitric acid extractable fraction was determined as well.

The AAS method required preliminary acid digestion of samples. Suspensions on the membrane filters (FPM) were digested by double extraction with 10 cm^3 of 5 M HNO_3 at 90°C for 2 h in closed teflon vessels. The extract was diluted to 50 cm^3 . Dry suspensions from the trap (80 - 100 mg) and bottom sediments (2 - 3 g) were acid digested for assaying Cd, Cu, Pb and Zn by extraction with 20 cm^3 of 5 M HNO_3 for 4 h at 130°C in closed teflon vessels or in conical flasks under reflux [1]. The extracts were diluted to 50 cm^3 . Mercury was assayed in the wet material. Samples of 100 - 150 mg of suspension or 3 - 4 g of bottom sediments were digested in a mixture of 8 cm^3 of concentrated nitric acid and 4 cm^3 of concentrated sulphuric acid with addition of 0.3 g of potassium persulphate, under conditions as above.

All reagents and inorganic standards of metals were supplied by MERCK (FRG) and were prepared for spectral analysis. The standardization was supplemented by NBS (USA) biological standards, mainly bovine liver. Water used for the prepara-

tion of the reagents, standards and samples was triple distilled, including repeat distillation from a quartz still. The laboratory equipment was made from polypropylene (AZLON, U.K.) and teflon.

The measurements were carried out on a Beckman model 1272 atomic absorption spectrophotometer equipped with the Massmann graphite cuvette and a deuterium lamp for background correction. Mercury was determined on a Laboratory Data Control (USA) double-beam monitor equipped with 30 cm long quartz cuvettes, 5 mm in diameter. Working conditions are reported in papers by Brzezińska [5, 9]. Parallel determinations of the metals in blanks (filters, reagents, water) were run. The spectrophotometric measurements were made in duplicate or triplicate.

For the NAA analysis, 50 mg of suspensions from the traps or 1/4 of a filter with suspension were taken, the same portion of the filter serving as blank. Further procedure was the same as for determination the metals in plankton [10]. In order to determine zinc, it was necessary to separate it from scandium, because ^{46}Sc isotope interferes with zinc determination due to similar gamma ray energy values (1120 and 1115 keV respectively). Consequently the irradiated sample was dissolved in a mixture of concentrated nitric and hydrofluoric acids (3 : 1) taken in an amount required for complete dissolution, the acids were evaporated, 6 M hydrochloric acid was added, evaporated, and the residue was dissolved again in this acid. Zinc was separated on a column filled with an anion exchanger Dowex 1 \times 8 (Cl^-), (100 - 200 mesh) the following fractions being collected: 1) 10 cm³ of 6 M HCl, 2) 10 cm³ of 0.5 M HCl, 3) 30 cm³ of 0.1 M HNO_3 . The third fraction contained zinc, which was assayed on the basis of the 1115 keV photopeak of ^{65}Zn .

Mercury was assayed after Żmijewska [35]. Samples of suspensions and standards (a solution of mercury in nitric acid) were irradiated at a neutron flux of the intensity of $10^3 \text{ cm}^{-2} \cdot \text{s}^{-1}$ for 20 h in a nuclear reactor EWA. Twenty four hours after activation the ampoules containing samples were opened and their contents were transferred to a round-bottom flask with a reflux condenser. One milligram of inactive mercury carrier and 5 cm³ of concentrated nitric acid were added. The mixture was refluxed until dissolution was obtained. After digestion, mercury together with the carrier were extracted with a chlorophorm thionalide solution ($1 \text{ g} \cdot \text{dm}^{-3}$) from a dilute (1 : 3) nitric acid solution. The gamma radiation of ^{197}Hg isotope was measured using a gamma-ray spectrometer with Ge-Li detector. With standards, the acid digestion step was omitted.

All determination by the NAA method were carried out in duplicate or triplicate.

5. RESULTS AND DISCUSSION

The precision of the metal assays in suspensions and bottom sediments is listed in Table 4. It was estimated on the basis of 8 - 10 determinations of a metal in the same sample or on the basis of 2 - 3 determinations in 3 - 10 various samples [14]. In this respect the precision includes only the analytical procedure together with acid digestion and disregards random errors due to sampling and inhomogeneity of the material [8, 10]. The inhomogeneity could be estimated for traps, for which the standard deviation was included, calculated for the whole trap on the basis of mean

Table 4. Estimated precision of trace metal determinations by AAS and NAA in suspended matter and bottom sediments ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight)

Metal and method	FPM		STPM		STPM ^a		Bottom sediments	
	Mean concentration	S.D. [%]						
Cd - AAS	16.2	7.6	2.65	17.0	2.86	5.8	0.10	8.0
Hg - AAS	27.0	4.4	0.55	5.7	0.52	11.5	0.37	5.4
Pb - AAS	164.5	9.8	94.0	10.2	92.0	7.5	56.4	8.7
Cu - AAS	889	6.5	203	13.9	217	10.6	19.9	6.3
Zn - AAS	1219	6.2	158	9.5	169	20.1	101.5	4.1
Zn - NAA	682	8.5	156	26.0				
Fe - AAS							3070	4.5
Fe - NAA	1350	52.0	30670	4.0				
Mn - AAS							45.5	5.2
Se - NAA	1.9	9.0	2.0	43.0				
Cr - NAA	10.0	43.0	84.0	5.0				
Cr - AAS							21.8	9.4
Co - NAA	0.5	9.0	8.2	7.4				
Co - AAS							4.4	6.3
Ag - NAA	2.8	7.0	1.7	30.0				
Sb - NAA	2.5	76.0	5.9	21.0				
Cs - NAA	0.11	18.0	5.4	7.0				
Ni - AAS							68.7	10.7
V - AAS							30.0	5.0

S.D. - standard deviation.

a - Precision for the whole trap calculated from the mean concentrations for separate cells.

metal concentrations in particular cells (Table 4). The inhomogeneity is responsible for high dispersion of data, which in the case of mercury and zinc exceeds twice the dispersion due to random analytical errors. Baumgartner *et al.* [2] studied the causes of the dispersion of the data during sampling bottom sediments and assaying metals in them by NAA method. They found that, due to the inhomogeneity of sediments the classification into sub-samples had major contribution (52 - 93 per cent) to the total random error of the determination of Cr, Sc, Co, Fe and Zn.

The concentration of metals in dry matter of suspensions separated by the filtration of water from the Southern Baltic (FPM), taken in various depths, varied over wide ranges (Table 5). Maximum observed concentrations determined with a probability of 0.95 by using critical values of Student's distribution [34] were twofold higher than mean concentrations for Hg, Cu, Pb, Zn, Cs and Fe, threefold higher for Cd, Co, Cr and Se and four- to fivefold higher for Sb and Ag. Histograms for the metal levels in suspensions (Fig. 3) are indicative of positively skewed distributions of all elements with the exception of Cs, whose distribution was very symmetric according to its physico-chemical properties. The degree of skewness of the distributions is particularly high with Cd, Pb and Cr (skewness coefficients ranging from 0.22 to

Table 5. Statistical evaluation of trace metal content in suspended matter from the Southern Baltic (1977 - 1978)

Metal	FPM [$\mu\text{g}\cdot\text{g}^{-1}$ dry weight]				STPM [$\mu\text{g}\cdot\text{g}^{-1}$ dry weight]				
	Number of samples	Mean conc.	Standard deviation	Observed range	Mode	Number of samples	Mean conc.	Standard deviation	Range
Cs	13 ^a	1.6	0.8	0.1 - 3.1	1.6	3	3.4	0.4	2.9 - 3.7
Se	13 ^a	5.5	5.2	1.6 - 17.1	3.5	3	2.0	0.2	1.8 - 3.1
Co	13 ^a	6.8	6.2	2 - 23	4.9	3	8.2	0.4	7.8 - 8.6
Cd	69	14.8	12.0	1.2 - 54	3.3	13	2.6	0.4	0.1 - 12.2
Hg (AAS)	64	35.8	18.7	2.8 - 85	33.4	18	0.49	0.15	0.32 - 0.69
Hg (NAA)	—	—	—	—	—	3	0.67	0.06	0.62 - 1.40
Ag	13 ^a	36.0	73.7	1.2 - 278	15.0	3	1.7	0.5	1.2 - 2.1
Sb	13 ^a	86.9	117.5	4 - 371	22.2	3	3.9	0.6	3.5 - 4.6
Pb	68	117	81	4 - 303	50	18	71.3	20.6	3.5 - 105
Cr	13 ^a	129	114	23 - 410	33	3	84	5.9	77 - 88
Cu	62	756	443	75 - 1650	511	13	249	46.5	46 - 336
Zn (NAA)	13 ^a	728	428	228 - 1770	468	3	156	16	143 - 174
Zn (AAS)	68	1206	789	320 - 3000	1031	13	150	15	35 - 236
Fe	13 ^a	4318	2661	380 - 10200	3500	3	30670	1500	29000 - 32000

^a - Suspended matter sampled in September 1980.

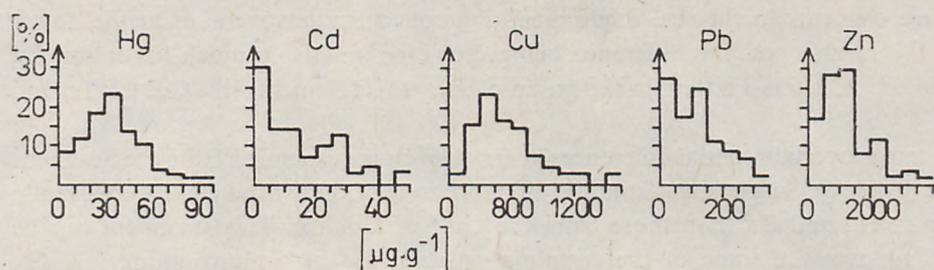


Fig. 3. Histograms of trace metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight) in suspended matter from the Southern Baltic.

Table 6. Average concentration levels of cadmium, mercury, lead, copper and zinc in suspended matter from different regions and water layers in the Southern Baltic

Metal	$\mu\text{g}\cdot\text{dm}^{-3}$			$\mu\text{g}\cdot\text{g}^{-1}$		
	Mean	Standard deviation	Mode	Mean	Standard deviation	Mode
Gulf of Gdańsk						
Cd	0.030	0.022	0.011	13.7	10.5	3.3
Hg	0.052	0.041	0.033	34.0	17.0	34.4
Pb	0.200	0.126	0.060	107	75.4	42.8
Cu	1.23	1.00	0.63	698	428	467
Zn	1.58	0.83	1.12	1096	692	750
Studied area, except the Gulf of Gdańsk						
Cd	0.019	0.012	0.012	17.4	13.5	3.3
Hg	0.035	0.018	0.028	40.7	22.5	30.0
Pb	0.150	0.100	0.140	132	88.0	29.0
Cu	1.39	1.03	1.16	893	391	533
Zn	1.50	1.37	1.20	1437	873	1208
Surface layer (0 to 5 m depth)						
Cd	0.037	0.029	0.012	13.3	9.7	3.3
Hg	0.051	0.041	0.031	36.0	21.8	35.1
Pb	0.228	0.159	0.110	90.4	52.3	33.3
Cu	1.65	1.05	1.31	703	423	650
Zn	1.99	1.36	1.39	1122	885	750
Intermediate layers						
Cd	0.007	0.006	0.011	9.7	8.9	3.6
Hg	0.040	0.024	0.034	37.4	27.2	33.4
Pb	0.080	0.062	0.050	102	66.5	136
Cu	0.59	0.24	0.52	657	260	600
Zn	1.03	0.64	1.07	1299	672	1182
Near-bottom layer						
Cd	0.028	0.020	0.012	20.3	13.9	3.6
Hg	0.045	0.027	0.028	37.0	16.0	33.4
Pb	0.193	0.120	0.150	156	91.0	136
Cu	1.35	1.00	0.73	907	518	600
Zn	1.42	1.01	1.09	1278	741	1182

0.88) thus indicating strong, but irregular effect of accidental, local sources of input of these elements to the sea. Predominating concentrations were, as a rule, lower than the mean ones, the difference being, however, relatively much lower for Cs, Se, Co, Hg, Cu, Zn, Fe than in the group of such toxic elements like Cd, Cr, Pb and Sb.

There are certain spatial differences in metal levels in suspension from the Southern Baltic (Table 6). Suspensions from the off-shore zone of the central coast were usually richer in Hg and Zn than those from the Gulf of Gdańsk. This statement can be extended over the some of the remaining metals, the maximum amounts of Cr, Ag and Fe being found in suspensions taken from the deep regions, i.e. from the Bornholm Deep. The level of Cd and Pb in one gram of dried suspended matter was higher at the bottom than in the upper layers whereas the distribution of Hg, Cu and Zn was rather uniform. Such spatial tendencies manifest themselves in the mean values, elevated strongly by rare cases of sharp local increases of the levels of some metals, whereas the modal values confirm significant regional differences only in the distribution of zinc. The differences with depth occur in the distribution of zinc and lead in the suspended matter taken from surface and intermediate layer.

The estimation of the quantity of a particular metal occurring in the form of suspension in a unit volume of water depends on two factors: the concentration of suspended matter in water and the metal concentration in the suspended matter. As far as the general view on the abundance of all 12 elements studied in suspension of the Baltic Sea is concerned, it is consistent in the two approaches, gravimetric (Table 5) and volumetric (Table 7). Distributions of volumetric concentrations are also positive skewed, but more concentrated.

Owing to relatively high concentrations of suspended matter (Table 1), waters

Table 7. Statistical evaluation of trace metal concentrations ($\mu\text{g}\cdot\text{dm}^{-3}$) in suspended matter (FPM) from the Southern Baltic (1977 - 1980)

Metal	No. of samples	Mean conc.	Standard deviation	Range	Mode
Cs	13	0.009	0.003	0.001 - 0.070	0.005
Se	13	0.011	0.008	0.021 - 0.030	0.005
Co	13	0.012	0.009	0.004 - 0.040	0.008
Cd	69	0.026	0.024	0.001 - 0.110	0.012
Hg	64	0.046	0.029	0.010 - 0.176	0.030
Ag	13	0.077	0.133	0.008 - 0.500	0.027
Sb	13	0.148	0.181	0.019 - 0.650	0.057
Pb	68	0.177	0.106	0.010 - 0.560	0.141
Cr	13	0.285	0.280	0.019 - 0.650	0.100
Cu	62	1.28	1.00	0.16 - 3.40	0.73
Zn ^a	68	1.56	0.99	0.20 - 4.90	1.15
Zn ^b	13	1.83	1.58	0.36 - 6.58	1.45
Fe	13	8.30	3.65	3.6 - 15.8	7.00

a - AAS.

b - NAA.

of the Gulf of Gdańsk are thus richer in Cd than those of the central coast of the Southern Baltic. With reference to the water body, it can be stated that the highest concentrations of Cd, Cu and Pb occur at the bottom than those in the intermediate layers. Among the remaining metals, remarkable is large accumulation of Cr, Sb, Zn and Fe in suspended matter of the western coast.

In spite of a comprehensive literature confined to metals in marine suspensions, it is difficult to find any spatial, and particularly temporal, regularities. It has commonly been accepted that the chemical composition of water, suspensions or marine organisms of polar regions can still provide a measure of natural levels of trace compounds in the environment. To evaluate the state of the pollution of the Baltic we determined trace metals in suspensions from the Admiralty Bay i.e. in the Atlantic Sector of the Antarctic Sea [7]. Harris and Fabris [20] determined Cd, Cu, Pb and Zn in the suspended matter of the Indian Sector of the Antarctic Sea. The suspended matter from the Indian Sector was on an average 4 - 8 times richer in these metals than that from the Admiralty Bay, and twofold richer in Cd, Pb and Zn than suspended matter of the Southern Baltic. Owing to differences in suspended matter concentration, arranging of these regions after abundance of suspended metals becomes just opposite. The mean metal content in suspended matter of the Southern Baltic is very close to the data characterising oceanic conditions for all elements, with the exception of Cd, Ag and Sb, the mean concentrations of which in the Baltic Sea are 2, 5 and 36 times higher, respectively. Abundance of Pb and Zn similar to those of the Southern Baltic were found by Buat-Menard and Chesselet in the Northern Atlantic (cited after [20]), whereas those of copper, and zinc were found by Duinker and Nolting in the North Sea, at the Rhine estuary [12, 13]. Weigel [32, 33] analyzed Baltic seston taken in 1973 from an open sea region. The mean metal contents in one gram of dry matter determined by him were as follows: 5.8 μg Cd, 123 μg Pb, 61 μg Cu and 733 μg Zn. The concentrations of lead and zinc, and even of cadmium, can be regarded as identical if one takes into account that much of suspensions analyzed by us were taken from a zone strongly affected by land. Differences in the estimation of copper are likely to be due to methodological factors, although certain increase in the concentration of this metal in the Baltic Sea due to increasing input of organic matter cannot be ruled out.

Suspended matter collected in traps (STPM) on the bottom of the Gulf of Gdańsk (Table 5) contained less metals than those filtered (FPM) from various water layers (Tables 5 and 6) and more than silts collected from the surface of the bottom (Table 8), with the exception of Co, Cs and Fe, which have a tendency to accumulate at the bottom. It should be mentioned that in the case of iron the contamination from the trap and the bottom may occur.

One of the main purpose of using the traps was collection of a material having the same composition as that of contemporary bottom sediments. Bearing in mind the rate of the sedimentation in the Baltic Sea estimated as 0.5 - 1.5 mm yr^{-1} [3, 31], the material trapped during 1-2 months (Table 7) would correspond to an about 0.1 mm thick layer of sediments. On the other hand, the 1-cm layer of the bottom deposits taken for analysis would be the outcome of approx. 10-yr sedimentation

Table 8. Mean concentrations and standard deviations or concentration ranges of trace metals ($\mu\text{g}\cdot\text{g}^{-1}$) in dry surficial sediments from the Baltic Sea (1976 - 78)

Metal	Gdańsk Basin, 1976		Baltic proper, 1976 (5 samples)	Danish Straits, 1976 (4 samples)	Bosex area [24], 1977 (2 cores)	Gdańsk Basin, 1978		Southern Baltic, 1978	
	silt (26 samples)	sand (21 samples)				silt (3 samples)	sand (4 samples)	silt (4 samples)	sand (5 samples)
Hg	0.19 ± 0.15	0.12 ± 0.10	0.02 - 0.36	0.06 - 0.22	0.14 - 0.19	0.31 ± 0.31	0.19 ± 0.17	0.03 ± 0.01	0.02 ± 0.02
Cd	2.6 ± 1.9	0.83 ± 0.78	0.01 - 0.29	0.08 - 0.15	5.5 - 6.3	0.39 ± 0.16	0.30 ± 0.36	0.50 ± 0.30	0.02 ± 0.01
Co	14.0 ± 4.2	11.9 ± 4.0	2.7 - 15.5	5.8 - 11.7	14 - 16	—	—	—	—
Cr	15.2 ± 9.0	4.0 ± 5.6	24.6 - 67.5	59.6 - 86.3	27 - 31	—	—	—	—
Cu	35.4 ± 12.2	5.6 ± 3.5	2.5 - 43.6	5.7 - 22.4	67 - 75	37.1 ± 22.5	15.0 ± 18.0	23.1 ± 8.3	1.9 ± 0.4
V	35.9 ± 18.4	11.2 ± 12.2	15.4 - 34.3	4.8 - 13.6	—	—	—	—	—
Mn	49.8 ± 16.7	25.2 ± 13.2	19.7 - 285	24.5 - 68.0	200 - 290	250 ± 82	28.8 ± 7.2	470 ± 162	25.5 ± 18.1
Ni	52.7 ± 24.7	34.8 ± 23.5	3.9 - 73.0	10.0 - 127	40 - 52	—	—	—	—
Pb	53.8 ± 20.7	10.4 ± 6.9	24.9 - 99.8	43.0 - 86.8	82 - 130	64.1 ± 5.5	9.2 ± 8.1	22.5 ± 9.7	5.4 ± 2.2
Zn	189 ± 43	28.0 ± 18.0	21.5 - 142	75.6 - 118	375 - 434	183 ± 93	35.4 ± 31.7	93.3 ± 65.6	6.2 ± 6.6
Fe ^d	—	—	—	—	18.0 - 19.4	32.5 ± 2.0	4.8 ± 4.6	9.3 ± 5.0	1.1 ± 0.1

a - $\text{mg}\cdot\text{g}^{-1}$.

of suspended matter which undergoes extensive transformations of their chemical composition. Owing to the vicinity of land and the mouth of the Vistula River, materials collected on the bottom of the southern region the of Gdańsk Deep may be mostly of continental origin; either directly (river-borne suspensions and air-borne particulate matter) or indirectly (coagulation of colloidal fraction [25] and precipitation of new, sparingly soluble compounds upon mixing together fresh water with sea water). The high dynamics of the sea bottom in this region causes that such calculations are rather rough estimates. They can, however, shed light on the fate of metals bound with suspensions (Table 9). The calculations reveal very large amounts of Pb, Zn, Cu, Cr, Cd and Hg deposited annually per 1 m² of the bottom of the Gulf of Gdańsk. A fraction permanently fixed in the bottom constitutes the major part of

Table 9. Approximate deposition rate of particulate metals in the Gulf of Gdańsk, calculated from sedimentation trap data

Rate [mg·m ⁻² yr ⁻¹]	Pb	Zn	Hg	Cr	Cu	Cd
Deposition with STPM	84.8	179	0.58	100	296	3.1
Accumulation in surficial silts	74.1	123	0.23	18	44	0.4
Accumulation as percentage of deposition	87	69	40	18	15	13

lead and zinc transported to the bottom. With the remaining metals, the mobile fraction predominates, whose mechanisms of further redistribution in the sea may be very different. Suess and Erlenkeuser [29], on the basis of own studies and those of Hallberg [19] have shown the enhanced contribution of Cd, Pb, Zn and Cu to the chemical composition of the Baltic bottom sediments, the enhancement being attributed to anthropogenic sources. The anthropogenic contribution for Zn was estimated by them to approx. 100 mg m⁻²yr⁻¹ in Kiel Bight, Bornholm Deep and Gotland Deep. With Cd, Pb and Cu the anthropogenic contribution could not be precisely estimated, but it was of the order of magnitude very close to our estimates listed in Table 9.

Concentrations of trace metals in bottom sediments of the Southern Baltic (Table 8) fall into the ranges reported for various regions of the Baltic Sea [4]. The dispersion of the data is, however, very large and is expressed in coefficients of variation of the order of 80 - 140 per cent for such metals as Hg, Cd, Cr, V, decreasing considerably for Co, Cu, Mn, Ni, Pb and Zn (20 - 60 per cent). Depending on the nature of a sediment, the content of organic matter in it and the site of residence in the sea, there are some regularities in concentration of the metals. Silts are usually much richer in metals than sands, similarly as an increase in organic carbon content leads to increased metal concentrations, in particular of Cu and Hg. Some of the metals, such as Pb, Zn and Cu pass in significant amounts to the bottom sediments in the gulfs, other such as Cd, Cr and Mn are rather transported to the deep sea regions together with the finest fraction of suspended matter. Emission of metals from land-based sources.

manifests itself in locally increased metal levels in silts and sands in which parallel increase of organic matter is noted (Table 2).

On going from suspended matter to bottom sediments there is not only the decrease in concentrations of the majority of studied metals in the series FPM > STPM > silts > sands, but also the significant rearrangements in respect of abundance of particular metals in various components of the marine environment (Table 10). In the water phase, the overwhelming quantities of Cd, Pb, Zn and Hg occur in solution. The contribution of the suspended fraction of the metals in their total concentration in water is the least for cadmium, the highest for copper. Coefficients of enrichment of suspended matter in metals are, however, very high and increase in the same order as the contribution of suspended fraction of metals from Cd (6×10^4) to Cu (4×10^5). Table 10 lists mean values of the coefficients calculated for

Table 10. Characteristics of the average distribution of cadmium, mercury, lead, copper and zinc in the Southern Baltic

Value	Cd	Pb	Zn	Hg	Cu
Concentrations in water [$\mu\text{g} \cdot \text{dm}^{-3}$]					
– mean	0.26	0.89	7.79	0.09	1.89
– modal	0.15	0.39	7.07	0.04	1.86
Particulate metals in the total concentration [%]	8.1	15.8	16.5	28.4	41.3
Coefficients of enrichment					
– FPM	60	140	160	390	400
– STPM	15	82	12	6	110
– silts	1.6	60	19	2.4	17
– sands	0.2	6	3	1.2	2

metal concentrations in suspended matter and water for each sample or from the metal concentrations in bottom sediments and suspended matter and from means of regional concentrations of the metals in filtered water from a particular region. Similar to that in the Southern Baltic affinity of metals to suspended matter in respect of accumulation coefficients and ranking of the elements after their abundance was observed by Naruse *et al.* [22] in the Gulf of Ise at the Pacific coast of Japan. Degradation of organic matter liberates considerable amounts of metal as early as during the first months after their deposition; coefficients of accumulation of Hg and Zn in suspended matter collected in traps were by 1 to 2, orders of magnitude lower than in suspensions filtered from the water, whereas coefficients of accumulation of Pb, Cd and Cu were two- to fourfold lower. Further decrease of the accumulation of the metals, down to the coefficient values of the order of $10^2 - 10^3$, takes place in silts. Carefully rinsed sands from open sea regions practically contain no more fraction of the metals extractable under the given conditions. The presence of some amounts of metals in sands from the Gulf of Gdańsk and the Puck Bay is always accompanied by a remarkable content of organic matter (Tables 2 and 8).

The ratio of metal concentrations in various kinds of suspended matter to their

concentrations in silts (Table 10) reveals a significant difference in the rate of the chemical transformation of organic matter in suspensions. Of the 5 metals considered, Hg is released from suspensions at the highest rate, followed by Cu and Cd. On the other hand, releasing of Zn and Pb occurs considerably less efficiently. The facility and efficiency with which mercury returns to marine environment provide serious ecological threat.

The rank order of the metal concentrations in suspended matter and bottom sediments is the outcome of a number of factors. In the Southern Baltic the rank order is as follows:

FPM	Fe > Zn > Cu > Cr > Pb > Sb > Ag > Hg > Cd > Co > Se > Cs
STPM	Fe > Cu > Zn > Cr > Pb > Co > Sb > Cs > Cd > Se > Ag > Hg
Bottom sediments (Gdańsk Basin)	Fe > Zn > Pb > Ni > Mn > V > Cu > Cr > Co > Cd > Hg
Bottom sediments (Southern Baltic)	Fe > Mn < Zn > Cr > Ni > V > Cu > Pb > Co > Cd > Hg
Earth crust	Fe > Mn > V > Cr > Ni > Zn > Cu > Co > Pb > Cs > Sb > Cd > Hg > Se > Ag

As far as the bottom sediments are concerned the rank order resembles much the natural abundance of the elements in the lithosphere (after Taylor, cited after Polański and Smulikowski [27]), and in the case of the so-called heavy metals it is identical. The main difference is that in the Gdańsk Basin certain shift of Zn and Pb occurred (in the open sea zone the shift of Zn) to the group of more abundant elements. Investigations of the Baltic bottom sediments carried out by Niemistö and Tervo [23] as well as by Olausson *et al.* (cited after [23]) have shown similar order of occurring elements to the natural one, with increasing tendency of occurring of Zn and Cu in the Northern Baltic, of Zn and Pb in the open sea and of Zn, Pb and Cu in the coastal zone. Slight differences in ordering the elements in the Baltic sediments after various authors can be due to regional conditions, they usually fall, however, within the dispersion due to random errors of analyses (Table 4). Taking into account all the data on trace metal contents in the sediments of the Baltic Sea it can be stated that absolute concentrations of Zn, Pb, Cd and Hg in the Baltic sediments are higher than the mean concentrations of these metals in the unpolluted regions [27]. The concentrations of all remaining metals (Fe, Mn, Cr, Ni, Co, V) are lower in the Baltic than in the clean regions the difference being so large, that even accounting for the metal fraction built in the crystal lattice of loamy minerals does not affect this estimate. The ordering of trace metals in suspended matter and bottom sediments of the Southern Baltic seems to be strongly influenced by high accumulation of metals in marine organisms, specially Cu, Pb, and Zn. It is also in accordance with the stability constants of these metals with humic and fulvic acids and proteins [18, 25].

AKNOWLEDGEMENTS

The investigations were carried out under three projects: R-18 "Protection of the Baltic Sea against Pollution", co-ordinated by the Ministry of Administration and Environment Protection, MR.I.15 "Fundamentals of economics in the marine environment", co-ordinated by the Institute of Oceanology of the Polish Academy of Sciences, and PR.05.532.13 "Hydrological, chemical and physical processes affecting pollution of the Baltic Sea" supported by US EPA.

The authors thanks are due to Dr Joanna Zachowicz and to Mr. Grzegorz Okołowicz, M. Sc., for characterization of the biological composition of suspended matter collected in traps; to Mrs Aleksandra Żelechowska, M. Sc., for carrying out determinations on CHN analyzer and to Mrs Urszula Kępińska, M. Sc., for determination of geological features of the materials.

REFERENCES

1. Andrulowicz, E., J. E. Portmann, *Determination of metal content of sediments in relation to dumping and discharge control*. ICES, CM. 1975/E: 22.
2. Baumgartner, D. J., D. E. Cawfield, J. B. Carkin, L. M. Male, *Variation in metal content of marine sediments used for assessment of environmental effects*. *Thalassia Jugosl.*, 13, 1977, 3/3, p. 253 - 264.
3. Bojanowski, R., E. Kochlewska, D. Skiba, *Determination of Pb-210 in bottom sediments of the Baltic Sea for geochronological purposes*. *Studia i Mater. oceanol. KBM PAN*, 1977, 19, p. 123 - 127 [in Polish].
4. Brüggemann, L., *Heavy metals*. In: *Assessment of the effects of pollution on the natural resources of the Baltic Sea*. ICES/STWG Editorial Board, 1980 [draft], p. 112 - 129.
5. Brzezińska, A., *The run-off of cadmium, copper, lead and zinc in the waters of the river Vistula*. *Studia i Mater. oceanol. KBM PAN*, 25, *Chemia Morza* (3), 1978/79, p. 99 - 111 [in Polish].
6. Brzezińska, A., *On the determination of cadmium, copper, lead and zinc in marine particulate matter by electrothermal atomization*. *Oceanologia* [this issue].
7. Brzezińska, A., R. Samp, *A preliminary study of the occurrence of trace metals in Admiralty Bay on King George Island*. *Studia i Mater. oceanol. KBM PAN*, 34, *Chemia Morza* (4), 1981, p. 113 - 126 [in Polish].
8. Brzezińska, A., A. Trzosińska, *Interlaboratory studies on the determination of trace metals in the marine environment*. *Chem. Anal.* 28, 1983, 1 - 2, p. 121 - 131.
9. Brzezińska, A., *The occurrence of mercury in the Southern Baltic Sea*. *Oceanologia* [this issue].
10. Brzezińska, A., A. Trzosińska, W. Żmijewska, L. Wódkiewicz, *Trace metals in some organisms from the Southern Baltic*. *Oceanologia* [this issue].
11. Cormody, D. J., J. B. Pearce, W. E. Yasso, *Trace metals in sediments of New York Bight*. *Mar. Poll. Bull.*, 4, 1973, 9, p. 132 - 135.
12. Duinkier, J. C., R. F. Nolting, *Dissolved and particulate trace metals in the Rhine Estuary and the Southern Bight*. *Mar. Poll. Bull.*, 8, 1977, p. 65 - 71.
13. Duinkier, J. C., *Processes affecting the behaviour of contaminants (metals and organochlorines) during estuarine mixing and in coastal areas, with particular reference to the Southern North Sea*. ICES, CM 1980/E: 34.
14. Eckschlager, K., *Błędy w analizie chemicznej*. PWN, Warszawa 1974, p. 137 - 139.
15. Erlenkeuser, H., E. Suess, H. Willkomm, *Industrialization affects heavy metal and carbon isotope concentrations in recent Baltic Sea sediments*. *Geochim. et cosmochim. Acta*, 38, 1974, p. 823 - 842.
16. Gordeyev, V. V., A. P. Lisicin, *Mikroelementy*. In: *Khimia okeana. 1: Khimia vod okeana*. Eds O. K. Bordovski and V. I. Iwanenkov, "Nauka", Moskva 1979, p. 337 - 375.

17. Grasshoff, K., *The hydrochemistry of landlocked basins and fiords*. In: *Chemical oceanography*, 2nd edition, Vol. 2. Eds J. P. Riley and G. Skirrow, Academic Press, 1975, p. 523 - 525.
18. Groot, A. J. de, W. Salomons, E. Allersma, *Processes affecting heavy metals in estuarine sediments*. In: *Estuarine chemistry*. Eds J. D. Burton and P. S. Liss, Academic Press, 1976, p. 131 - 157.
19. Hallberg, R. O., *Paleoredox conditions in the Eastern Gotland Basin during the recent centuries*. Merentutkimuslait. Julk./Havsforkningsinst. Skr., 238, 1974, p. 3 - 16.
20. Harris, J. E., G. J. Fabris, *Concentrations of suspended matter and particulate cadmium, copper, lead and zinc in the Indian Sector of the Antarctic Ocean*. Mar. Chem., 8, 1979, 2, p. 163 - 179.
21. Joanny, M., M. Chaussepied, F. Corre, *Métaux-traces dans les sédiments marins. Présentation des résultats d'une calibration internationale*. Centre National Pour L'exploitation des Océans, Centre Océanologique de Bretagne, Brest 1980.
22. Naruse, Y., R. Ando, F. Tsuchiyama, H. Sugiyama, *Adsorption of heavy metals on suspended matter*. Bull. Jap. Soc. Sc. Fish., 45, 1979, 11, p. 1417 - 1421.
23. Niemistö, L., V. Tervo, *Preliminary results of heavy metal contents in some sediment cores in the Northern Baltic Sea*. XI Conf. Baltic Oceanogr., Rostock 1978, paper No 52.
24. Niemistö, L., V. Tervo, *Preliminary results of some harmful substances in sediments of the Bosex area*. XI Conf. Baltic Oceanogr., Rostock, 1978, paper No 53.
25. Pempkowiak, J., *Humic substances in the bottom sediments of the Baltic Sea*. Polish Academy of Sciences, Department of Oceanology, Sopot 1977, Ph. D. thesis [in Polish].
26. Pempkowiak, J., G. Kupryszewski, *The input of organic matter to the Baltic from the Vistula River*. Oceanologia, 1980, 12, p. 79 - 95.
27. Polański, A., K. Smulikowski, *Geochemia*. Wyd. Geologiczne, Warszawa 1969, p. 60.
28. Rózdżyński, K., *Bottom sedimentation trap*. Studia i Mater. oceanol. KBM PAN, 31, Miernictwo Oceanograficzne (3), 1980, p. 317 - 323 [in Polish].
29. Suess, E., H. Erlenkeuser, *History of metal pollution and carbon input in the Baltic Sea sediments*. Meyniana 27, 1975, p. 63 - 75.
30. Soutar, A., S. A. Kling, P. A. Crill, E. Duffrin, *Monitoring the marine environment through sedimentation*. Nature, 266, 1977, p. 136 - 139.
31. Voipio, A., L. Niemistö, *Sedimentological studies and their use in pollution research*. ICES, C.M. 1979/C: 46.
32. Weigel, H. P., *Atomabsorptionmessungen von Blei, Cadmium, Kupfer, Eisen und Zink im Seston der Ostsee*. Helgoländer wiss. Meeresunters., 28, 1976, p. 200 - 216.
33. Weigel, H. P., *On the distribution of particulate metals, chlorophyll and seston in the Baltic Sea*. Mar. Biol., 44, 1977, p. 217 - 222.
34. Zar, J. H., *Biostatistical analysis*. Prentice Hall Inc., Biological Science Series, 1974.
35. Żmijewska, W., *Determination of mercury in biological material by neutron activation analysis*. Chem. Anal., 21, 1976, 4, p. 853 - 861.