The determination of Cu, Pb, Cd and Zn in the southern Baltic water, suspension and sediments *

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Trace metals
Baltic Sea

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Abstract

This paper presents the results of the determination of Cu, Pb, Cd, and Zn in the solution and suspension of the southern Baltic water, which were obtained by dc anodic stripping voltammetry (ASV) and in sediments by atomic absorption spectroscopy (AAS) technique. The respective mean total concentrations of analysed metals in the sea water and suspension were: Cu -0.58 ± 0.10 $\mu g \cdot dm^{-3}$; Pb -0.57 ± 0.14 $\mu g \cdot dm^{-3}$; Cd -0.09 ± 0.02 $\mu g \cdot dm^{-3}$, and Zn -13.0 ± 2.5 $\mu g \cdot dm^{-3}$. 68% of Pb and Cd appear in the suspension form while 75% of Cu and 85% of Zn in the soluble form. On the other hand the mean concentrations of analysed metals in sediments amounted to: Cu -57 ± 7 $\mu g \cdot g^{-1}$ dry weight; Pb -209 ± 54 $\mu g \cdot g^{-1}$ dry weight; Cd -4.3 ± 0.5 $\mu g \cdot g^{-1}$ dry weight and Zn -273 ± 20 $\mu g \cdot g^{-1}$ dry weight, respectively.

1. Introduction

The mean salinity of the surface sea water of the southern Baltic varies from 7‰ to 8‰, while in the case of the deep water it fluctuates from 10‰ to 16‰ (Brügmann, 1980; Głowińska, 1963; Kullenberg, 1981). The seasonal changes of salinity of sea water of the coastal areas are also caused by the supply of large quantities of river water which contain large amounts of Cu, Cd, Pb, and Zn, both in suspension and soluble forms. The elements

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in suspension exhibit different degrees of binding and the forms which are insoluble in river water may behave quite differently after being transported into the sea environment (Bojanowski, 1981). This last statement concerns mostly independent mineral phases (characterised by small stability) and ions bounded on the surface of suspension particles by weak adsorption forces (Bojanowski, Samuła-Koszałka, 1979).

2. Methods

2.1. Reagents and solutions

All acids and other reagents were of Suprapur quality (Merck), except for acetate buffer (pH = 4.5) which was prepared from analytical grade reagents.

Doubly distilled mercury was used to fill a hanging mercury drop electrode (Kemula, Kublik, 1958).

Nitrogen was purified by bubbling through vanadium solution with zinc amalgam.

All glassware used was rinsed first with 3M HCl and 7M HNO_3 and then with doubly distilled water before usage.

Stock solutions (1 $mg \cdot dm^{-3}$) of Cu(II), Cd(II), Pb(II), and Zn(II) were prepared by diluting commercial standards (Merck, Titrisol) with 0.1 M HNO_3. From these solutions working standards of suitable concentration were prepared by dilution with doubly distilled water.

2.2. Sea water sampling and analysis

Water samples for metal analysis were collected in acid-washed polyethylene bottles in July 1980 in different places of the southern Baltic (Fig. 1). Immediately after being brought into the laboratory the sea water was

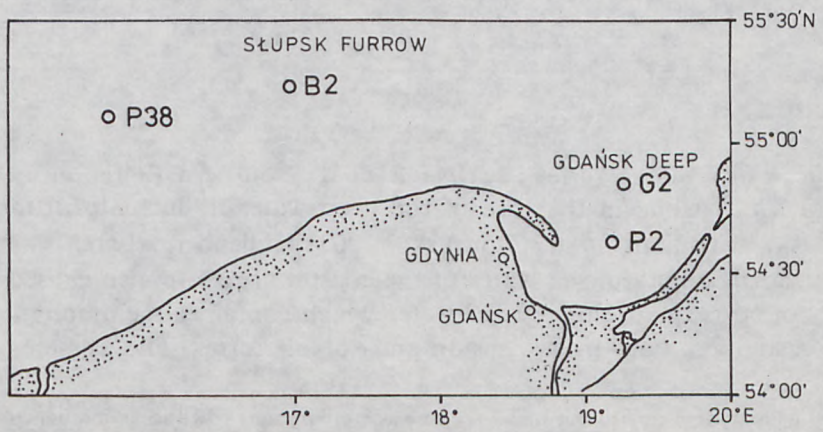

Fig. 1. Location of the sampling stations

filtered through a Sartorius' celullose acetate filter (pore size 0.45 μm, presoaked in 3M HCl and 1M HNO_3). The filtered samples of volume 250 cm^3 were acidified with 0.25 cm^3 of concentrated HNO_3 and stored until analysed. Samples of 10 cm^3 were deaerated by purging with high purity nitrogen for 10 minutes and analysed for Cd, Pb, Cu, and Zn by dc anodic stripping voltammetry (ASV) – *Polarograph type OH-102*, Radelkis, Hungary (Bolałek, 1981; Davidson, Withfield, 1977; Kremling, 1973; Nürnberg, Valanta, 1975; Topping, 1974; Trens, 1972). The experimental conditions which were used by us are presented in Table 1. Quantitation was performed by the method of double standard addition. The precision of the metal determination was between 5 and 10%. The blanks for Cu, Pb, and Zn constituted less than 20% of the value in the sea water samples, whereas for Cd – less than 35%.

The samples of used suspensions were mineralized by mixed acids: 6M HCl and 40% HF in a Teflon autoclave according to the procedure given by Skwarzec *et al.* (1984).

Table 1. The conditions of determination of trace metals in sea water and suspension using dc anodic stripping voltammetry (ASV) technique (all potential relative to the saturated calomel electrode SCE)

Parameters	Dissolved form				Suspended form			
	Cu	Pb	Cd	Zn	Cu	Pb	Cd	Zn
Deposition potential [V]	−1.0	−1.0	−1.0	−1.2	−0.8	−0.8	−0.8	−1.0
Peak potential [V]	−0.1	−0.35	−0.6	−0.95	0.1	−0.28	−0.42	−0.75
Electrodeposition time [min]	5	5	5	3	5	5	5	3
pH solution	2	2	2	4.5*	4.5*	4.5*	4.5*	4.5*
Scan-rate [V/min]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

* Solution buffered with acetate buffer

2.3. Sediment sampling and analysis

Samples of sediments were taken in the southern Baltic using a long cover. The samples were dried at 110°C and homogenized prior to analysis. The mineralization of 2 g sediment (dry weight) was performed in a platinum flask with 20 cm^3 of 30% H_2O_2, 10 cm^3 of concentrated HNO_3, 20 cm^3 of 40% HF, and 20 cm^3 of 70% $HClO_4$. After evaporation the dry residue was converted into chloride salts which were dissolved in 100 cm^3 of 0.1M HCl. Cd, Cu, Pb, and Zn content determinations were performed with an *Instrumentation Laboratory IL-353* atomic absorption spectrophotometer. All determinations were carried out using the air-acetylene absorption technique. The calibration of the apparatus was done using mixed standards which contained from 0.02 to 5 mg of a given element *per* 1 dm^3.

Table 2. Comparison of concentrations of some metals [$\mu g \cdot g^{-1}$ dry weight] in the sediment sample provided by the International Laboratory of Marine Radioactivity IAEA* with our data using atomic absorption spectroscopy (AAS) technique. Mean and standard deviation are given

Sample	Zn	Cd	Cu	Pb
Sediment ($n = 5$)	484 ± 16	12.5 ± 0.5	78 ± 2.6	136.7 ± 8.3
IAEA certified values	437	11.20	72.42	119.8

* These values are given in a Report IAEA No 24 *Intercomparison of trace element measurements in marine sediment sample*, SD-N-1/2, June 1985

The accuracy and precision of this method were satisfactory as estimated by an analysis of the standard material (sample code SD-N-1/2) (Table 2).

3. Results and discussion

3.1. Copper

The total mean concentration of Cu in the southern Baltic water amounts to 0.58 ± 0.10 $\mu g \cdot dm^{-3}$. The results of individual analyses fluctuate between 0.35 and 1.35 $\mu g \cdot dm^{-3}$ (Table 3). They are about 3 times lower than the results obtained by Brzezińska (1978a, b), but one may say that they are consistent with the results obtained by Schmidt (1980), Kremling and Petersen (1984) as well as Brügmann (1984) for the southern Baltic. In the places we investigated about 25% of the total amount of Cu was bound to the suspension, but the greatest share of the suspension form was obtained for the waters taken at station B-2 (about 42%). The highest concentration of Cu – reaching 344 $\mu g \cdot g^{-1}$ – was also noticed there (Table 3). The increase of Cu content in the suspension is probably connected with its bioaccumulation by mesozooplankton (Szefer, 1985; Szefer *et al*, 1985) as well as its complexing process by organic matter (Kremling *et al*, 1981) and by humic substances (Pempkowiak, 1983). That is why the concentrations of Cu in the suspension are much higher than in bottom sediments (Table 4).

3.2. Lead

The mean total concentration of Pb in the southern Baltic water amounts to 0.57 ± 0.14 $\mu g \cdot dm^{-3}$ and the results of particular analysis range from 0.20 to 2.09 $\mu g \cdot dm^{-3}$. Those results correspond well with the results obtained previously from the different zones of the southern Baltic by Brügmann (1974a, b, 1984), Brzezińska (1978a, b) and Bojanowski (1981). Unlike in case of Cu, one may observe differences in the contents of Pb in particular zones.

Table 3. The concentration of trace metals at four stations of the southern Baltic (n = number of individuals)

Station	Depth [m] and concentration	Salinity [‰]	Dissolved form		Suspended form			Total concentration	EF in suspension*
			[μg·dm^{-3}]	[%]	[μg·dm^{-3}]	[%]	[μg·g^{-1} dry weight]	[μg·dm^{-3}]	[·10^5]
1	2	3	4	5	6	7	8	9	10
			Copper						
P-2	surface layer 0–10	7.71– 7.68	0.36±0.03	74	0.13±0.05	26	102	0.49±0.03	
(Gulf of Gdańsk)	deeper layer 70–78	8.48–10.73	0.42±0.04	79	0.12±0.04	21	111	0.56±0.07	2.8
	mean concentration (n = 12)		0.38±0.05	76	0.12±0.04	24	105	0.50±0.07	
	concentration range		0.33–0.46		0.07–0.19			0.40–0.63	
G-2	surface layer 0–20	7.77– 7.78	0.34±0.02	63	0.20±0.04	37	167	0.54±0.06	
(Gdańsk Deep)	deeper layer 90–105	12.01–12.82	0.33±0.05	45	0.40±0.07	55	344	0.73±0.09	7.6
	mean concentration (n = 20)		0.34±0.07	58	0.25±0.06	42	259	0.59±0.09	
	concentration range		0.26–0.66		0.07–0.52			0.40–0.91	
B-2	surface layer 0–20	7.89– 7.92	0.63±0.15	87	0.09±0.03	13	72	0.72±0.16	
(Słupsk Furrow)	deeper layer 70–89	11.51–14.01	0.61±0.12	86	0.10±0.03	14	66	0.71±0.14	1.6
	mean concentration (n = 18)		0.64±0.20	89	0.08±0.04	11	103	0.72±0.21	
	concentration range		0.33–1.15		0.02–0.20			0.38–1.35	
P-38	surface layer 0–10	8.01– 8.02	0.39±0.14	76	0.12±0.01	24	92	0.51±0.15	
(Bornholm Basin)	deeper layer 70–88	15.56–17.59	0.42±0.09	82	0.09±0.02	18	56	0.51±0.08	2.0
	mean concentration (n = 14)		0.41±0.07	79	0.11±0.02	21	80	0.52±0.06	
	concentration range		0.21–0.06		0.09–0.13			0.35–0.75	
	mean concentration (n = 64)		0.44±0.08	75	0.14±0.04	25		0.58±0.10	

1	2	3	4	5	6	7	8	9	10
			Cadmium						
P-2	surface layer 0–10	7.71–7.68	0.03±0.01	33	0.06±0.01	67	42	0.09±0.02	
(Gulf of Gdańsk)	deeper layer 70–78	8.48–10.73	0.03±0.01	33	0.06±0.03	67	84	0.09±0.03	25
	mean concentration ($n = 12$)		0.02±0.01	33	0.06±0.02	67	74	0.09±0.02	
	concentration range		0.02–0.03		0.03–0.09			0.06–0.12	
G-2	surface layer 0–20	7.77– 7.78	0.03±0.01	33	0.06±0.01	67	48	0.09±0.01	
(Gdańsk Deep)	deeper layer 90–105	12.01–12.82	0.03±0.01	43	0.04±0.01	57	34	0.07±0.01	22
	mean concentration ($n = 20$)		0.02±0.01	33	0.06±0.02	67	66	0.09±0.02	
	concentration range		0.02–0.03		0.03–0.10			0.06–0.13	
B-2	surface layer 0–20	7.89–7.92	0.02±0.01	25	0.06±0.02	75	67	0.08±0.01	
(Słupsk Furrow)	deeper layer 70–89	11.51–14.01	0.03±0.01	43	0.04±0.01	57	61	0.07±0.01	23
	mean concentration ($n = 18$)		0.03±0.01	38	0.05±0.01	62	68	0.08±0.01	
	concentration range		0.02–0.06		0.04–0.06			0.07–0.08	
P-38	surface layer 0–10	8.01– 8.02	0.02±0.01	25	0.06±0.01	75	44	0.08±0.02	
(Bornholm Basin)	deeper layer 70–88	15.56–17.59	–	–	–	–	–	–	22
	mean concentration ($n = 14$)		0.02±0.01	25	0.06±0.02	75	44	0.08±0.02	
	concentration range		0.01–0.02		0.01–0.07			0.03–0.09	
	mean concentration ($n = 64$)		0.03±0.01	32	0.06±0.02	68		0.09±0.02	

1	2	3	4	5	6	7	8	9	10
			Lead						
P-2	surface layer 0–10	7.71– 7.68	0.10±0.01	50	0.10±0.04	50	75	0.20±0.06	
(Gulf of Gdańsk)	deeper layer 70–78	8.48–10.73	0.16±0.04	41	0.23±0.07	59	323	0.39±0.08	17
	mean concentration ($n = 11$)		0.14±0.03	44	0.18±0.06	56	240	0.32±0.11	
	concentration range		0.09–0.20		0.09–0.35			0.20–0.46	
G-2	surface layer 0–20	7.77– 7.78	0.13±0.02	39	0.20±0.08	61	167	0.33±0.06	
(Gdańsk Deep)	deeper layer 90–105	12.01–12.82	0.13±0.02	16	0.82±0.21	84	563	0.95±0.29	63
	mean concentration ($n = 18$)		0.15±0.04	16	0.80±0.29	84	952	0.95±0.18	
	concentration range		0.11–0.28		0.11–1.98			0.26–2.09	
B-2	surface layer 0–20	7.78– 7.92	0.14±0.05	24	0.44±0.13	76	492	0.58±0.09	
(Słupsk Furrow)	deeper layer 70–89	11.51–14.01	0.17±0.02	39	0.26±0.11	61	221	0.43±0.14	18
	mean concentration ($n = 19$)		0.14±0.04	29	0.35±0.14	71	245	0.49±0.16	
	concentration range		0.07–0.49		0.03–0.44			0.45–0.73	
P-38	surface layer 0–10	8.01– 8.02	0.13±0.01	27	0.34±0.09	73	283	0.47±0.08	14
(Bornholm Basin)	deeper layer 70–88	15.56–17.59	0.23±0.05	40	0.35±0.08	60	219	0.58±0.11	
	mean concentration ($n = 13$)		0.18±0.05	35	0.34±0.11	65	251	0.52±0.14	
	concentration range		0.09–0.38		0.34–0.35			0.45–0.73	
	mean concentration ($n = 61$)		0.18±0.03	32	0.39±0.12	68		0.57±0.14	

1	2	3	4	5	6	7	8	9	10
			Zinc						
P-2	surface layer 0–10	7.71– 7.68	9.7± 1.4	89	1.8±0.5	11	1466	11.5± 0.4	
(Gulf of Gdańsk)	deeper layer 70–78	8.48–10.73	9.7± 0.5	84	1.2±0.4	16	1003	10.9± 1.0	1.2
	mean concentration ($n = 12$)		9.2± 1.3	88	1.3±0.6	12	1122	10.5± 1.5	
	concentration range		7.4–11.0		0.5–2.8			7.9–11.8	
G-2	surface layer 0–20	7.77– 7.78	14.1±3.4	93	1.1±0.2	7	897	15.1± 3.0	
(Gdańsk Deep)	deeper layer 90–105	12.01–12.82	17.5± 0.4	88	2.5±0.7	12	1832	20.0± 1.0	1.3
	mean concentration ($n = 19$)		15.0± 5.2	89	1.7±0.5	11	1935	16.8± 5.4	
	concentration range		9.2–24.0		0.6–3.9			11.4–25.8	
B-2	surface layer 0–20	7.89– 7.92	9.5± 4.1	75	3.3±1.1	25	2756	12.8± 3.9	
(Słupsk Furrow)	deeper layer 70–89	11.51–14.01	10.2± 2.8	76	3.2±0.4	24	3170	13.4± 2.3	3.0
	mean concentration ($n = 17$)		10.6± 4.0	79	2.8±0.9	21	3203	13.4± 2.8	
	concentration range		4.6–19.4		0.3–3.7			5.9–23.1	
P-38	surface layer 0–10	8.01– 8.02	12.2± 3.4	89	1.5±0.1	11	1178	13.7± 3.5	
(Bornholm Basin)	deeper layer 70–88	15.56–17.59	6.2± 1.6	71	2.4±0.6	29	2361	8.6± 1.8	1.9
	mean concentration ($n = 14$)		9.2±3.0	83	2.0±0.3	17	1769	11.2±3.3	
	concentration range		4.6–15.7		1.4–3.0			6.6–17.3	
	mean concentration ($n = 62$)		11.1± 2.6	85	1.9±0.5	15		13.0± 2.5	

* Trace metal enrichment factors in suspension

Table 4. The mean levels of metals in the sediment (segment 0–6 cm) taken from the southern Baltic. All the metal levels are given in $\mu g \cdot g^{-1}$ dry weight basis ($\pm$1.S.D; $n = 6$)

Station	Cu	Pb	Cd	Zn
P-2 (Gulf of Gdańsk)	67±3	256±38	4.4±0.5	264±19
G-2 (Gdańsk Deep)	58±2	168±25	3.7±0.4	275±20
B-2 (Słupsk Furrow)	56±2	145±21	4.3±0.4	285±20
P-38 (Bornholm Basin)	47±2	268±39	4.6±0.5	267±19

Its highest concentrations were noticed in the samples of sea water taken at station B-2 (0.95 ± 0.18 $\mu g \cdot dm^{-3}$) while the lowest at station P-2 (0.32 ± 0.11 $\mu g \cdot dm^{-3}$, Table 3). Generally it may be stated that the concentration of Pb in the bottom layer is little higher than in the surface layers. It becomes obvious if we take into consideration both the sedimentation processes and the possibility of Pb desorption from the bottom sediments to waters. This metal gets to the water mostly from the air over of the southern Baltic (Brzezińska, Garbalewski, 1980) and remains there in the form of suspension (68%—Table 3) showing correlation only with the concentration of the suspension (Bojanowski, Samuła-Koszałka, 1976).

The contents of Pb in the suspension range from 240 to 952 $\mu g \cdot g^{-1}$ and the values of Pb enrichment factors in the suspension are largest among the analysed metals and amount from 1.5 to $6.3 \cdot 10^6$ (Table 3).

3.3. Cadmium

The mean total concentration of Cd in the solution and suspension amounts to 0.09 ± 0.02 $\mu g \cdot dm^{-3}$ and generally ranges from 0.03 to 0.13 $\mu g \cdot dm^{-3}$. This metal appears mainly in the suspended form (68% —Table 3). A considerable content of Cd in suspension (from 34 to 74 $\mu g \cdot g^{-1}$) can probably be caused by the accumulation of this metal by marine organisms (Skwarzec *et al*, 1984). The value of Cd enrichment factor in suspension is about $2 \cdot 10^6$ (Table 3).

3.4. Zinc

Zn shows the highest values of concentrations of all the analysed metals. The mean concentration of this metal for the investigated regions of the southern Baltic is about 13.0 ± 2.5 $\mu g \cdot dm^{-3}$ and the results of particular determinations range vary from 5.9 to 23.0 $\mu g \cdot dm^{-3}$. Those results are in a good agreement with the results obtained previously for different zones of the southern Baltic, by Kremling (1973), Kremling and Petersen (1978), and Brügmann (1974a, b). Only 15% of Zn appears in the suspension where its content is from 897 to 3203 $\mu g \cdot g^{-1}$, while in the bottom sediments it is never higher than 285 $\mu g \cdot g^{-1}$ (Table 3 and 4). Zn is easily accumulated by

mesozooplankton where its concentration coefficient reaches 10^5 (Szefer, 1985; Szefer *et al*, 1985). Comparing Zn with all previously analysed metals it may be observed that its affinity to suspension is low (Table 5) and its values of the enrichment factor in suspension are about 1.2 to $3.0 \cdot 10^5$ (Table 3).

Table 5. The selectivity factors* (SF) for Zn, Pb, Cu, and Cd in suspensions from the southern Baltic (calculated using the levels of metal expressed on the wet weight basis)

Station	Cu/Pb	Cu/Zn	Cu/Cd	Pb/Zn	Pb/Cd	Zn/Cd
P-2 (Gulf of Gdańsk)	0.32	2.28	0.16	7.21	0.50	0.07
G-2 (Gdańsk Deep)	0.14	6.28	0.37	45.55	2.67	0.06
B-2 (Słupsk Furrow)	0.05	0.47	0.08	9.48	1.50	0.16
P-38 (Bornholm Basin)	0.14	1.28	0.09	9.04	0.63	0.07

* Dividing the levels of two metals (M_1/M_2) for suspension by the determined ratio of M_1/M_2 in the sea water we obtain the value of SF which is the index of certain preference in favour of M_1

4. Conclusions

On the basis of the results obtained it can be stated that Pb and Cd appears mostly in the suspended form whereas Cu and Zn appear mostly in the dissolved form. The partion coefficients of metals between the suspension and solution decrease in the sequence: Pb > Cd > Cu > Zn, while metals enrichment factors in the suspension range from $1.2 \cdot 10^5$ to $6.3 \cdot 10^6$ and diminish in the order: Pb > Cd > Cu > Zn.

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