

ACTA HYDROBIOL.	15	2	145—166	KRAKÓW 1973
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**Rozprzestrzenienie metali ciężkich w wodach płynących  
w rejonie występowania naturalnych złóż  
oraz przemysłu cynku i ołowiu**

**The spreading of heavy metals in flowing waters  
in the region of occurrence of natural deposits  
and of the zinc and lead industry**

Wpłynęło 30 marca 1972 r.

**Abstract** — The basic chemical composition and the concentration of Cu, Zn, Pb, Cd, Mn, Cr, Co, Mo, Sr, and Ba were investigated in flowing waters (channels, streams, and rivers) in the region of occurrence of natural deposits of zinc and lead, and of the mining and metallurgic industry exploiting these deposits. Among other things it was found that from the region of such an industrial centre the migration of zinc, lead, and cadmium by the water courses may be fairly considerable. In the water of the successive receivers of wastes the most rapid decrease in lead and the lowest in zinc content was found with the increase in the distance from the source of pollution. The natural occurrence of lead and zinc ores in the deeper rock layers does not to any extent influence the surface waters with pH about 8.1 and with high total hardness — which occur in the investigated region. The increase in the content of zinc, lead, and cadmium in the water of the investigated water courses is mainly connected with the industrial pollution. The quantitative level of these three heavy metals shows a distinct tendency to increase in the autumn-winter season. The occurrence of calcium-dolomite rocks in the catchment basin of the investigated water courses is revealed in the chemism of the water by an exceptionally high content of magnesium and a low content of manganese and copper.

From industrial centres various waste substances are released into the air and the water, and are deposited on the surface of the earth (e.g. in the form of solid wastes stored away on dumps). Such substances may find their way into the surface waters not only directly but also indirectly through the above-mentioned media. Above all, the settling of industrial dusts from the air, the washing away by rainfall and sweeping by the

\* Praca wykonana w ramach problemu resortowego PAN nr 21.

winds of the solid wastes stored on dumps (the pulverization of ashes, sinters, dried sediments after flotation, etc.) have a direct influence on the properties of the wastes. The heavy metals are among the more troublesome components of industrial pollution. Many branches of the industry appear to release these metals, the zinc and lead industry being one of them.

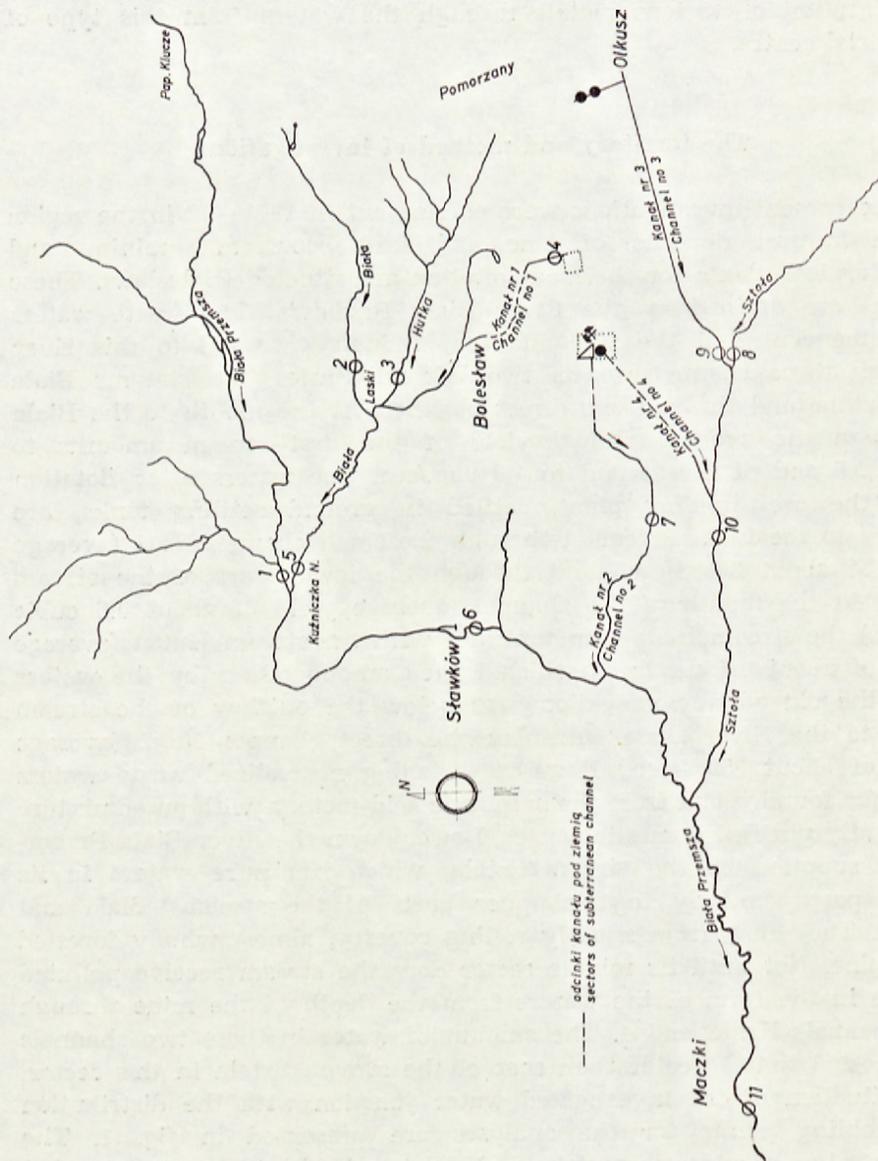
In England a considerable pollution of the water with zinc and lead, brought about by the old mines of these ores with faulty water economy, attracted attention as early as the end of the XIX century (Jones 1964). In the regions of the zinc industry with properly arranged water economy, as generally occurs in our country, the effect of zinc and lead pollution on the surface waters is naturally limited, may nevertheless play an important role in the balance of the pollution of streams and rivers (with zinc, lead, suspended solids, and the reagents used in the process of ore dressing). The problem of the pollution of surface waters with zinc and lead has increased in importance in recent years, especially as the situation of the highly industrialized countries (U.S.A., West Germany) clearly indicates that the concentration of these metals may reach high levels even in great rivers and bring about many difficulties for the consumers of their water (Kopp, Kroner, undated, Haberer, Norman 1971, Kölle et al. 1971). In the Soviet Union the industrial pollution of rivers with zinc and lead was investigated by, among others, Žukov, Mongait (1948), and Zavodnov et al. (1965). From the heavy metals occurring in the surface waters especially dangerous are, those which strongly accumulate in the organism (Hg, Cd, Pb) and hence may more rapidly exceed the threshold of acute action. It is worthy of note that lately many authors have claimed that the toxicity of many metals not only accumulates but in some combinations (Cu + Zn, Cu + Cd, Zn + Ni) many times exceeds the total sum (Jones 1964, Haberer, Normann 1971).

In this country the available data on the influence of industrial pollution containing heavy metals on the surface waters are relatively scarce, as was previously reported (Pasternak 1971). Particularly little information has been obtained on the degree of migration of these kinds of metals to the waters flowing in the regions of occurrence of the zinc and lead industry. On the basis of foreign literature, Koziorowski, Kucharski (1964) reported on the composition of wastes obtained in the process of flotation of zinc and lead ores, on the methods of the purification of such wastes, and on their unfavourable influence on the water environment. The pragmatic approach to the problem of the effect of the zinc industry on the adjacent surface waters reveals a lack of information which could make it possible to determine what part of the content of zinc, lead, and other metals in these waters may be attributed to the natural occurrence of these ores

in the rocks of the catchment basin, and what to their industrial exploitation. The principal aim of the present work was to obtain at least preliminary materials in this problem and to determine the degree of migration of various metals through the waters from this type of industrial centre.

### The territory and method of investigation

The present investigations were carried out in 1971—72 in the region where natural deposits of zinc and lead occur and mining and metallurgical plants for their exploitation are situated (Bolesław). These regions are drained by the River Biała Przemsza. The waste waters from the centre of the zinc and lead industry are fed to this river through three channels to its two left tributaries, the streams Biała and Sztoła, and through one direct channel. At the mouth to the Biała Przemsza the average annual yield of the first stream amounts to about 1.5 and of the second to 1.9 c.m./sec. The waters after flotation from the ore dressing plant, settled in ground settling tanks, are drained to the Biała Przemsza through the small channel No 1 (average yield of about 200 l/sec.) and through the lower part of the stream Biała. At the mouth of the channel (average yield of about 0.6 cubic m./sec.) the stream Biała communicates with the stream Hutka (average yield of about 0,4 c.m./sec.) which is, fed among others by the waters from the old adits. Some kilometres below the outflow of the stream Biała to the River Biała Przemsza the direct channel No 2 (average yield of about 350 l/sec.) flows in, bringing neutralized waste waters from the foundry and from the sulphuric acid factory, with an admixture of slightly purified domestic wastes. Lower down the River Biała Przemsza is supplied by the stream Sztoła, which has pure waters in its upper part, similarly to the upper parts of the streams Biała and Hutka. They flow from slightly rolling country, almost wholly forested with pine. Not until its middle sector does the stream receive polluted waters in the form of the waters from the depth of the mine through the channels Nos 3 and 4. The amount of water in these two channels is almost 3 times greater than that of the stream Sztoła in this sector. The situation of the investigated water junction with the distribution of sampling points for the analyses are presented in fig. 1. The concentration of microelements was also determined in the water sampled from the mine depth. For comparison, the investigations comprised also the next receiver of the waters of the Biała Przemsza, i.e. the River Vistula. The sampling point for the water from the Vistula was localized several kilometres above the city of Kraków. The annual mean yield of the River Biała Przemsza in the region of the first inflow of the



Ryc. 1. Plan sieci badanych cieków oraz rozmieszczenie punktów (1—12) poboru prób wody (z wyjątkiem rzeki Wisły)  
 Fig. 1. Plan of the water network and the localization of sampling points (with the exception of the River Vistula)

polluted water of the stream Biała amounts to about 3.0 c.m./sec., a few kilometres lower at Sławków it is 4.5, and in its low sector at the locality Maczków about 6.3 c.m./sec. In the region of the present investigations the corresponding yield of the River Vistula amounted to about 70 c.m./sec.

The substratum of the investigated part of the catchment basin of the River Biała Przemsza and its tributaries is chiefly formed of Triassic limestones (mainly shell stones) with orebearing dolomites (zinc and lead ores) covered with glacial sands. Hence, permeable sandy soils in a great percentage having the granulometric composition of loose sands, especially in the vicinity of the Błędownska desert, occur on the major part of this territory. The degree of afforestation of the whole catchment basin of these rivers is fairly high.

The samples of water for determination of the total chemical composition and of the content of more important microelements were taken from the surface layer into polyethylene bags. That part of the sample of water which was taken for the determination of microelements, with the exception of strontium, was concentrated. This was carried out by means of evaporation of the water in order to avoid complicated chemical treatments of the sample (i.e. extraction with various organic reagents or the method of ion substitution) leading to qualitative changes of the investigated constituents (Allen et al. 1970) and to determine not only the dissolved but also colloidal forms of zinc and lead in the water. According to Lloyd (1960), the colloidal suspension of zinc may also injure aquatic organisms. If any mineral suspension occurred in the sample, it was removed by the sedimentation method (without coagulation). The samples of water were acidified with concentrated  $\text{HNO}_3$  prior to evaporation. The obtained dry residue was dissolved in 0.1 n  $\text{HNO}_3$  (checked for the content of the investigated elements) and transferred to flasks, the acid, weakened by calcium and magnesium carbonates, being made up with drops of concentrated  $\text{HNO}_3$  to maintain the pH of the solution at about 1. The organic substance occurring in the dry residue of the water was burned at 360—400 °C before dissolving, 1 ml of concentrated  $\text{HNO}_3$  and of perchloric acid being added at the end of combustion. The analyses of those parts of the residue which had not been dissolved in 0.1 n  $\text{HNO}_3$ , carried out using emission spectrography, indicated that the error resulting from the low solubility of sulphates of some elements is insignificant, with the exception of barium. Strontium was determined in the direct samples of water, which were only condensed to one half of their volume when its concentrations were very low. Some investigators even use flame photometry for the determination of strontium (Pridnikov et al. 1971). The determination of other microcomponents of water without condensation is in principle only possible by means of the very costly

neutron activation method (Bhagat et al. 1971) or anode stripping voltametry (Allen et al. 1970). In the present investigations all microelements were determined using atomic absorption spectroscopy (Standard Methods 1970, Hemsley 1971, Paus 1971). To improve the accuracy of the determination of barium and molybdenum, whose atoms excited at the temperature obtained with the use of air and acetylene reveal specific properties disturbing the absorption, the determinations were carried out in the reducing flame (David 1968, Ramakrishna et al. 1969, Rubeska, Moldan 1969). The use of nitrous oxide in the mixture leading to a temperature of 2950°C requires specific adaptation of the laboratory.

The general chemical properties of the investigated waters (the content of macroelements), with the exception of iron, were determined according to the methods reported by Just and Hermanowicz (1964) and by Standart Methods (1970). Iron was determined using an atomic absorption spectrophotometer.

### Discussion of results

The results of determination of the physico-chemical properties of the waters of the investigated water courses are presented in Tables I and II. It should be stressed at the start, for a better understanding of these properties, that a few kilometres above the inflow of the stream Biała the River Biała Przemsza receives a very large load of organic wastes from the paper pulp factory in Klucze, while besides a similar pollution the River Vistula also receives the waste waters of the coal and chemical industry as well as other wastes. As may be seen from the obtained data, the waters of the investigated rivers differ in some of their properties to a considerable degree. Above all this concerns the content of organic substances (oxidability), mineral suspended solids, oxygen, sodium, sulphates, chlorides, and the reaction. Their only common property, which results from the occurrence of rocks rich in calcium and magnesium in the substratum of the catchment basin of these rivers, is the high total hardness. A lower water hardness was found only in the upper sector of the stream Biała, in whose catchment basin patchy silts, usually poor in these components, occur under sands. Particularly high hardness is characteristic of flotation effluents and metallurgic waters (Table II). However, this is already the result of human industrial activity (the processes of flotation and neutralization of waste waters from the metallurgic plant and from the factory of  $H_2SO_4$ ).

The main receiver of the polluted water of the investigated industrial centre — the River Biała Przemsza in the sector above the mouth of the

Tabela I. Fizyko-chemiczne właściwości wody badanych rzek i potoków

Table I. Physico-chemical properties of the water of investigated rivers and streams

Rzeka (r) Potok (p) Stream (Miejscowość) (Locality)	Data Date	Temperatura wody °C Water temperatur	Tlen rozpuszcz. Oxygen dissolved mg O <sub>2</sub> /l	Stopień nasylenia Oxygen saturation %	Utlenialność mg O <sub>2</sub> /l Oxydability	pH	Alkaliczność meq/l Alkalinity	Twardość ogólna Total hardness mg/l	mg/l						Fe µg/l
									Ca	Mg	K	Na	Cl'	SO <sub>4</sub>	
Biała Przemsa (r) (Kuzniczka N.)	Wartości średnie Mean values	-	1.95	-	52.0	7.2	3.30	13.3	79.3	9.5	2.26	8.00	22.0	61.0	630
Biała (p) (Laski)		-	8.96	-	3.1	7.0	1.20	6.1	32.2	6.9	1.16	2.16	3.7	48.0	59
Hutka (p) (Laski)		-	8.90	-	3.0	7.7	3.50	13.0	63.6	17.8	2.32	7.52	14.0	55.7	43
Biała (p) (Kuzniczka N.)		-	7.80	-	3.5	7.4	2.85	18.2	77.2	32.1	2.59	10.88	14.8	182.5	48
Biała Przemsa (r) (Szawków)	19.V. 1971	13.9	0.80	7.7	103.8	7.2	3.15	15.9	68.6	27.3	1.44	8.48	22.5	110.9	1019
	13.VII. "	17.9	1.28	13.4	99.2	7.2	3.20	14.5	87.2	9.8	1.36	7.20	19.5	84.5	1680
	7.IX. "	12.4	6.24	58.0	41.0	7.2	3.30	16.1	74.3	24.7	1.36	4.80	18.5	104.7	4825
	26.X. "	8.7	4.96	42.4	67.8	7.1	2.90	16.1	82.2	20.0	1.88	8.24	33.0	112.8	1540
	29.I. 1972	1.7	4.65	33.3	62.7	7.2	2.85	16.8	85.8	20.8	2.00	10.56	37.0	124.8	925
10.V. "	13.5	4.16	39.6	46.7	7.3	3.15	15.0	68.6	23.4	1.64	8.16	26.0	90.7	910	
Szoła (p) powyżej ujścia kanałów above the mouth of the channels	19.V. 1971	14.8	8.00	78.3	3.2	8.2	3.45	12.3	22.2	39.9	0.32	1.36	3.5	43.2	170
	13.VII. "	18.1	7.04	73.8	3.1	8.2	3.50	12.2	54.3	20.0	0.56	1.52	3.2	40.8	60
	7.IX. "	11.9	9.28	85.3	2.5	8.2	3.45	12.7	48.6	25.6	0.72	1.44	3.5	50.4	49
	26.X. "	6.1	11.04	88.7	4.0	8.2	3.55	13.1	52.5	25.1	0.88	1.80	3.0	55.2	25
	29.I. 1972	0.3	11.94	82.2	1.7	8.0	3.55	12.7	44.3	28.2	0.68	2.16	2.8	48.0	38
10.V. "	14.6	8.00	78.0	1.9	8.4	3.30	12.2	36.4	30.8	0.68	1.28	3.5	50.4	60	
Szoła (p) poniżej ujścia kanałów below the mouth of the channels	19.V. 1971	11.2	8.96	81.1	5.2	8.0	3.50	12.9	40.0	31.7	0.88	4.00	11.0	48.0	365
	13.VII. "	12.0	8.32	76.6	1.7	8.0	3.60	12.6	65.7	14.5	0.80	4.16	10.8	38.4	170
	7.IX. "	10.7	9.60	85.9	2.4	8.0	3.60	13.7	60.0	23.0	1.04	3.92	10.8	56.6	373
	26.X. "	9.4	10.72	93.1	2.1	8.1	3.60	13.2	61.5	20.0	1.32	7.40	13.2	53.7	86
	29.I. 1972	9.0	9.76	84.0	1.2	8.0	3.55	13.0	48.6	26.9	1.08	5.92	11.8	50.9	75
10.V. "	11.6	7.20	65.7	3.0	8.0	3.50	13.0	47.9	27.3	0.84	3.92	11.5	48.0	108	
Biała Przemsa (r) (Maczki)	19.V. 1971	14.0	3.68	35.4	45.0	7.6	3.00	14.9	52.9	32.5	1.48	8.32	19.5	105.1	1575
	13.VII. "	18.7	4.16	44.1	36.8	7.4	2.95	14.8	82.2	14.5	1.52	8.32	24.8	98.4	963
	7.IX. "	13.8	5.60	53.6	56.8	7.3	2.75	15.6	79.3	19.5	1.60	6.40	22.5	121.0	1017
	26.X. "	8.8	6.56	56.2	51.8	7.3	2.80	16.2	81.5	20.8	2.52	9.20	29.0	125.8	1687
	29.I. 1972	1.6	8.64	61.7	37.1	7.3	3.00	18.3	87.2	26.4	2.24	11.60	37.0	146.0	1325
10.V. "	14.3	4.80	46.5	24.6	7.4	2.85	16.0	69.3	27.3	1.96	12.24	30.2	124.8	4100	
Wisła (r) (Sołejowice)	19.V. 1971	15.2	5.10	50.3	10.4	7.2	2.20	11.9	57.2	16.9	7.56	80.00	146.0	76.8	2075
	13.VII. "	21.9	4.96	55.9	9.8	7.2	2.05	12.8	61.8	17.1	7.80	96.00	158.5	111.9	1080
	7.IX. "	18.1	5.76	60.4	13.0	7.1	3.00	20.3	92.9	31.7	13.00	200.00	338.0	179.2	1352
	26.X. "	11.4	6.72	61.1	19.7	7.3	2.85	17.2	78.6	26.9	11.96	146.40	262.0	124.3	1735
	29.I. 1972	0.5	7.84	54.3	18.2	7.1	2.85	18.6	76.5	34.3	13.00	176.00	278.0	190.0	2500
10.V. "	14.9	4.80	47.0	9.2	7.2	2.25	14.7	65.8	23.9	11.24	145.60	207.0	182.5	1125	

Tabela II. Zawartość ważniejszych metali ciężkich w wodach odpadowych kopalni i huty cynku (w wodzie dołowej  $\mu\text{g/l}$ , a w wodzie po flotacji i z huty w  $\text{mg/l}$ ) oraz inne chemiczne właściwości tych wód

Table II. Content of more important heavy metals in the waste waters from the mine and zinc foundry (in the water from the mine depth  $\mu\text{g/l}$ , and in the flotation effluent and from the foundry in  $\text{mg/l}$ ), and other chemical properties of these waste waters

Rodzaj wody Kind of water	Data Date	Cu	Zn	Pb	Cd	Mn	Fe	pH	Twardość ogólna Total hardness	Alkalicz- ność Alkalinity	$\text{SO}_4$ mg/l	Tlen roz- puszczony Oxygen dissolved mg $\text{O}_2/\text{l}$
Woda dołowa z kopalni Water from the mine depth $\mu\text{g/l}$	19.V. 1971	5.2	675	300	2.5	34	925	-	-	-	-	-
	13.VII. "	8.0	1800	153	2.0	34	1075	8.0	15.0	3.6	33.2	-
	7.IX. "	5.0	267	49	1.8	18	157	8.0	15.3	3.6	54.8	-
	26.X. "	2.0	221	47	1.3	8	65	8.1	13.3	3.7	29.2	-
	29.I. 1972	2.5	375	40	3.7	5	25	-	-	-	-	-
10.V. "	3.0	300	25	3.0	4	25	-	-	-	-	-	
Woda ze stawu osadowego po flotacji Water from the sedimentation pond after flotation mg/l	15.VII. 1971	-	0.50	2.26	-	śl tracce	0.4	8.6	59.2	1.12	899	35.2
	5.IX. "	-	0.48	10.30	-	0.01	0.8	7.8	52.5	4.20	957	47.2
	23.X. "	-	0.70	1.26	-	0.10	1.5	8.1	38.5	2.24	621	20.0
	15.XI. "	-	1.07	4.86	-	0.50	2.3	9.5	20.6	2.24	921	29.6
	19.I. 1972	-	0.28	3.12	-	0.14	2.5	8.0	48.5	2.38	823	14.4
21.III. "	-	1.70	1.37	-	0.15	14.0	8.0	50.2	3.64	777	22.4	
Woda kanału nr 2 (z huty) Water in channel no 2 (from the foundry) mg/l	27.IX. 1971	-	6.42	0.13	-	-	-	średnio 7.0	najczęściej Mean	najczęściej Most frequently	najczęściej Most frequently	najczęściej Most frequently
	23.X. "	-	6.45	0.14	-	-	-	-	-	-	-	-
	15.XI. "	-	5.69	0.08	-	-	-	-	-	-	-	-
	15.I. 1972	-	6.20	0.45	-	-	-	-	-	-	-	-
2.III. "	-	9.50	0.30	-	-	-	-	-	-	-	-	
Woda kanału nr 3 Water in channel no 3 $\mu\text{g/l}$	10.V. 1972	2.8	250	34.2	3.3	12.5	61.0	8.1	12.9	3.45	55.7	6.7

stream Biała, which releases the first pollutions from this centre — has water with a very high content of suspended and dissolved organic matter, with low or medium oxygenation, neutral reaction, and with a considerable content of iron and aluminium. The sulphitation waste waters of the cellulose plant do not flow into the river.

In this sector the content of zinc, lead, cadmium, and some other heavy metals in the water of the River Biała Przemsza does not distinctly differ from the amounts of these elements in the relatively pure river waters (Konovalov et al. 1966, Kopp, Kroner — undated, Pasternak, Antoniewicz 1970, 1971). In relation to pure waters on the sandy and limy substratum in the water of this part of the river only a certain increase in chromium and copper content may be observed. This increase is probably due to the inflow of some mineral pollution from the cellulose plant at Klucze.

The flotation effluents flowing out of the ore dressing plant through channel No 1 and through the lower sector of the stream Biała are characterized by a high total hardness and by an exceptionally high content of suspended solids (usually 30—100 mg/l), of oxygen (from aeration), iron, sodium (90—110 mg Na/l), potassium (about 10 mg K/l), by a highly alkaline reaction, and considerable oxidability (20—35 mg O<sub>2</sub>/l). This last named property is mainly connected with the occurrence in these waters of organic compounds such as (ethyl-sodium) xanthogenate and pine oils, which are introduced as reagents in the process of ore flotation. With higher concentrations xanthogenate and the products of its decomposition (carbon sulphide) are noxious for aquatic organisms, especially if the level of chlorides in the water is high (Solski et al. 1972). The content of chlorides in these waters may be reckoned among such levels. According to the modern view, the degree of hydrolysis of xanthogenate decreases with an increase in the pH of the water; aeration does not increase it.

The pollution of water after flotation with zinc and lead is very variable in time and usually high (Table II), the amount of lead being here particularly high. With a few exceptions its content is several times as great as that of zinc. Besides these two microelements such waters contain considerable amounts of manganese.

The waters of the stream Biała and of its tributary, the Hutka, flowing from the locality Pomorzany, are quite clean up to the mouth of the channel No 1 (Table I). Only their chemical character is changed after their confluence into one water course (the lower Biała) and after the inflow of the flotation effluents (fig. 1) through the channel No 1. Already in the sector of the stream Biała near the mouth these changes become visible to certain degree. In this part of the stream the water is almost entirely free from industrial mineral suspensions and organic pollution. Only the increased total hardness (resulting from

Tabela III. Zawartość pierwiastków śladowych w wodach badanych rzek i potoków w  $\mu\text{g/l}$   
 Table III. Content of trace elements in the water of the investigated rivers and streams in  $\mu\text{g/l}$

Rzeka (r) River Potok (p) Stream (Miejscowość) (Locality)	Data Date	Cu	Zn	Pb	Cd	Mn	Cr	Co	Sr	Ba	Mo
Biaża Przemysła (r) (Kućniczka N.)	Wartości średnie Mean values	12.20	55.0	6.75	2.0	121.2	40.0	2.2	400	104.0	6.0
Biaża (p) (Laski)		1.5	77.0	2.50	1.5	50.0	2.5	1.0	100	60.0	1.5
Hutka (p) (Laski)		2.5	79.5	8.25	2.0	12.5	3.5	1.7	350	95.0	2.5
Biaża (p) (Kućniczka N.)		4.0	161.0	19.3	2.0	12.5	6.2	1.6	375	100.0	3.8
Biaża Przemysła (r) (Sławków)	19.V. 1971	14.0	159.0	15.0	2.5	188.0	-	-	-	-	-
	13.VII. "	13.0	102.0	9.0	2.0	178.0	50.0	2.25	525	105.0	6.8
	7.IX. "	3.7	75.0	6.0	1.8	100.0	100.0	3.25	355	104.2	6.3
	26.X. "	18.0	60.0	17.0	1.3	100.0	50.0	2.25	550	82.5	9.4
	29.I. 1972	18.7	88.0	30.0	3.7	360.0	12.5	2.25	350	112.5	5.0
	10.V. "	15.0	50.0	14.3	1.8	120.0	25.0	5.00	550	100.0	10.0
Sztosza (p) powyżej ujścia kanałów above the mouth of the channels (Bukowno)	19.V. 1971	2.0	64.0	5.0	2.5	9.0	-	-	-	-	-
	13.VII. "	6.0	87.0	5.0	2.0	4.0	43.7	1.50	425	100.0	5.0
	7.IX. "	2.5	20.0	6.0	1.8	6.0	12.5	1.93	295	104.2	3.5
	26.X. "	12.0	21.0	12.0	0.8	2.0	31.2	1.75	425	77.5	5.6
	29.I. 1972	2.5	18.0	12.5	2.7	3.7	6.2	2.12	520	87.5	5.0
	10.V. "	2.0	50.0	9.3	1.5	7.5	12.5	3.00	250	87.5	2.5
Sztosza (p) poniżej ujścia kanałów below the mouth of the channels (Bukowno)	19.V. 1971	10.7	1400.0	175.0	16.7	100.0	-	-	-	-	-
	13.VII. "	7.0	333.0	13.0	2.7	4.0	43.7	2.50	375	105.0	2.5
	7.IX. "	3.8	812.0	244.0	11.0	47.0	75.0	2.50	400	119.8	8.7
	26.X. "	4.0	253.0	44.0	2.5	10.0	37.5	1.50	350	82.5	5.0
	29.I. 1972	2.5	250.0	25.0	4.5	6.2	16.2	2.12	520	118.8	3.8
	10.V. "	2.0	267.5	19.5	2.5	25.0	12.9	6.00	175	100.0	5.0
Biaża Przemysła (r) (Maozki)	19.V. 1971	10.7	500.0	20.0	3.7	131.0	-	-	-	-	-
	13.VII. "	12.0	300.0	6.0	3.5	178.0	43.8	1.75	625	105.0	9.0
	7.IX. "	13.8	421.0	14.0	4.0	114.0	87.5	3.25	580	104.2	7.5
	26.X. "	21.0	1489.0	22.0	4.2	400.0	43.8	2.00	575	75.0	10.0
	29.I. 1972	12.5	1000.0	27.5	6.7	450.0	12.5	1.75	350	125.0	5.0
	10.V. "	18.8	807.5	19.5	5.0	205.0	25.0	7.00	625	94.0	5.0
Wisza (r) (Soiejowice)	19.V. 1971	16.0	900.0	37.0	10.0	194.0	-	-	-	-	-
	13.VII. "	16.0	400.0	13.0	5.0	150.0	87.5	3.00	1500	82.5	5.0
	7.IX. "	10.0	340.0	24.0	7.3	313.0	112.5	4.75	1425	104.2	11.3
	26.X. "	20.0	532.0	31.0	8.5	230.0	62.5	3.50	1750	58.0	15.6
	29.I. 1972	37.5	1250.0	27.5	13.7	675.0	31.3	2.50	1600	63.0	7.5
	10.V. "	17.5	665.0	25.0	6.3	250.0	37.5	9.00	1200	75.0	12.5

the very high content of magnesium) and the content of sulphides is noted in it.

Also the content of microelements in the water of the stream Biała next to its outflow to the Biała Przemsza reveals no great changes in comparison with their primary amounts in the clean water before the mouth of the channel No 1 (Table III). Usually only the content of zinc and lead distinctly increases. The content of copper is maintained at the same level as in the clean waters of this region. A certain amount of copper which gets into the flotation effluents as a result of its use as one of the reagents in his process, is probably precipitated already in the section of the channel with xanthogenate in the form of sulphides and other compounds. Among others, the sulphide anion is released in the decomposition of xanthogenate. In periods of low water level in the stream Biała this situation is somewhat worse.

Such small changes in the chemism of the waters of the lower sector of the stream Biała under the influence of the flotation effluents would seem to result from the fivefold dilution of these polluted waters by the clean water of the stream and from its great capacity for self-purification. This capacity results primarily from the occurrence of wide, shallow overflows along almost the whole length of its bed, densely covered with various flowering plants.

On account of the low concentration in the water of the final sector of the stream Biała of various macro- and microelements and owing to the new, about threefold, dilution which this water undergoes in the River Biała Przemsza, the influence of this stream on the chemism of the water of the Biała Przemsza is very small. This is revealed in the determination of the chemical properties of the water from the river slightly below the mouth of the stream Biała (fig. 1, point 5).

The neutralized metallurgic waters (Table II) fed directly to the Biała Przemsza through the channel No 2 are in general characterized by a neutral reaction, very high total hardness resulting mainly from the content of magnesium, very large amounts of sulphates and aluminium, a medium content of suspended solids, and a small content of iron.

Though the amount of water flowing through the channel No 2 is not very great, it brings into the River Biała Przemsza a considerable load of zinc and lead. The concentration of these elements in its water is usually very high (Table II) in spite of the precipitation of considerable amounts of these elements from the crude metallurgic waters in the process of neutralization (Table II). Unlike the flotation effluents, the waste waters from the plant contain greater amounts of zinc than of lead.

Similarly as the clean water of the stream Hutka, the clean water of the upper sector of the stream Sztoła up to the mouth of the

channel No 3 has an alkaline reaction, good oxygenation, an exceptionally low content of sodium, potassium, chlorides, and low oxidability (Table I). A characteristic feature is also the content of magnesium, rarely noted in Polish natural surface waters. This peculiarity is most probably connected with the occurrence of dolomite rocks and permeable soil cover in the substratum of the catchment basin of these streams. The average yield of the stream Sztoła next to the mouth of the channel No 3 is about 300 l/sec.

The content of microelements in the clean waters of the upper Sztoła and Hutka is on the whole low. Particularly small amounts of copper and manganese are found. The content of zinc and lead exceeds only slightly the most frequently encountered level of these components in the clean waters of rivers and lakes (Konovalov et al. 1966, Weiler, Chawla 1969, Pasternak, Antoniewicz 1971, Więclawski 1972). Hence it seems that the natural influence of the presence of rocks containing zinc and lead ores in the deeper layers of the substratum of the catchment basin on the flowing surface waters is fairly small. It must be noted here that also the action of air pollution on these water courses is insignificant, the territory of their catchment basin not being situated on the line of the prevailing winds and lying at a fairly considerable distance from the source of emission, i.e. from the plant. The dusts from the metallurgic plant in the investigated industrial centre are mainly concentrated on the territory lying to the east and, according to Ząbczyński (1970), amounts to 38.8 t Zn/sq.km and 2.86t Pb/sq.km/year. Furthermore, no great influence of dusts on the chemism of the water of these streams is to be expected since they are partly supplied by Karstic springs.

The weak natural effect of the ore-bearing rocks occurring in the deeper substratum on the chemism of the water of these two streams may also result from the weak solubility of carbonates, sulphides, lead sulphates, and zinc occurring in the rock, in the alkaline and well oxidized waters of these territories, or from the susceptibility of these salts to secondary precipitation from the waters of such a reaction (also together with iron hydroxides — Solomin, Gončarova 1968). It seems that this weak effect may also be connected with the great drainage by the mines of the ground waters of quaternary level. In the clean waters of these two waters courses only chromium appeared in relatively large amounts at some periods.

In the stream Sztoła, below the inflow of the industrial channels Nos 3 and 4, the basic properties of the water undergo fairly small changes, the reason being that the basic chemism of the waters drawn from the mine (Table II) differs only insignificantly from the chemical composition of the water from the upper section of the Sztoła (Table I). As may be inferred from the results of the analyses, this phenomenon

is connected with the small inflow of pollution from the territory of surface industrial plants into the waters of the channels. In the water of the Sztola below the mouth of the channels some increase in the content of mineral suspended solids, the changes in the temperature (a decrease in summer and an increase in winter), and a small increase in the content of chlorides, sodium, potassium, and iron were observed. Due to the inflow of the water of the channels Nos 3 and 4 to the Sztola, the quantitative composition of microelements is radically changed.

The underground waters of the mine drawn up in the exploitation of the deposits, and then on the surface dumped into the waters of the stream Sztola through the above-mentioned channels, are considerably polluted, mainly with zinc, lead, and cadmium (Table II). The content of zinc and lead in these waters is similar or even higher than in the strongly polluted waters of the River Rhine and its tributaries (Haberer 1968) and of some rivers in the U.S.A. (Kopp and Kroner, undated). Here it must be stressed that beside the determined dissolved and colloidal compounds a considerable amount of lead and cadmium is brought into the surface waters with the waters from the depth of the mine in the form of suspended solids of variable granulometric composition. According to the preliminary experiments, about 60 per cent of the total content of zinc occurs in the suspension of the water from the depth of the mine. More detailed information in this matter will be obtained after the determination of the content of microelements in the bottom sediments of the investigated water courses (work on this problem is being carried out). Besides, the waters from the depth of the mine are characterized by a small content of manganese and copper — similar to that in the clean waters of the Hutka and Sztola. On the sector of the channels Nos 3 and 4 the content of zinc and lead in these waters varies only insignificantly.

Thus the above-mentioned changes in the composition of microelements in the waters of the lower sector of the stream Sztola beneath the points of inflow of waters from the depth of the mine, are for the most part revealed in an increase in the content of zinc, lead, and cadmium. They result not only from the above-described contents of microelements in the mine water but also from the very slight dilution of these waters in the natural water of the Sztola, poorer in these components. The volume of the waters of the channels exceeds several times that of the Sztola at the mouth of the first channel No 3. Moreover, in the quantitative composition of microelements in the water of the lower section of the stream Sztola only an insignificant increase in the content of manganese, copper, and chromium, and an exceptionally large increase in the content of cadmium is noted in relation to the clean water of the upper part of the stream and to that from the

depth of the mine. This supports the thesis, given above, based on the content of microcomponents in these waters, that, they do not receive any great inflow of other industrial pollution.

In the water of the River Biała Przemsza some kilometres below the mouth of the channel No 2 and of the Sztoła the values of the basic chemical parameters change to a not too great degree in relation to the point situated higher (Sławków). In general, in this sector only an increase in the total hardness, in the content of iron and sulphates, and a decrease in the oxidability are found in the water of the river (Table I). The increase in the content of iron is probably connected with the inflow of pollution from the wire-works in Sławków.

In this sector of the River Biała Przemsza the concentration of microcomponents in the water undergoes such greater changes as a result of the inflow through the channel No 2 of waste waters from the zinc plant, strongly polluted with some heavy metals<sup>1</sup>, and of the waters of the stream Sztoła. Above all the content of zinc, manganese, and cadmium significantly increases in comparison with the higher section of the river. At some periods in this point of the river (Maczki) the concentration of zinc in the water even exceeds 0.1 mg Zn/l, this being considered among others by Tomasz (1962) a threshold value, above which it begins to act more or less noxiously on some small aquatic organisms. It seems that this considerable increase in the content of zinc in the water of the Biała Przemsza has been to a high degree brought about by the inflow of metallurgic waters, which are exceptionally rich in this component. On the other hand, at this point of the river no great increase in the content of lead was observed, the amount of copper being similar to that usually noted higher up the river (Sławków). The trend of the content of chromium, molybdenum, cobalt, strontium, and barium in the water of the Biała Przemsza at these two points is similar to that of copper (Table III). In general, the content of strontium in the water of the River Biała Przemsza is in the range most often found by Haberer (1968 a) in the polluted waters of the southern part of West Germany. It is also worthy of note that in Maczki the water of the Biała Przemsza is drawn for the purpose of water-supply.

The results of the investigations of the water from the next recipient of the River Biała Przemsza, i.e. the River Vistula, indicate that the average content of the majority of the determined heavy metals in the more remote sectors of the observed water course does not diminish at all but, on the contrary, increases. However, it must be said that besides the described source of pollution a number of others localized

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<sup>1</sup> Average content of Cu, Cd, and Mn in the water of the channel is 2.5, 162.0 and 1200 mg/l respectively.

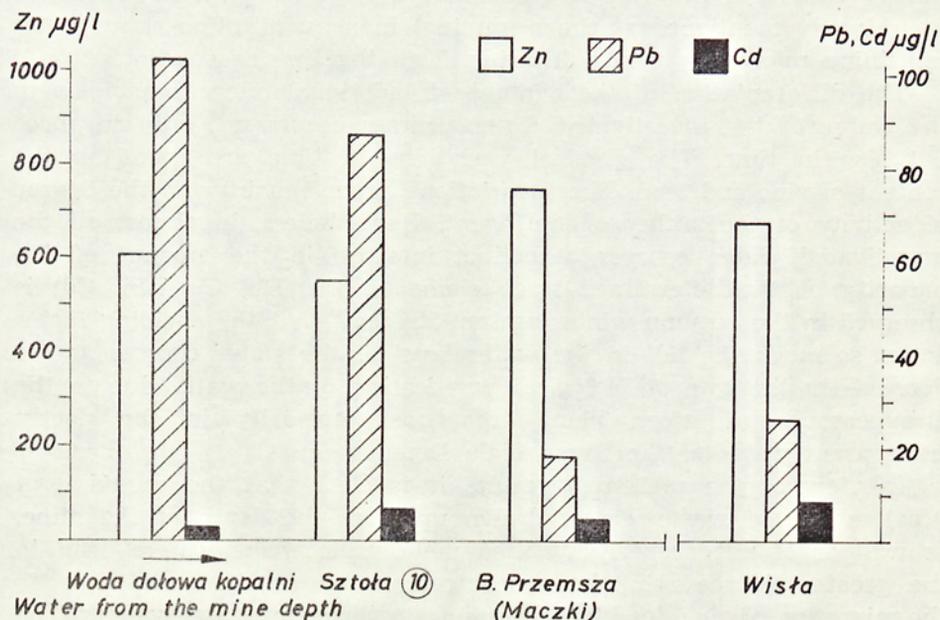
in the catchment basin of the Upper Vistula contribute to it. The water of the River Vistula above the city of Kraków contains above all large amounts of cadmium, strontium, manganese, zinc, and, periodically, copper. Higher contents of the last constituent are among the concentrations which distinctly influence the growth and propagation of trout (with rather low hardness of water), according to the experiments of McKim and Benoit (1971). As far as the content of barium is concerned, its determinations in the investigated water should be regarded as reduced because part of its not readily soluble components failed to dissolve in the nitric acid and remained in the sediment (as was already mentioned at the beginning) in a quantitative ratio to the remaining microcomponents differing from that in the solution.

The differentiation of the content of individual microcomponents in the water of the investigated water courses occurs not only in space but also in time. The greatest variations in time are found in the content of zinc and lead. These variations depend mainly on the degree of activity of the anthropogenic agent. Nevertheless, in almost all the investigated water courses a distinct increase in the amount of the majority of the determined trace elements (Zn, Pb, Cu, Mn, Cd) is observed in the autumn-winter season. It seems that the deciding factor is not so much the fall in the water level of the water courses as the decrease in the rate of biological purification of the water due to the disappearance of green plant organisms, especially in the poorly transparent water of the River Biała Przemsza.

In view of the presented results it is clear that the dumping of great masses of waste waters drawn up from the depth of the mine, as well as of not properly purified metallurgic waste waters, lead to the greatest increase in the concentration and at the same time to the migration of zinc, lead, and cadmium in the investigated waters. The share of strongly polluted flotation effluents supplied by the industrial centre is at present small. However, this situation may change completely if in future additional masses of waters polluted with zinc and lead (e.g. from the new mine Pomorzany) are conducted into some tributary of the stream Biała.

The average values of the concentration of zinc and lead in the water on the various sectors of the outflow of the waters from the depth of the mine are presented in fig. 2. These data suggest that the content of lead in the water already strongly decreases on the first kilometres as it flows away from the source of pollution, but then changes only insignificantly over a long distance. This is probably connected with the difference in weight between the compounds of zinc and lead in favour of the latter, or with a somewhat different ability of less readily soluble salts of these compounds for quantitative precipitation from the well-oxidized alkaline mine water. Lead sulphate

is much less soluble in water than zinc sulphate. The lowest solubility in water and the greatest stability in the solution is shown by lead carbonate, which is formed under the influence of free  $\text{CO}_2$ . It is also probable that in a certain measure this phenomenon may be connected with the more intensive sorption of lead than of zinc on the surface of the suspended solids in the investigated medium (Hellman 1970) or with a greater amount of it in the suspension itself, and hence its easier mechanical precipitation from the water. Any selective action of epiphyte or planktonic algae occurring in the channels with mine



Ryc. 2. Średnie wartości stężenia cynku, ołowiu i kadmu w wodzie na poszczególnych odcinkach drogi odpływu dołowych wód kopalnianych (strzałka oznacza kierunek przepływu wody)

Fig. 2. Mean content of zinc, lead, and cadmium in the water of individual sectors of the outflow of the waters from the depth of the mine (the arrow indicates the direction of the water flow)

water does not come into consideration (C o w g i l l 1970, G r o t h 1970). The capacity of precipitation of lead from water on a relatively short sector of the water course is a very favourable phenomenon in a water environment polluted with heavy metals. If absorbed for a longer time by the water organisms (accumulation capacity) the lead salts may be toxic for some of them already with a content of 0.1 mg Pb/l (Haberer, Normann 1971). It must be mentioned here that the toxicity of lead as well as of other heavy metals is inversely proportional to the hardness of the water (J o n e s 1964; M o u n t 1966). Moreover,

it must be stipulated that because of the very complicated character of the problem, the range of the biological tolerance of the concentrations of metals must for the present be taken with caution. In the waters of the Przemsza and its tributaries, rich in calcium and magnesium, the toxic action of metals may be much weaker.

As opposed to lead the content of zinc, though somewhat changing locally along the flow of the mine waters, remains within the range of high values over several kilometres of the water course. It seems that the agent favouring this longer persistence of zinc in the water is the pH value of the water of the River Przemsza (and also of the Vistula), lower than that of the inflowing industrial waste waters (Table I), and the occurrence of the great number of various active organic compounds which may form soluble complex compounds with zinc in the water of this river. The possibility of the formation and occurrence of such combinations in the waters are indicated in the papers of Gončarova et al. (1968), Nazarova, Eremenko (1971), and Tovstopiat et al. (1971). In the conclusions of their investigations Nazarova and Eremenko (1968) suggest that in the conversion of forms and in the circulation of heavy metals in the waters the complex combinations play an important part when the concentration of any metal exceeds the solubility of its hydroxide. In the maintenance of the high level of zinc in the water of the Biała Przemsza some part is probably played by the salts of iron and aluminium hydroxides and by the above-mentioned suspension, which also reveals a considerable sorption capacity in relation to zinc (Lobčenko, Kaplin 1968, Lobčenko, Solomin 1968, Hellmann, Griffatong 1969).

The great volume of outflowing waste waters from the investigated centre suggests that the drawing up of the underground waters in the exploitation of mines in this centre is fairly great. This drawing up leads to the formation of a depression funnel around it (at present with the radius of about 8 km) and to a deficit in drinking water. Hence, one of the important elements of preventing the negative effects of the discussed industrial centre on the water relations in the surrounding territories is — besides the purification of the most polluted water bodies — to secure a supply of drinking water for the population of the region. It seems probable that a source of such water may be the waters from the depth of the mine. As may be inferred from the obtained results of analyses, the mine waste waters drained away to the River Biała Przemsza are satisfactorily clean as far as their basic chemical properties are concerned, so that after removing the suspension and the major part of the load of zinc and lead they can meet the requirements of good drinking water. Because of the occurrence of subcolloidal particles in the suspension of these waters (trituated rock substratum) which settle with great difficulty, this suspension cannot

be removed in settling tanks. Among other methods, the removal of the suspension and of the majority of heavy metals from such waters may be performed by coagulation and filtration. The purification installations proposed by Kölle et al. (1971) used hitherto in waterworks are not capable of removing the pollution of heavy metals from flowing waters.

In some Canadian mines not only the waste water from the process of ore-dressing but also the waters from the depth of the mine are purified before release to the receiver. The waters from the mine depth are already purified underground (collective work 1970). After this treatment calcium is the first reagent added to the waters collected in special containers. The sediment is filtered off on vacuum filters. Finally it should be mentioned that the considerable amounts of suspensions brought into the water courses with the waste waters of the zinc industry result in the silting-up of their bottoms and in impeded contact with the ground waters in the valley.

### Conclusions

1. From the region of the centre of the zinc and lead industry the migration of some heavy metals through the water courses over considerable distances may be fairly great.

2. From the investigated microcomponents the greatest amounts of zinc and lead and the least of copper migrate to the waters of the neighbouring streams.

3. In the water of the successive receivers of wastes the content of lead decreases the most rapidly and that of zinc the slowest as the distance from the source of pollution increases.

4. The natural occurrence of zinc and lead ores in the deeper rock layers has little influence on the surface waters of pH about 8.1 and high total hardness occurring in the investigated region. The increase in the content of zinc, lead, and cadmium in the water of the investigated streams is mainly connected with the direct inflow of various industrial wastes to these water courses.

5. Due to the possibility of a considerable dilution of waste water flowing from the investigated industrial centre into the receivers, the degree of pollution with zinc, lead, and cadmium in the neighbouring water courses is not yet so high as seriously to endanger the organisms living in the sections of the river environment more remote from this centre. However, short-lasting, accidental, extreme concentrations of these metals in the metallurgic wastes and hence the appearance of distinct toxic influences in the River Biała Przemsza and further on, cannot be disregarded.

6. The quantitative level of the content of zinc, lead, copper,

manganese, and cadmium in the water of the investigated water courses reveals a distinct tendency to increase in the autumn-winter period.

7. The occurrence of calcium and dolomite rocks in the catchment basin of the investigated water courses is revealed in the chemical composition of the water by a high content of magnesium and a low one of manganese and copper.

#### STRESZCZENIE

Praca zawiera wyniki badań nad rozprzestrzenianiem się metali ciężkich w wodach płynących z rejonu występowania naturalnych złóż cynku i ołowiu oraz eksploatującego te złoża przemysłu górniczo-hutniczego (Bolesław). Stężenie pierwiastków śladowych (tabela II i III) w różnych zanieczyszczonych wodach przemysłowych, poflotacyjnych, hutniczych, odpadowych z kopalni, odprowadzanych kanałami oraz w wodzie dalszych naturalnych ich odbieralników (rzeka Biała Przemsza i jej dopływy oraz Wisła), rozpatrywano na tle ogólnego chemizmu tych wód (tabela I). Plan sieci badanych cieków z wyjątkiem odcinka Wisły) oraz rozmieszczenie punktów poboru prób wody, przedstawiono na ryc. 1. Kanałem nr 1 są odprowadzane wody poflotacyjne z zakładu wzbogacania rud, kanałem nr 2 wody hutnicze a kanałami 3 i 4 odpadowe wody z kopalni. Badania były wykonywane w 1971—72 r. Zawartość mikroskładników w wodach oznaczano przy pomocy atomowego spektroskopu absorpcyjnego.

Między innymi wyniki te pozwoliły stwierdzić, że z rejonu ośrodka przemysłu cynkowo-ołowiowego wynoszenie drogą wodną na dalszą odległość niektórych metali ciężkich może być dość znaczne. Spośród badanych mikroskładników do cieków odwadniających okolice badanego ośrodka przemysłowego w największej ilości migruje cynk i ołów a w najmniejszej miedź. Naturalna obecność w głębszych warstwach skalnych rud cynku i ołowiu wpływa na wody powierzchniowe o pH około 8,1 i znacznej twardości ogólnej (jakie występują na badanych terenach) stosunkowo słabo. Znaczny wzrost w wodzie naturalnych cieków stężenia cynku, ołowiu i kadmu wiąże się więc przede wszystkim z dopływem do tych cieków różnych przemysłowych zanieczyszczeń.

Skażenie poflotacyjnych i hutniczych wód cynkiem i ołowiem, jakkolwiek zmienne w czasie, jest z reguły wysokie (tabela II). W pierwszych wodach kilkakrotnie przeważa ołów nad cynkiem, a w drugich — odwrotnie. Spora ilość cynku, ołowiu i kadmu dostaje się do okolicznych, naturalnych cieków również z wodami dołowymi kopalni (tabela II i III). Poza oznaczonymi rozpuszczalnymi związkami tych metali z kopalnianymi wodami migruje też znaczna ich ilość w postaci zawiesiny. W rezultacie istnienia możliwości znacznego rozcieńczenia się w odbiornikach zanieczyszczonych wód, odprowadzanych z badanego ośrodka przemysłowego, stopień skażenia cynkiem, ołowiem i kadmem okolicznych wód płynących nie jest jeszcze tak duży, aby mógł poważnie zagrażać organizmom żyjącym w bardziej odległych od tego ośrodka punktach środowiska rzeczno. Nie można jednak wykluczyć występowania okresowo bardzo dużych awaryjnych stężeń tych metali w wodach hutniczych i w następstwie tego zwiększenia wpływów toksycznych. Sytuacja ta może w przyszłości ulec pogorszeniu, jeśli doprowadzeniu do potoku Biała większej masy zanieczyszczonych wód (z nowej kopalni) nie będzie towarzyszyło zwiększenie oczyszczania najbardziej uciążliwych ścieków.

W wodzie kolejnych odbiorników zanieczyszczeń, w miarę oddalania się od ich źródła, najszybciej redukuje się zawartość ołowiu, a najwolniej cynku

(ryc. 2). To stosunkowo szybkie wytrącanie się z wody już na pierwszych kilometrach biegu cieką dużej części ołowiu zachodzi, jak się wydaje, głównie na drodze fizyko-chemicznych procesów. Selektywne oddziaływanie występujących w kanałach z wodami kopalnianymi poroślowych oraz planktonowych glonów do tak znacznych ubytków tego pierwiastka nie mogło by doprowadzić. Ilościowy poziom w wodzie badanych cieków cynku, ołowiu, miedzi, manganu i kadmu, mimo zmienności w czasie ładunku przemysłowych zanieczyszczeń w jesienno-zimowym okresie, wykazuje wyraźną tendencję wzrostową (zmniejszenie oddziaływania czynnika biologicznego). Występowanie w podłożu zlewni badanych cieków skał wapiennych i dolomitowych, ujawnia się w składzie chemicznym ich wody wyjątkowo dużą zawartością magnezu, a małą manganu i miedzi.

Objętość zczyrywanych wód kopalnianych badanego ośrodka, jak wynika z oddziaływań kanałów je odprowadzających, jest bardzo znaczna. Spowodowało to powstanie na tym obszarze dużego leja depresyjnego (ok. 8 km). W związku z tym jednym z ważnych elementów zapobiegania ujemnym skutkom oddziaływania tego rodzaju obiektów przemysłowych na stosunki wodne jest nie tylko oczyszczanie zanieczyszczonych wód, lecz także zaopatrzenie ludności tego obszaru w odpowiednią wodę pitną. Po uprzednim pozabawieniu subkoloidalnej zawiesiny oraz nadmiaru cynku i ołowiu źródłem takiej wody mogły by się stać właśnie wody dołowe kopalni. Uzdatnianie ich wymaga jednak zastosowania nie tradycyjnych metod. Duża ilość zawiesiny w zanieczyszczonych wodach tego rodzaju przemysłu powoduje nadmierną kolmatację dna cieków i odcięcie ich od kontaktu z wodami gruntowymi doliny.

#### REFERENCES

- Allen H. E., W. R. Matson, K. H. Mancy, 1970. Trace metal characterization in aquatic environments by anodic stripping voltametry. *J. Water Poll. Control Fed.*, 42, 573—581.
- Bhagat S. K., W. H. Funk, R. H. Filby, K. R. Shah, 1971. Trace element analysis of environmental samples by neutron activation method. *J. Water Poll. Control Fed.*, 43, 1214—2423.
- Cowgill U. M., 1970. The hydrochemistry of Linsey Pond, North Brandford, Connecticut. 1. Introduction, field work and chemistry by X-ray emission spectroscopy. *Arch. Hydrobiol.*, 68, 1—95.
- David D. J., 1968. The suppression of some interferences in the determination of molybdenum by atomic-absorption spectroscopy in air-acetylene flame. *Analyst.*, 93, 79—82.
- Gončarova T. O., N. J. Kužekova, E. N. Titkova, B. T. Kaplin, 1968. Vzaimodejstvie ionov Ni, Co, Cu, Zn v rastvorach s guminowymi kislotami. *Gidrochim. Mat.*, 48, 103—111.
- Groth P., 1971. Untersuchungen über einige Spurenelemente in Seen. *Arch. Hydrobiol.*, 68, 305—375.
- Haberer K., 1968. Ergebnisse spurenanalytischer Untersuchungen an Fließgewässern in Süddeutschland. *Vom Wasser*, 35, 72—75.
- Haberer K., 1968 a. Der natürliche Strontiumgehalt in Oberflächen-Gewässern. *Vom Wasser*, 35, 100—108.
- Haberer K., S. Normann, 1971. Metallspuren im Wasser — ihre Herkunft, Wirkung und Verbreitung. *Vom Wasser*, 38, 157—182.
- Hellmann H., A. Griffatong, 1969. Die Absorption von Schwermetallen an den Schwebstoffen des Rheines — eine Untersuchung zur Entgiftung des Rheinwassers. *Deutsche Gewässerk. Mitt.*, 6, 160—164.

- Hellman H., 1970. Die Absorption von Schwermetallen an den Schwebstoffen des Rheins — eine Untersuchung zur Entgiftung des Rheinwassers (ein Nachtrag). Deutsche Gewässerker. Mitt., 14, 42—47.
- Hemsley J., 1971. The use of atomic absorption in water pollution control. Water Poll. Control. 90, 611—618.
- Jones J. R. E., 1964. Fish and river pollution. London, Butterworths L. T. D.
- Just J., H. Hermanowicz, 1964. Fizyczne i chemiczne badanie wody do picia i potrzeb gospodarczych. Warszawa, PZWL.
- Konovalov G. S., A. A. Ivanova, T. Ch. Kolesnikova, 1966. Redkije i rassejannye elementy (mikroelementy) v vode i vovzešennych veščestvach rek evropejskoj teritorij SSSR. Hidrochim. Mat., 42, 94—111.
- Kopp J. F., R. C. Kroner, (undated). Trace metals in waters of the United States, a five-year summary of trace metals in rivers and lakes of the United States (1962—1967). U. S. Dep. Interior Fed. Wat. Poll. Control, Admin. Cincinnati, Ohio.
- Koziorowski B., J. Kucharski, 1964. Ścieki przemysłowe. Warszawa, Wyd. Nauk.-Techn.
- Kölle W., Dorth, G. G. Smiricz, H. Sontheimer, 1971. Aspekte der Belastung des Rheines mit Schwermetallen. Vom Wasser, 38, 183—196.
- Lobčenko E. E., N. T. Kaplin, 1968. Rol vzvešennych veščestv v samoočiščenij prirodnych vod ot jonov medi i cinka. Hidrochim. Mat., 48, 151—155.
- Lobčenko E. E., G. A. Solomin, 1969. Izučenie adsorbciionnych svojtv glinistych mineralov. Soobščenie v konstanty adsorbciionnych ravnovesij pri neposredstvennom obmene Ca, na Cu i Zn. Godroshim. Mat., 49, 194—201.
- Loyd R., 1960. The toxicity of zinc sulphate to rainbow trout. Ann. Appl. Biol., 48, 84—94.
- McKim J. M., D. A. Benoit, 1971. Effects of long-term exposures to copper on survival, growth and reproduction of brook trout (*Salvelinus fontinalis*). J. Fish. Res. Bd Can., 28, 655—662.
- Mount D. J., 1966. The effect of total hardness and pH on the acute toxicity of zinc to fish. Int. J. Air Water Poll., 10, 49—56.
- Nazarova A. A., B. Ja. Eremenko, 1968. Kompleksnye svedinenija metallov s limonnoj kislotoj. Hidrochim. Mat., 48, 64—71.
- Nazarova A. A., B. Ja. Eremenko, 1971. O kompleksoobrazovanej cinka i kadmija s dietilaminam. Hidrochim. Mat., 56, 107—110.
- Pasternak K., A. Antoniewicz, 1970. Wstępne badania nad zawartością niektórych mikroskładników w wodach powierzchniowych południowej Polski — Preliminary investigations on the content of some trace components in surface waters of Southern Poland. Acta Hydrobiol., 12, 111—124.
- Pasternak K., 1971. Zawartość miedzi, cynku i manganu w wodzie zbiornika zaporowego w Goczałkowicach oraz kilku innych zbiorników — The content of copper, zinc, manganese in the water dam reservoir at Goczałkowice and of several other reservoirs. Acta Hydrobiol., 13, 159—177.
- Pasternak K., A. Antoniewicz, 1971. Zmienność zawartości miedzi, cynku i manganu w wodzie kilku rzek, potoków i stawów karpowych — The variability of copper, zinc, and manganese content in the water of some rivers, streams, and carp ponds. Acta Hydrobiol., 13, 251—268.
- Paus P. E., 1971. Application of atomic absorption spectroscopy to the analysis of natural waters. Atomic Absorption Newsletter, 10, 69.
- Praca zbiorowa, 1971. Filter process for mine water uses lime as initial agent. Pit a Quarry, 3, 33.
- Prudnikov E. D., Ju. S. Šapkina, M. P. Semov, 1971. Plamenno-spektro-

- fotometričeskoje opredelenie mikrokoličestw litija, rubidija, cezija i stroncija v vodach. *Izv. Vyss. Uc. Zav., Ser. Chim. Techn.*, 14, 196—197.
- Ramakrishna T. V., P. W. West, J. W. Robinson, 1969, The determination of molybdenum by atomic absorption spectroscopy. *Anal. Chim. Acta*, 44, 437—439.
- Rubeška J., B. Moldan, 1969. Atomic absorption spectrophotometry. London, ILIFTE Books L. T. D.
- Solomin G. A., T. O. Gončarova, 1968. Rol gidrookisej v samočiščenij prirodnych vod ot ionov tjaželych metallov. *Gidrochim. Mat.* 46, 143—149.
- Solski A., K. Łyskawa, E. Rzewuska, 1972. Wzrost toksycznego działania ksantogenianu etylo-sodowego na organizmy wodne pod wpływem wolnego chloru. *Mat. Bad. IGW*, 21, Ser. Ochr. Wód przed Zanieczyszcz. 9.
- Standard Methods for the examination of water and wastewater, 1971. 13th Edition. Washington, APHA.
- Thomas E. A., 1962. Zink in Trinkwasser als Algengift. *Arch. Mikrobiol.*, 42, 246—253.
- Tovstopjat E. C., V. Ja. Eremenko, A. A. Nazarova, 1971. Kompleksnyje soedinenija tjaželych metallov a aminokislotami, vstrečajuščimisja v prirodnych vodach. *Gidrochim. Mat.*, 56, 91—106.
- Weiler R. R., V. K. Chawla, 1969. Dissolved mineral quality of Great Lakes waters. *Proc. 12th Conf. Great Lakes*, 801—818. Intern. Ass. Great Lakes Res.
- Więclawski F., 1972. Badania zmian zawartości metali ciężkich w wodach jeziorowych Pojezierza Mazurskiego — Investigations on the changes in the content of heavy metals in lake waters of the Masurian Lake District. *Acta Hydrobiol.*, 14, 149—163.
- Zavodnov S. S., E. E. Lobčenko, N. G. Fečenko, 1965. O zagraznenij medju i cinkom rek Severnoj Osetii i processach ich samočiščanija. *Gidrochim. Mat.*, 40.
- Ząbczyński S., 1970. Wpływ zanieczyszczenia powietrza na gleby i kształtowanie się produkcji rolniczej. *Post. Nauk Roln.*, 5, 3—18.
- Zukov A. J., I. L. Mongait, 1948. Rudoobogatitelnye fabryki, *Proizvodstv. Stoč. Vody*, red. T. E. Boldyreva, Moskva.

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## ERRATA

Strona Page	Wiersz — Line		Zamiast Instead of	Winno być Ought to be
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194				
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Table II				
column 13		4		1
column 24		19	33	3
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Table III				
column 5		11	39,2	29,2
column 17		11	30,4	29,1
203				
Table IV	1		w	z
218				
Table II	1		limnicznych	limnicznych, $n \cdot 10^3$
	4		reservoirs	reservoirs, $n \cdot 10^3$
223				
Table III	2		wodnego	wodnego, $n \cdot 10^3$
	4		environment	environment, $n \cdot 10^3$