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SPATIAL ARRANGEMENT OF HEAVY METALS IN THE DAM-RESERVOIR SEDIMENTS IN THE CONDITIONS OF ANTHROPOMIXION

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FORMY SPECJACYJNE METALI CIĘŻKICH W OSADACH DENNYCH ZBIORNIKA ZAPOROWEGO W WARUNKACH ANTROPOMIKSJI

Wykazano, że rozmieszczenie metali ciężkich w osadach dennych badanego zbiornika jest silnie zróżnicowane przestrzennie. Stanowi ono wypadkową ruchów wody, stopnia troficzności, procesu biokumulacji oraz antropopresji. Jako wynik specyficznego ruchu wody transportującego biomasę wewnątrz ekosystemu, wykształciła się strefa, w której kumulacja metali ciężkich jest zintensyfikowana. Strefa ta (o powierzchni około 150 ha) została w przybliżeniu zlokalizowana. Znajduje się on w północno-zachodniej części zbiornika a maksymalne stężenia oznaczanych metali w tym rejonie wynoszą: dla kadmu 30 mg/kg, dla niklu 55 mg/kg, dla chromu 130 mg/kg, dla ołowiu 160 mg/kg, dla miedzi 1000 mg/kg, dla cynku 1300 mg/kg. Zlokalizowanie stref podwyższonego zanieczyszczenia ma znaczenie z punktu widzenia ewentualnych zabiegów rekultywacyjnych dla poprawienia jakości wody w zbiorniku oraz ogólnego stanu ekosystemu.

Summary

The results of research on the role of water mass movements arising as a result of anthropopresion, in heavy metals arrangement in sediments have been presented on the example of dam reservoir in Rybnik. The carried out thermo-visual measurements of the thermally polluted Rybnik dam-reservoir revealed spatial diversification of water temperature. The zones of diverse dynamics of water mass movements have been shown, including the zone of intensive water flow and the zone of stagnation. It has been proved that the values of these concentrations are strongly diverse in space. This is the result of the eutrophication grade, bioaccumulation process, and anthropomixtion. As a result of specific water movement, which transports biomass inside the ecosystem, the zone, developed in which the transfer of heavy metals to the sediments is intensified. This zone of about 150 ha in area was located. The maximum concentrations of metals described in this area are: for cadmium – 30 mg/kg, for nickel – 55 mg/kg, for chromium – 130 mg/kg, for lead – 160 mg/kg, for copper – 1000 mg/kg, for zinc – 1300 mg/kg. In the case of mobile fractions, potentially capable of freeing themselves from sediments the concentration values are: for cadmium – 14 mg/kg, for nickel – 15 mg/kg, for chromium – 4 mg/kg, for lead – 8 mg/kg, for copper – 100 mg/kg, for zinc – 600 mg/kg. The participation of mobile fractions of metals in their total quantity was: for zinc – 46%, for cadmium – 46%, for nickel – 27%, for copper – 10%, for lead – 5%, for chromium – 3%. The relationship between the total concentrations of metals likewise their mobile forms and the content of organic matter in sediments, points to the role of biomass of plankton organisms and detritus as bio-sorbent in the process of transporting and transferring metals from water to sediments. With reference to water mass dislocation effect inside the reservoir under the influence of anthropogenic factor, in the situation when this factor is stronger than the factors which cause natural water movements, author suggests using the term anthropomixion.

INTRODUCTION

Along with water masses translocation, pollutants including heave metals are moved within the ecosystem [6–11]. The soluble pollutants are circulating together with water until chemical or biochemical reactions cause their precipitation and deposition as sediments [1, 2, 12, 13, 21].

Heavy metals are among the most persistent toxic compounds discharged to water ecosystems [14, 21, 22, 33]. Rivers and creeks entering a water reservoir together with atmospheric precipitation enrich the reservoir with heavy metals which accumulated in sediments are constituting a permanent element of the ecosystem, practically not removable outside the ecosystem [12–14].

The bottom sediments of which a substantial part is of clay characteristic absorbs on the surface large amounts of metals [1, 27, 28, 15, 32]. These metals in a particular environment (oxygen deficiency, pH, redox potential) form salts from which, to a lesser or higher degree, they can be released into water [4, 8, 17, 30].

The degree of bottom sediments pollution depends on the amount of discharged pollutants load, exposition time and inters reservoir processes. The phenomenon of enrichment with metals depends mainly on the precipitation of individual compounds. The processes depend on changes of some environment parameters such as pH, ORP, and changes in the concentration of precipitated compounds. The process of adsorption on the organic particles surface and hydrated Fe-Mn oxides are especially important [1, 2, 8, 15, 30, 31].

Organic matter is transported to the reservoir with the inflowing waters as a part of allochtonic suspended solids [8, 11, 24,]. They precipitate also on the water surface from the atmosphere [4, 11, 13, 25]. A part is also the result of inter-reservoir biological and chemical processes. The decaying biomass settles on the reservoir bottom as *detritus* [3, 10, 27]. The organic suspended solids do have a large active surface. They are absorbers for various pollutants including heavy metals [1, 5, 8, 11, 15]. Entering as a part of suspended solids which circulate in the water depth, the organic matter takes part in pollutants transportation and allocation [4, 7, 8].

The spatial distribution of settled on the bottom suspended solids, together with pollutants is the result of horizontal (transferal) and vertical (settling) motions. The transferal movement is occasionally disturbed by circulation caused by winds on the water surface, especially during the spring and autumn mixing periods. In the anthropomixion conditions there is an additional factor, i.e. water mass movements caused by anthropopressure [6–8].

In soils or in bottom sediments the total concentration of heavy metals is determined [4, 19, 21]. For this purpose it is necessary to know the participation of metal fractions which are capable of releasing themselves in particular conditions from sediments into water, as well as the participation of fractions which are permanently connected with them [23–26]. An additional knowledge is necessary, i.e. the partition of the metals fractions which could be released to the water under specific conditions. Also the fraction permanently fixed to the sediments has to be known [20, 28, 29].

The aims of the work were:

- the speciation fractions of heavy metals in bottom sediments in the Rybnik reservoir,

- determination of concentration and share of mobile and immobilized fractions,
- indication of the threats due to potential possibility of metals dissolution in the water,
- elaboration of a spatial map of bottom sediments polluted by mobile (liable) forms of heavy metals,
- investigation of the correlation between the concentration of organic matter and concentration of heavy metals.

In the previous work [7] the spatial distribution of total heavy metals concentration in bottom sediments was presented. Here, in the background of previous investigations, the results concerning mobile and immobilized forms of metals are presented. For evaluation of the purity and possibilities of the water ecosystem utilization it is important to determine not only the level of pollution, but also to determine the localization of the polluted sediments [7, 8, 16–18, 32, 26]. Determination of the regions with higher metals deposition is important in respect to future recultivation (restoration) of the reservoir [7, 8, 25].

MATERIAL AND METHODS

The Rybnik reservoir was formed in 1972, and should be considered as a technological object of the Power Plant RYBNIK S.A. The reservoir has a soil dam and is supplied with waters of the Rivers Ruda and Nacyna. It is located on the border line of the Raciborz Valley and the Rybnik Plateau. The reservoir, together with inundations: Grabownia, Gzel and Pniowiec, separated form the main reservoir by side dams is the most important one in the region. This is a unique ecosystem in Poland. The anthropogenic character is determined by thermal pollution due to discharge of cooling waters by the Power Plant Rybnik S.A., and anthropomixion character as a result of the forced water flow caused by the power plant [4, 5]. The total surface, together with the lateral inundations is 555 ha, while the main reservoir has an area of 465 ha. Its length is 7 km [5–8]. At the maximal exploitation bank level of 221.00 m above sea level, the capacity of the main reservoir is 21.4 million m^3. Together with the lateral inundations the total capacity is 24.0 mln m^3.

Heavy metals immobilized on sediments particles in water reservoirs are present usually in five basic forms adsorbed on the mineral particles, bounded as hydroxides and carbonates, bound to iron and manganese oxides, complexes with organic matter and clay minerals. The low concentration of heavy metals in various fractions and very often of amorphous character is the reason why they are not detectable by common methods of determination [2, 13, 17].

In order to distinguish the chemical forms in which heavy metal are present in bottom sediments of the investigated reservoir, the 6-step extraction proposed by Tessier and modified by Calmano and Forstner [2, 29] given below was used:

Step 0 – extraction of metals from the pore liquid (intestinal),
Step 1 – extraction of exchangeable forms of metals,
Step 2 – extraction of metals bound to carbonates metals,
Step 3 – extraction of metals bound to Fe-Mn oxides and amorphous iron oxides (weakly reducible phase),
Step 4 – extraction of metals bound to amorphous and weak crystalline iron oxides (medium reducible phase),

Step 5 – metals bound to organic matter and sulfides,
Step 6 – extraction of metals bound to silicates and crystalline iron oxides (residuum).

With the aim of determination of the concentration and spatial distribution of organic matter and heavy metals, in November 2002 using the Birge-Eckman sampler, 125 samples were collected in transversal sections. The samples were collected according to the following procedure: 25 sampling sites were selected, each in the radius of 50 m, 5 samples were taken. The samples were mixed together for averaging.

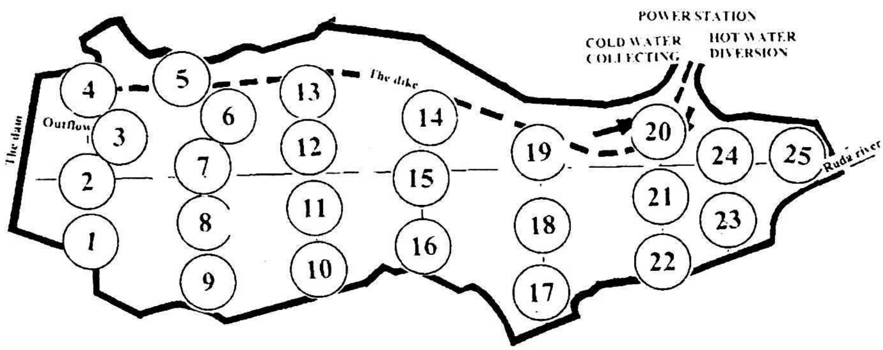

Fig. 1. Rybnik reservoir – sampling points

In the averaged samples the organic matter was determined at the temperature of 450°C. Samples dried at 25°C were used for determination of the following metals: cadmium (Cd), nickel (Ni), chromium (Cr), lead (Pb), copper (Cu) and zinc (Zn). Atomic adsorption spectrophotometer technique according to Calmano-Forster and Tessier [2, 29] was used for metals determination. In the phases of extraction the concentration of heavy metals were measured in the eluates. The fractions 0 to 2 are mobile compounds, fractions 3 to 6 are immobilized compounds. It has to be stressed that although metal carbonates are not soluble in neutral and basic conditions, they can be dissolved in acid environment under anaerobic conditions, and are counted as soluble. Extrapolation of results permitted drawing of isolines of areas of the highest and lowest concentration of organic matter and the mobile fractions of heavy metals in bottom sediments.

RESULTS

In Tables 1 and 2 the concentration of mobile and immobilized fractions of heavy metals in bottom sediments is given. In Figures 2–7 the spatial distribution of mobile fractions of the various metals is presented.

Table 1. Concentration of mobile – A, and constant – B, fractions of heavy metals in bottom sediments [mg/kg]

Metals	Zn		Pb		Cd		Cr		Cu		Ni	
sample points	A	B	A	B	A	B	A	B	A	B	A	B
1	143.64	108.36	0	27.08	3.9	2.37	2.33	11.65	43.55	26.51	1.74	5.75
2	602.51	652.49	7.16	101.34	14.54	7.52	4.17	127.83	50.71	1053.29	13.23	36.82
3	574.71	656.29	7.78	93.92	11.63	9.7	4.29	97.61	59.97	976.03	15.1	34.37
4	572.76	747.24	8.35	109.55	8.3	31.46	4.38	152.22	76.05	810.95	15.76	44.09
5	324.91	359.09	4.77	54.76	6.76	4.68	2.36	67.74	21.87	202.13	5.79	15.54
6	581.35	513.65	5.16	92.27	10	8.73	3.54	92.04	28.45	572.55	11.86	31.06
7	607.37	696.63	5.71	151.09	13.68	15.62	3.29	136.11	52.62	936.38	11.84	45.29
8	629.35	572.65	4.46	96.34	7.68	13.1	3.44	126.96	35.96	780.04	11.3	42.13
9	484.96	562.04	5.35	75.96	6.96	9.69	2.77	74.62	29.7	464.3	9.27	32.37
10	471.02	615.98	5.4	87.38	8.05	10.63	2.28	122.22	122.67	712.33	11.08	34.26
11	57.39	33.79	1.04	19.19	2.18	1.28	2.69	7.47	25.99	37.71	0.45	4.62
12	65.13	52.47	2.11	18.34	6.05	4.47	0.97	12.74	64.26	45.04	1.19	6.46
13	32.58	59.52	0.7	17.49	4.94	6.44	2.5	10.73	23.71	75.29	0.16	5.79
14	51.3	42.07	2.78	14.03	6.25	3.92	1.44	9.08	101.81	23.19	0.23	5.88
15	75.57	50.43	1.11	14.35	6.78	3.9	3.04	8.91	59.73	58.87	1.31	5.47
16	56.76	37.34	2.89	16.75	4.59	3.5	2.37	7.47	36.47	55.15	0.52	4.6
17	125.98	57.42	3.43	21.47	5.75	3.43	2.7	14.92	33.06	65.52	1.66	7.12
18	589.39	831.81	5.89	112.81	16.67	17.42	4.44	157.56	30.71	896.29	10.11	43.8
19	625.97	954.03	4.46	90.51	12.38	11.12	3.47	111.93	29.6	806.1	10.16	43.72
20	56.3	123.7	0.74	16.05	4.26	4.6	3.18	9.11	47.99	26.82	0.97	5.61
21	320.05	240.05	0.94	42.08	11.2	7.59	2.05	42.18	44.82	274.78	9.34	17.3
22	86.89	259.11	4.66	20.41	6.47	2.12	3.17	13.07	90.56	17	2.21	8.14
23	236.71	151.39	1.72	34.18	7.43	7	1.52	17.56	42.73	66.47	2.44	9.23
24	445.18	802.82	2.61	91.37	21.23	13.37	2.25	118.45	26	86.1	4.32	31.07
25	484.74	789.26	3.82	90.95	7.68	13.39	4.4	138.3	5.43	103.87	5.5	36.31

Table 2. Percentage [%] of mobile – A, and constant – B, fractions of heavy metals in bottom sediments

Metals	Zn		Pb		Cd		Cr		Cu		Ni	
sample points	A	B	A	B	A	B	A	B	A	B	A	B
1	57.00	43.00	0.00	100.00	62.20	37.80	16.67	83.33	62.16	37.84	23.23	76.77
2	48.01	51.99	6.60	93.40	65.91	34.09	3.16	96.84	4.59	95.41	26.43	73.57
3	46.69	53.31	7.65	92.35	54.52	45.48	4.21	95.79	5.79	94.21	30.52	69.48
4	43.39	56.61	7.08	92.92	20.88	79.12	2.80	97.20	8.57	91.43	26.33	73.67
5	47.50	52.50	8.01	91.99	59.09	40.91	3.37	96.63	9.76	90.24	27.14	72.86
6	53.09	46.91	5.30	94.70	53.39	46.61	3.70	96.30	4.73	95.27	27.63	72.37
7	46.58	53.42	3.64	96.36	46.69	53.31	2.36	97.64	5.32	94.68	20.72	79.28
8	52.36	47.64	4.42	95.58	36.96	63.04	2.64	97.36	4.41	95.59	21.15	78.85
9	46.32	53.68	6.58	93.42	41.80	58.20	3.58	96.42	6.01	93.99	22.26	77.74
10	43.33	56.67	5.82	94.18	43.09	56.91	1.83	98.17	14.69	85.31	24.44	75.56
11	62.94	37.06	5.14	94.86	63.01	36.99	26.48	73.52	40.80	59.20	8.88	91.12
12	55.38	44.62	10.32	89.68	57.51	42.49	7.08	92.92	58.79	41.21	15.56	84.44
13	35.37	64.63	3.85	96.15	43.41	56.59	18.90	81.10	23.95	76.05	2.69	97.31
14	54.94	45.06	16.54	83.46	61.46	38.54	13.69	86.31	81.45	18.55	3.76	96.24
15	59.98	40.02	7.18	92.82	63.48	36.52	25.44	74.56	50.36	49.64	19.32	80.68
16	60.32	39.68	14.71	85.29	56.74	43.26	24.09	75.91	39.81	60.19	10.16	89.84
17	68.69	31.31	13.78	86.22	62.64	37.36	15.32	84.68	33.54	66.46	18.91	81.09
18	41.47	58.53	4.96	95.04	48.90	51.10	2.74	97.26	3.31	96.69	18.75	81.25
19	39.62	60.38	4.70	95.30	52.68	47.32	3.01	96.99	3.54	96.46	18.86	81.14
20	31.28	68.72	4.41	95.59	48.08	51.92	25.87	74.13	64.15	35.85	14.74	85.26
21	57.14	42.86	2.19	97.81	59.61	40.39	4.63	95.37	14.02	85.98	35.06	64.94
22	25.11	74.89	18.59	81.41	75.32	24.68	19.52	80.48	84.19	15.81	21.35	78.65
23	60.99	39.01	4.79	95.21	51.49	48.51	7.97	92.03	39.13	60.87	20.91	79.09
24	35.67	64.33	2.78	97.22	61.36	38.64	1.86	98.14	23.19	76.81	12.21	87.79
25	38.05	61.95	4.03	95.97	36.45	63.55	3.08	96.92	4.97	95.03	13.15	86.85

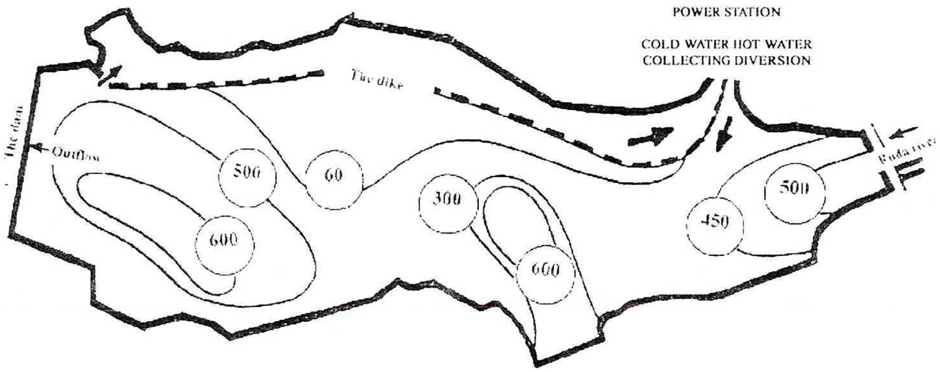

Fig. 2. The mobile form of zinc (Zn) in bottom sediments – Rybnik reservoir

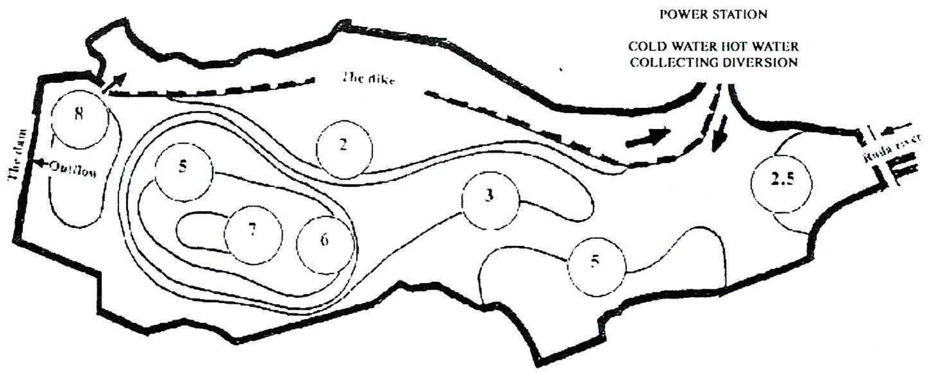

Fig. 3 The mobile form of lead (Pb) in the bottom sediments on the Rybnik dam-reservoir

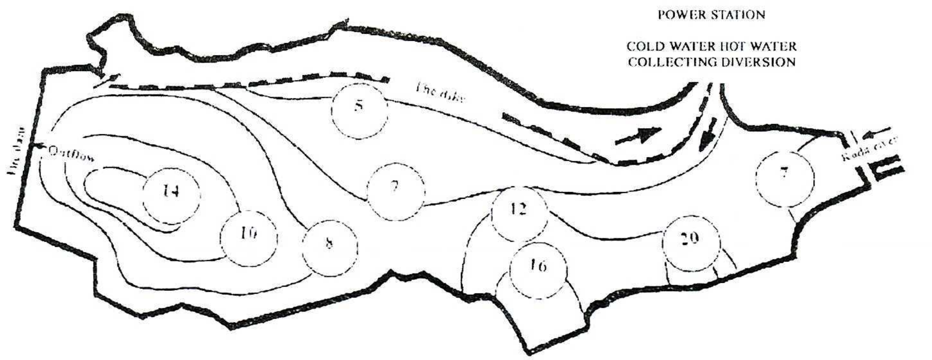

Fig. 4. The mobile form of cadmium (Cd) in the bottom sediments on the Rybnik dam-reservoir

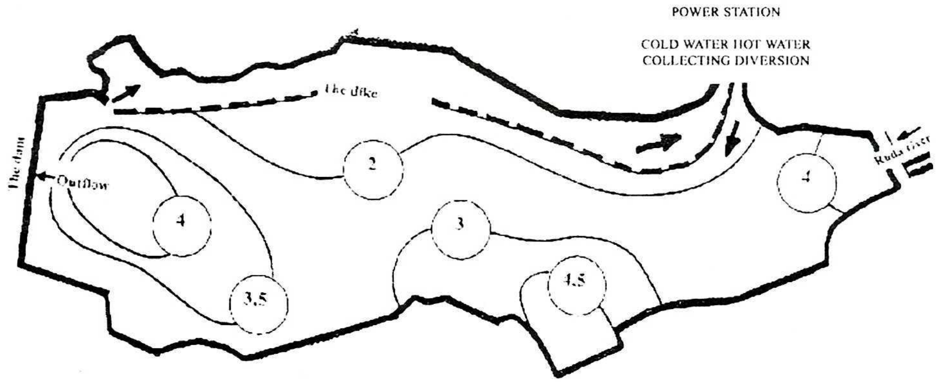

Fig. 5. The mobile form of chromium (Cr) in the bottom sediments on the Rybnik dam-reservoir

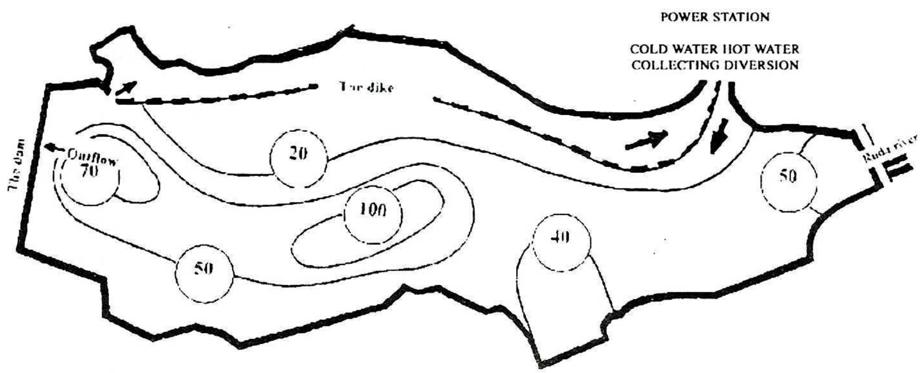

Fig. 6. The mobile form of copper (Cu) in the bottom sediments on the Rybnik dam-reservoir

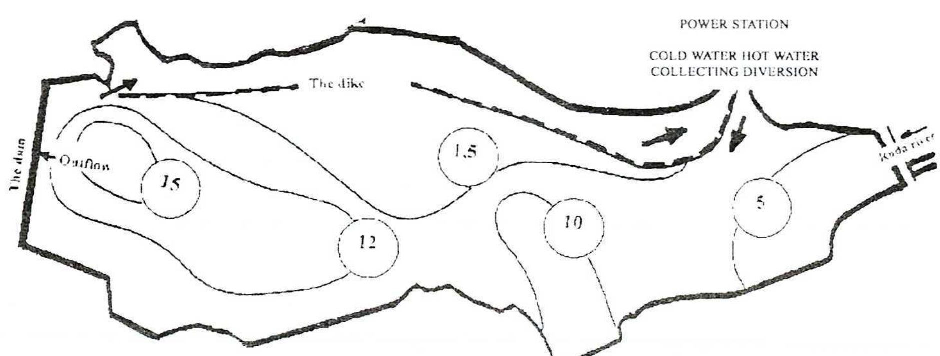

Fig. 7. The mobile form of nickel (Ni) in the bottom sediments on the Rybnik dam-reservoir

DISCUSSION

It is interesting, that there is a high dispersion of concentration value of individual metals especially the occurrence of transects of very big concentration gradients. The maximal concentrations of mobile fraction of all metals were found in the dammed section of the reservoir in the deepest part. In the case of zinc, copper and chromium higher concentrations were found in the vicinity of the River Ruda inflow, upstream to the discharge of warm water (Figs. 2, 5, 6).

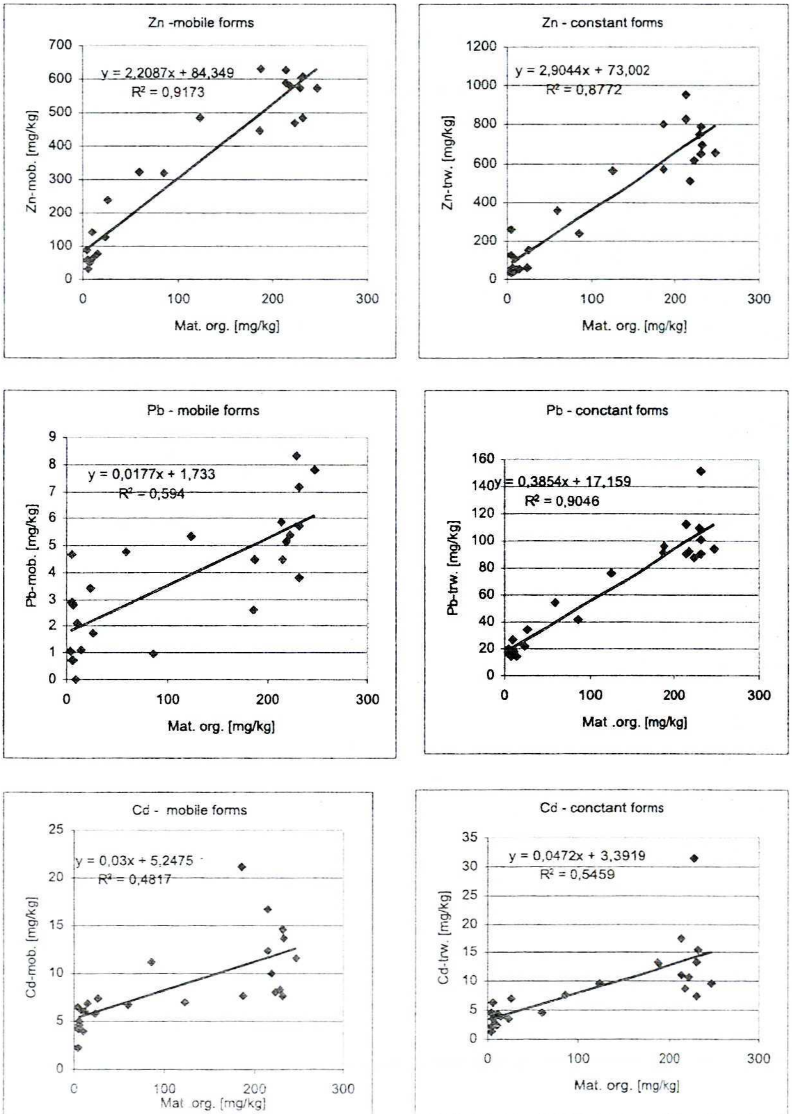

Fig. 8. The relationships between the organic matter and concentrations of mobile and constant fractions of heavy metals in bottom sediments – reservoir Rybnik, part I

There is a correlation between the concentration of organic matter in bottom sediments and concentration of the mobile or immobilized heavy metals fractions. The correlation for each metal was presented in Figures 8 and 9.

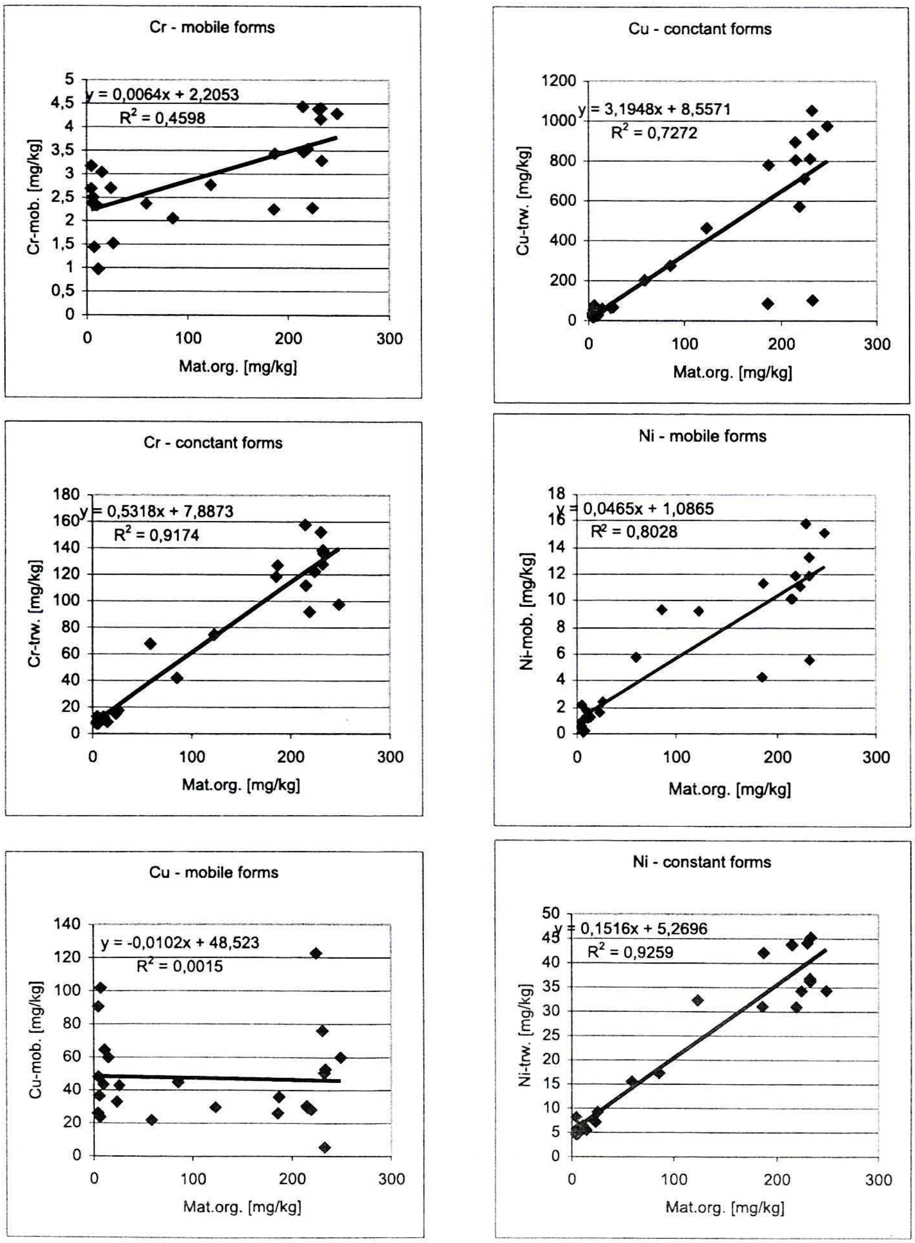

Fig. 9. The correlation between the concentration of organic matter and mobile and immobilized fraction concentration of heavy metals in bottom sediments – reservoir Rybnik, part II

These graphs are showing that the metals form organo-metalic compounds. This indicates the role of biomass, mainly of plankton organisms. Metals are transferred from water to the biomass, bound on the surface and entering the cells, and are later transferred to bottom sediments.

Spatial distribution of heavy metals in bottom sediments, including the mobile fraction is definitively depended on the water movement within the reservoir. That is clearly visible on the thermo vision map (Fig. 10).

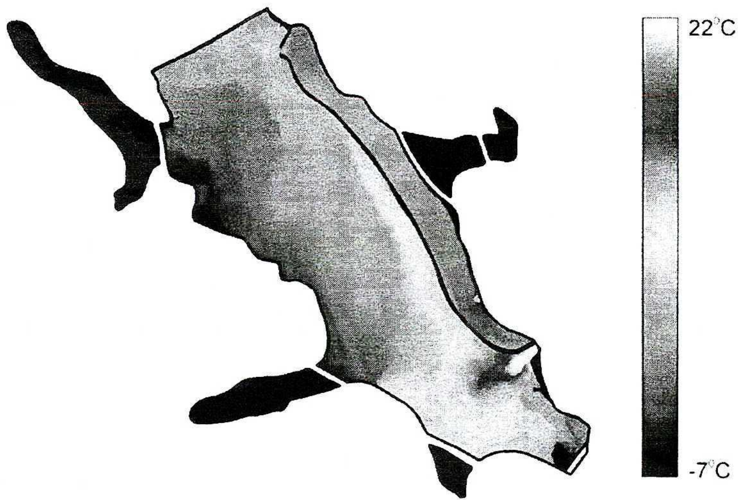

Fig. 10. The infra-red map of Rybnik dam-reservoir – January 2003

Heavy metals in appropriate conditions can get released from sediments and create in the water environment toxic compounds. The higher share of mobile metals fractions, the greater threats to ecological state of the ecosystem. In Figure 11 the average share values of mobile and immobilized fraction of each metal is shown.

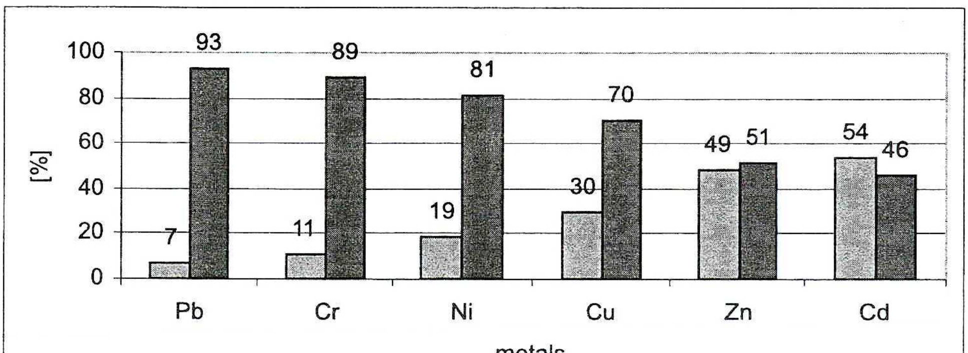

Fig. 11. The average participation of the mobile and constant forms of heavy metals in the bottom sediments on Rybnik dam-reservoir

The average participation of immobilized forms of lead (Pb), chromium (Cr), nickel (Ni) and copper (Cu) is high and is respectively 93%, 89%, 81% and 72%. It means that the threat to the reservoir environment is low. The highest average value of mobile fraction was measured for cadmium (51%) and zinc (49%) which potentially can be released from the bottom sediments to the water. For comparison the average mobile fraction of metals in bottom sediments in selected barrage reservoirs in the Silesia region is given in Figure 12.

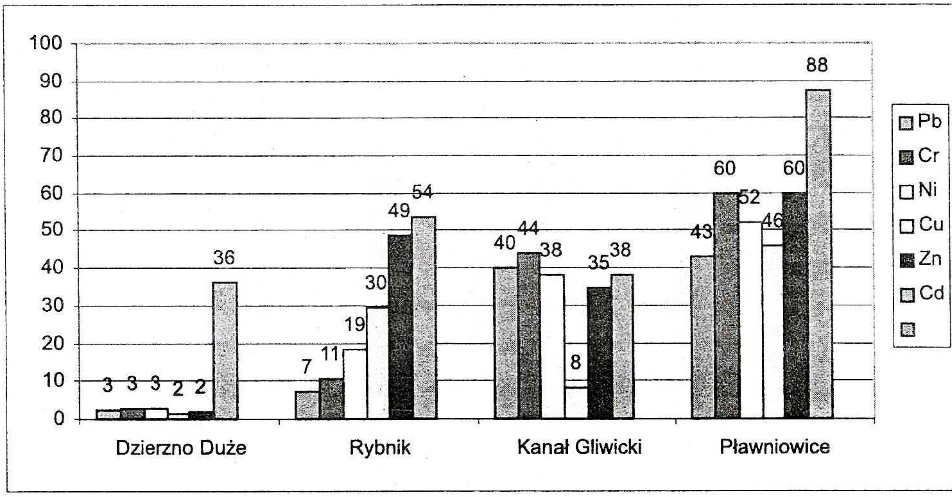

Fig. 12. The average participation of heavy metals mobile forms in the selected reservoirs in the Upper Silesia Region of Poland

It becomes evident that in all cases cadmium poses the main threat. Attention has been drawn to higher shares of mobile fractions in reservoirs with water of low hardness (Pławniowice, Rybnik), and definitively lower shares in water of high hardness (Dzierżno Duże, Kanał Gliwicki). This is in connection with the buffering degree [5–8]

CONCLUSIONS

The results of investigations permitted formulation of the following conclusions:

1. Spatial distribution of heavy metals in the reservoir bottom sediments, including mobile fractions depends on water movement within the reservoir and differences in thermal conditions.
2. Under anthropomixion there is a strong spatial differentiation in heavy metals mobile and immobilized fraction in bottom sediments.
3. The concentration of mobile fraction of heavy metals in bottom sediments is distinctively correlated to the concentration of organic matter. This indicates the role of plankton organisms in transport of pollutants within the ecosystem and transfer from the water to bottom sediments.
4. As far as the potential release from bottom sediments cadmium (Cd) zinc (Zn) and copper (Cu) pose the highest threat to the ecological condition of the Rybnik reservoir.

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