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The environmental fate of metals from zinc and lead mining area in surface water (Przemsza River, southern Poland)

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Abstract: The chemical composition of surface waters of the Przemsza River flowing through Upper Silesia (in southern Poland) is strongly affected by Zn and Pb ore, and less by Carboniferous hard coal deposits. The chemical type of surface water is $Ca\text{-}HCO_3$. In the waters, three groups of metals and metalloids were found that directly interfere with the mineralization of the deposit. Although genetically related to the same deposit, each group exhibits a different fate in the environment. A typical deposit association is Pb-Zn-Ag-As-Sb-Hg. The first group of metals in surface waters is consistent with the typical association of the ore Zn-Pb-Cd-(Tl), the second includes Ag-Sb-Hg, and the third includes the additives in the zinc and lead ore Co-Ni-Mo-Mn:

$$\begin{bmatrix} \mathrm{Ca} & \mathrm{HCO_3\ or\ SO_4} \\ \uparrow\downarrow + & \uparrow\downarrow \\ \mathrm{Na} & \mathrm{Cl} \end{bmatrix} + \Big[\big[\mathrm{Zn}-\mathrm{Pb}-\mathrm{Cd}-(\mathrm{Tl})\big]+\big[\mathrm{Ag}-\mathrm{Sb}-\mathrm{Hg}\big]+\big[\mathrm{Co}-\mathrm{Ni}-\mathrm{Mo}-\mathrm{Mn}\big]\Big].$$

Depending on the pH-Eh conditions, metals and metalloids precipitate out of the solution or sorb on solid particles. The concentrations of individual groups of metals are interdependent but show different environmental fates along the river course. The natural process of the enrichment of surface waters with Zn-Pb-Cd-(Tl) is by water circulation in a rock matrix naturally rich in the metals and draining groundwaters by the river. Under oxidizing and slightly alkaline conditions, Ag-Sb-Hg incorporated into the soluted chemical compounds, may, when the physicochemical parameters of the waters change, be adsorbed and/or precipitated. The presence and ratio of concentrations of Co-Ni-Mo-Mn with respect to zinc are almost identical, differing only in concentration.

Keywords: Zn-Pb ore, Upper Silesia region, Przemsza River, metals pollution, thallium, cadmium, mercury

INTRODUCTION

The environmental fate of metals or metalloids of anthropogenic origin is dictated by a number of external factors. The main three include geological structure, hydroclimatic conditions, and chemical factors (Nordstrom 2011, Newman 2018). The latter include a wide spectrum of parameters determining the behavior of a pollutant in individual compartments of the environment. Among the many physical and chemical properties of a pollutant that characterize its content in water, the following are particularly important: (a) concentration, (b) polarity (water solubility), (c) vapor

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pressure (volatilization), (d) Henry's law constant H (gas solubility), (e) octanol-water partition coefficient K_{ow} (hydrophobicity index), (f) organic carbon normalized distribution coefficient K_{oc} (organic soil sorbent capability), (g) sorption, (h) diffusivity, etc. (Pachana et al. 2010). Of the many parameters, only the selected ones are important but all of them may partially influence the final chemical type of the water.

The presence of individual metals in surface waters and their mutual relationships of concentrations are strongly associated with mining of Zn and Pb ore deposits in the region of Upper Silesia in southern Poland (Fig. 1). Carboniferous hard coal deposits also occur in the area, but no longer have an impact on the dispersion of metals in groundwaters and surface waters (Lis & Pasieczna 1997). It is to be emphasized that the main load of metals and metalloids discharged into the Przemsza River in the south and east parts of Upper Silesia is from the discharge of mine waters, post-industrial, post-smelting sewage and post-flotation sewage, or the historical areas of the Zn-Pb ore processing and waste landfilling (Cabała et al 2009).

The occurrence of surface and groundwaters in the Przemsza River basin is associated with the Quaternary and older formations, e.g., Jurassic, Triassic, Carboniferous, and Permian. The water conditions of the river basin depend strongly on precipitation, losses due to evaporation and large-scale discharge of mine waters.

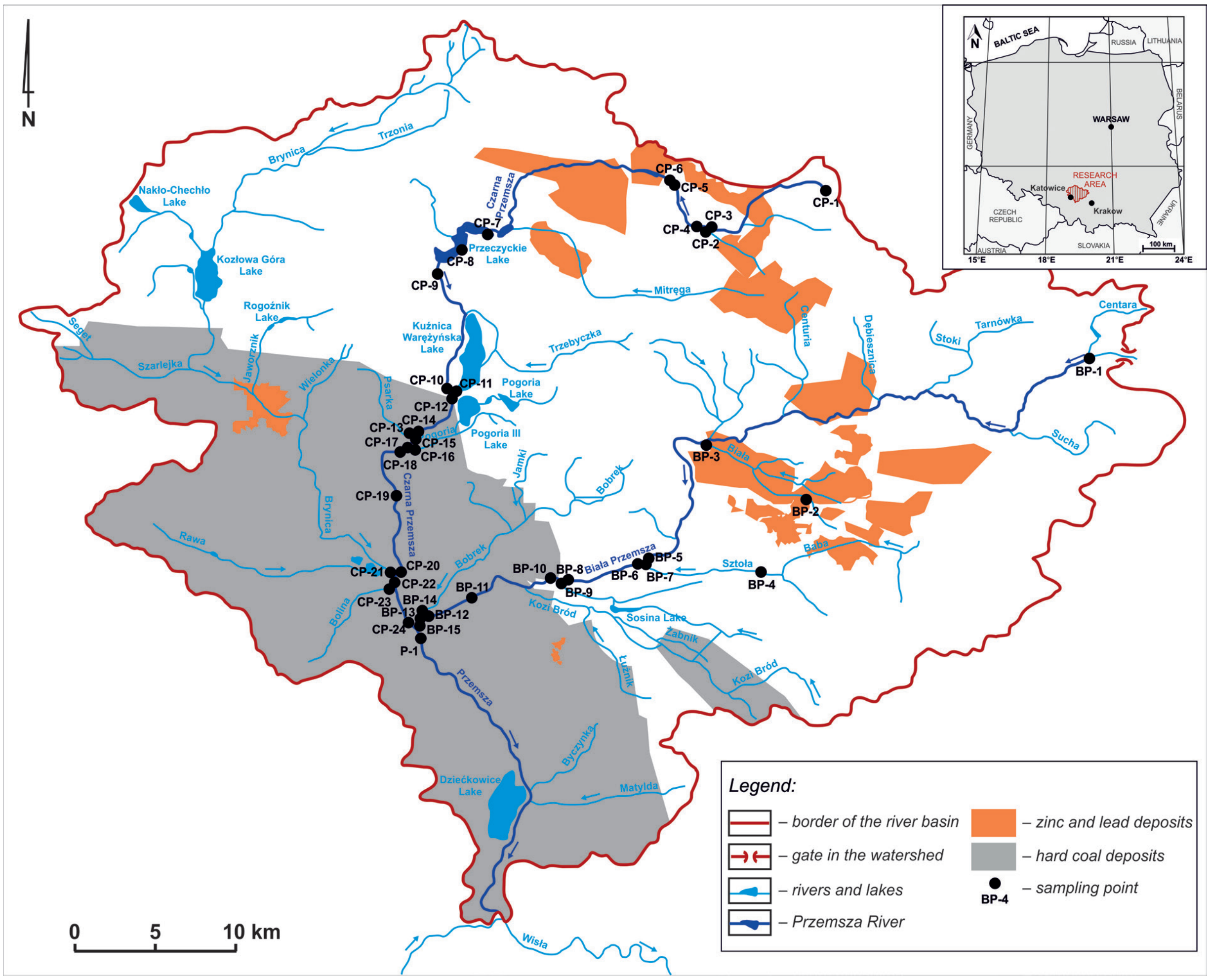

Fig. 1. *The Przemsza River location with sampling points (based on data on ibris.pl and geoportal.pgi.gov.pl)*

Moreover, in the last few decades, the natural conditions of the river have been disturbed due to drinking water transfer from the other drainage basins, river regulation, construction of water reservoirs, and development of depression cones in mines (Chełmicki red. 2001, Treichel et al. 2015, Rzętała 2016).

The main purpose of this work is to identify the chemical type of surface water in a river in relation to anthropopressure, particularly with the mining of zinc and lead ore deposits. On the basis of the chemical composition of water, the work aims to indicate the origin of individual elements related to the mineralization of the Przemsza River catchment. The results of the analysis also allow for the separation of environmental pollution from the geogenic component of the total content.

The Przemsza River is a 100 km-long left-bank tributary of the Vistula River in southern Poland. The catchment of the river, with over 2000 km^2 of surface area, covers the eastern part of the Upper Silesia Upland and the western part of the Cracow Upland. The Przemsza drainage basin comprise the subbasins of the Czarna Przemsza and Biała Przemsza rivers which are called the Przemsza River in their lower section. However, in this study we use the term "The Przemsza River drainage basin" for the entire drainage basin (Fig. 1).

Geological setting and ore mineralization

The river basin covers an area of two tectonic units. The upper course of the Czarna Przemsza and Biała Przemsza rivers drain the Krakow-Silesian monocline, while the rest, the greater part, is within the Upper Silesian Basin.

The tectonic structure of the Krakow-Silesian monocline was shaped by orogenic movements. During the Variscan orogeny, angular incompatibility was formed at the junction of the Triassic and Jurassic during the Old Kimmerian phase. Subsequent changes in this area occurred during the Alpine orogeny, during the Larami phase, at the turn of the Cretaceous and Paleogene. At that time, the Miechów Basin was created and the described tectonic unit became a monocline. Mesozoic rocks are inclined to the northeast. The folding of the Flysch Carpathians had the greatest influence on the present shape of that area. As a result of these orogenic movements, in the Oligocene and Miocene, the Silesian-Krakow monocline was disturbed by numerous faults with relative heights exceeding 100 m, which have a significant impact on the present relief of this area (Burda 2014a).

The Upper Silesian Basin was shaped by orogenesis movements during the Variscan orogeny. The western part is strongly folded, with numerous overthrusts. Discontinuous deformations have a much greater dimensions within the Upper Silesian Basin. As a result, staircase faults with discharges usually from 100 to 150 m are common in this area, although sometimes they reach larger heights. The area of the Upper Silesian Basin is characterized by numerous exposures of Carboniferous formations. Rocks of this age lie at an angle of less than 15° (Burda 2014b).

The catchment of the Przemsza River, including the catchments of the Biała Przemsza and Czarna Przemsza rivers, is rich in zinc-lead ores and hard coal deposits. Coal mining and the related energy industry have a much smaller impact on environmental pollution with metals than the several hundred-years long history of metal extraction (Lis & Pasieczna 1997). Therefore, this study focuses on zinc-lead deposits. Ore deposits have been mined here for zinc, cadmium and lead. Barium, silver, and thallium, as well as sulfur, arsenic, selenium, and tellurium, were of less importance. Taking into account the enrichment of the main elements in relation to average earth crusts levels (Clark values) in the carbonate rocks, the contents of zinc, iron, lead, cadmium, sulfur, silver, thallium, barium, selenium, tellurium, and arsenic are outstanding (Gałkiewicz & Śliwiński 1983). The main sulfide minerals in the area are sphalerite, marcasite, pyrite, and galena, with occasional vurcite and brunckite occurrences. Sphalerite commonly contains admixtures of iron, cadmium, lead, and manganese, to a lesser extent silver and antimony, and traces of thallium, germanium, copper, gallium, indium, cobalt, molybdenum, nickel, and bismuth. Iron sulfides, as a rule, contain admixtures of arsenic, thallium, antimony, lead, and zinc, and less of manganese, copper, nickel, molybdenum, cobalt, silver, and cadmium. Galena has admixtures of metals such as zinc, iron, manganese, silver, and copper, and to a lesser extent arsenic, thallium, indium, germanium, cobalt, nickel, molybdenum, bismuth, and cadmium (Gałkiewicz & Śliwiński 1983). There is some lateral variation in their concentrations. In the studied area of the Przemsza River catchment, zinc concentrations are associated with the domination of iron and enrichment with cadmium and silver. Quantitatively, thallium and arsenic correlate with iron whereas silver correlates with zinc. More intense manifestations of barium are also visible. A certain differentiation is visible in the concentrations of arsenic, antimony, and silver in accordance with the orientation along the SW-NE line, where silver moves towards the SW, and arsenic and antimony towards NE (Gałkiewicz & Śliwiński 1983).

The main chemical component of the ores is zinc and, with a several times lower concentration, lead. Of course, sulfur is the dominant component of sulfide ores. The more important of the accompanying metals are cadmium and silver. Cadmium correlates with zinc with relative ratios of 0.005 Cd to 1 Zn and silver with zinc and lead, with an average ratio of 0.0001 Ag to 1 Zn + Pb. Sulfur is accompanied by selenium and tellurium (Gałkiewicz & Śliwiński 1983). Generally, the mineral composition of ores is dominated by the simple paragenesis of Zn-Pb-Fe sulfide minerals (Cabała 2001, Cabała & Sutkowska 2006). In the ore minerals, apart from Zn, Pb, and Fe, there are accompanying elements: Ag, Cd, Tl, and As. The above-mentioned features and the low crystallization temperature of ores allow them to be classified as epigenetic, low-temperature Mississippi Valley (MVT) hydrothermal deposits (Cabała & Konstantynowicz 1999, Cabała & Sutkowska 2006).

METHODS

The hydrochemical study of the selected reaches of the Przemsza River included the collection of surface water samples and analysis. Samples were collected from the main channel and its tributaries (Fig. 1). The field research was carried out at the turn of August and September 2019. *In situ*, at all 40 measurement points, the physical and chemical parameters of tested waters were determined (pH value, redox potential Eh, temperature, and electric conductivity EC) using a multi-parameter WTW Multi 340i meter. The samples were taken from the middle of the stream at a depth of about 30 cm below the water table. A total of 40 water samples were taken, and 15 of them were subjected to inorganic chemical analysis. In the laboratory, a range of inorganic substances was determined, including chlorides Cl^- (titration – ISO 9297:1989), bicarbonates HCO_3^- (titration – ISO 9963-1:1994), major elements (inductively coupled plasma optical emission spectrometry (ICP-OES – ISO 11885:2007), and minor elements (Tab. 1 and Tab. 1a – attached as a supplementary file in the online version) (inductively coupled plasma – mass spectrometry (ICP-MS) using a Perkin Elmer Elan 6100 Spectrometer – ISO 17294-1:2004 and ISO 17294-2:2003). Overall, each consisted of the determination of 47 components. Chemical analyses of water samples were performed in an accredited Hydrogeochemical Laboratory (No. AB 1050) in the Department of Hydrogeology and Engineering Geology at AGH UST in Krakow in August 2019. In the remaining samples, only chloride concentration was determined as a nonreactive indicator of anthropopressure on local surface waters (Tab. 2). Chlorides were used for marker analysis as a conservative substance, which indicates the maximum extent of spread in the soil-water environment. Moreover, chlorides are mainly attributable to anthropogenic sources, while sulphates usually constitute a natural component (Crawford & Lee 2015). Therefore, we used chloride concentrations as a reference for the variability of other hydrochemical compounds.

During the water sampling, the discharge in the river was estimated at 40 points corresponding to the hydrochemical sampling points. Transverse profiling of the river bed was performed at every point. For 15 "main" points, the flow velocity was measured with a current meter (Hydrometric Current Meter with stick probe OTT companies), and in the remaining points (25) by the floating method using a float floating on the water surface. The flow studies were used to calculate the total substance loads in the river.

Table 1
*Concentrations of selected metals in a surface water [μg/L]**

No.	Ag	Br	Cd	Co	Hg	Mn	Mo	Ni	Pb	Sb	Sr	Tl	Zn
CP-1	6.898	121.25	0.337	0.423	2.091	2.105	5.172	3.320	1.463	19.439	143.018	0.174	*5*
CP-9	8.863	*50*	*0.15*	0.268	2.037	86.071	2.736	1.701	1.104	13.510	124.793	0.137	17.177
CP-11	7.347	*50*	0.316	0.259	1.781	22.978	2.605	2.024	1.992	11.935	154.724	0.142	*5*
CP-19	7.149	*50*	0.400	0.414	1.457	48.161	2.036	3.008	2.022	8.522	243.173	*0.05*	23.861
CP-21	9.132	1996.45	0.985	1.538	1.572	383.461	1.881	12.984	4.218	6.010	1254.668	1.161	75.185
CP-23	28.430	13200.00	0.331	0.600	1.178	27.799	3.957	4.013	0.143	4.538	10332.346	*0.05*	34.520
CP-24	14.618	2952.77	0.648	1.203	1.574	313.557	6.507	16.584	3.191	7.904	1352.848	0.577	39.926
BP-1	8.024	122.49	0.657	0.473	1.163	20.649	2.358	4.569	1.941	5.212	183.980	*0.05*	*5*
BP-2	2.059	401.88	98.697	3.152	0.206	395.285	20.833	15.195	103.372	2.757	220.563	12.817	1926.174
BP-3	4.503	533.36	75.467	2.958	0.252	486.491	34.452	13.159	71.426	3.302	236.133	12.325	1491.192
BP-4	2.026	1039.11	51.753	2.817	0.251	432.970	38.906	12.580	59.086	3.235	245.501	12.260	1149.080
BP-10	*0.5***	58.27	69.799	2.896	*0.05*	415.532	1.220	11.975	25.282	0.351	329.326	3.495	4814.519
BP-11	*0.5*	*50*	52.637	3.678	*0.05*	490.490	1.303	11.266	6.624	0.246	377.949	4.207	3669.381
BP-15	*0.5*	*50*	1.658	0.951	*0.05*	35.736	2.192	6.913	40.653	0.738	111.053	0.836	1006.424
P-1	5.577	2493.26	10.748	1.549	0.223	306.448	19.498	15.360	33.498	2.910	1110.223	4.649	356.927

* Full range of chemical analyses is given in Table 1a attached as a supplementary file in the online version of the article.

** Half of the quantification limit in italic.

Table 2
Chlorides concentration in surface water of the Przemsza River

No.	pH [–]	*T* [°C]	EC [µS/cm]	Cl^- [mg/L]	No.	pH [–]	*T* [°C]	EC [µS/cm]	Cl^- [mg/L]
CP-1*	8.8	10.4	900	32	CP-21	8.0	14.7	3220	551
CP-2	8.2	15.2	864	57	CP-22	8.0	20.5	2100	322
CP-3	7.7	14.9	594	30	CP-23	8.1	15.4	*>20 000*****	6257
CP-4	7.7	14.9	593	33	CP-24	8.0	14.3	3160	753
CP-5	7.8	16.3	820	61	BP-1**	8.3	11.4	873	76
CP-6	7.7	17.5	628	35	BP-2	*n.m.*	*n.m.*	*n.m.*	32
CP-7	8.3	23.3	586	42	BP-3	*n.m.*	*n.m.*	*n.m.*	32
CP-8	9.1	24.4	457	36	BP-4	*n.m.*	*n.m.*	*n.m.*	25
CP-9	8.3	14.3	545	30	BP-5	8.6	11.6	1260	106
CP-10	8.5	17.7	609	32	BP-6	8.4	11.4	1275	115
CP-11	8.6	13.2	588	35	BP-7	8.1	14.9	2.9	417
CP-12	8.7	22.4	464	35	BP-8	8.4	11.6	977	45
CP-13	8.9	18.7	553	43	BP-9	8.5	11.6	1218	60
CP-14	8.5	17.4	590	34	BP-10	8.6	10.4	1075	46
CP-15	8.6	17.6	582	36	BP-11	8.6	12.3	1173	71
CP-16	8.6	18.0	585	35	BP-12	8.9	11.0	728	24
CP-17	7.5	20.4	948	82	BP-13	8.5	11.5	1148	68
CP-18	7.8	19.7	900	64	BP-14	8.3	11.7	600	33
CP-19	8.6	13.3	713	51	BP-15	8.5	11.1	1363	116
CP-20	8.1	19.2	745	65	P-1***	8.2	14.2	2740	514

* CP – The Czarna (Black) Przemsza River, ** BP – The Biała (White) Przemsza River, *** P – The Przemsza River (after the rivers merge), **** value *>20 000* above the measuring range of the EC probe, *n.m.* – no measurement.

RESULTS

In environmental studies, four genetic types of surface waters were pre-identified (Fig. 2). They are related to (i) uncontaminated spring waters with a chemical composition similar to the calcium-bicarbonate groundwaters $Ca\text{-}HCO_3$ (points: CP-1 and BP-1), (ii) characteristics of the Czarna Przemsza (CP-9, 11, 19 and 24) and (iii) Biała Przemsza waters (BP-4, 10, 11 and 15), and also (iv) waters from the tributaries of the Przemsza River heavily polluted due to the discharge of sewage and mine waters composed of Na-Cl (CP-21 and CP-23). The chemical characterization of the waters discharged to the Przemsza River in the 1990s was 0.5–5 mg/L for zinc, 1–2 mg/L for lead, and approx. 150 mg/L for sulphates with an alkaline water pH of 7.9 to 8.2 and a suspension of 50–80 mg/L (Wójcik et al. 1990, Ciszewski 1998).

In order to characterize the chemical state of surface water in the Przemsza River (2019), initially non-reactive chloride concentrations were used in the study as a preliminary indicator of the level of surface water pollution (Tab. 2). The base level of chlorides (CP-1) in the water is about 30 mg/L and remains quasi-constant in the upper, about the 50th km long course of the Biała Przemsza and Czarna Przemsza rivers. Chloride concentration in both rivers increases rapidly ca. 3 times, down to about the 60th kilometer of the river course. The rapid increase in chloride pollution is directly related to the inflow of the polluted tributaries: the Bolina, Brynica and Bobrek rivers. This is a consequence of the discharge of sewages from zinc-lead ore mines as well as from coal mines to these tributaries (Girczys & Sobik-Szołtysek 2003). The maximum chloride concentration determined in the catchment area was 6257 mg/L (CP-23 in the Czarna Przemsza tributary). The chloride load along the entire length of the Czarna Przemsza changes by 3.4 kg/s, and for the Biała Przemsza by 0.89 kg/s. In the CP-23 point, water with maximum sulphate concentration (361 mg/L) is the most polluted in the conducted survey. Sulphate load along the entire length of the Czarna Przemsza changes by 0.82 kg/s, and for the Biała Przemsza by 1.4 kg/s. Relating the amount of pollutant load to the total mineralization of the studied waters, it transpires that the pollution increment for the Czarna Przemsza River is 8.2 kg/s (between the CP-1 and CP-24 points), while for Biała it is 6.4 kg/s (between the BP-1 and BP-15 points). Among the other anions, the concentration of bicarbonates ranges from 209 to a maximum of 409 mg/L, while sulphates range from 33 to max. 361 mg/L. Among the cations, sodium has the highest concentration, corresponding to the concentration of chlorides. Sodium is in the range of 6 to max. 3093 mg/L. The remaining main ions are present in concentrations: calcium from 56 to max. 386 mg/L, potassium from 1 to max. 88 mg/L and magnesium from 7 to max. 218 mg/L.

The highest concentrations of metals in the river were, of course, determined for zinc (max. 4810 μg/L, avg. 974 μg/L). The highest values are recorded in the Biała Przemsza, where active zinc and lead mining took place. Here, the average concentration of Zn is 2009 μg/L, but it is important that in the spring area and the upper course of the Biała Przemsza River, upstream the mining area, the concentration of zinc is below the detection level <10 μg/L, and it is similar to the spring area of the Czarna Przemsza River. Zinc concentrations over the detection level are also observed in river reaches with a lack of tributaries This phenomenon is also noticeable for the remaining elements, although not so clearly. The highest lead concentration in surface water was determined at 103 μg/L (avg. 24 μg/L) in the Biała Przemsza at the point BP-10. Correspondingly, high concentrations were found for cadmium 99 μg/L (avg. 24 μg/L) and thallium 13 μg/L (avg. 4 μg/L) at this point.

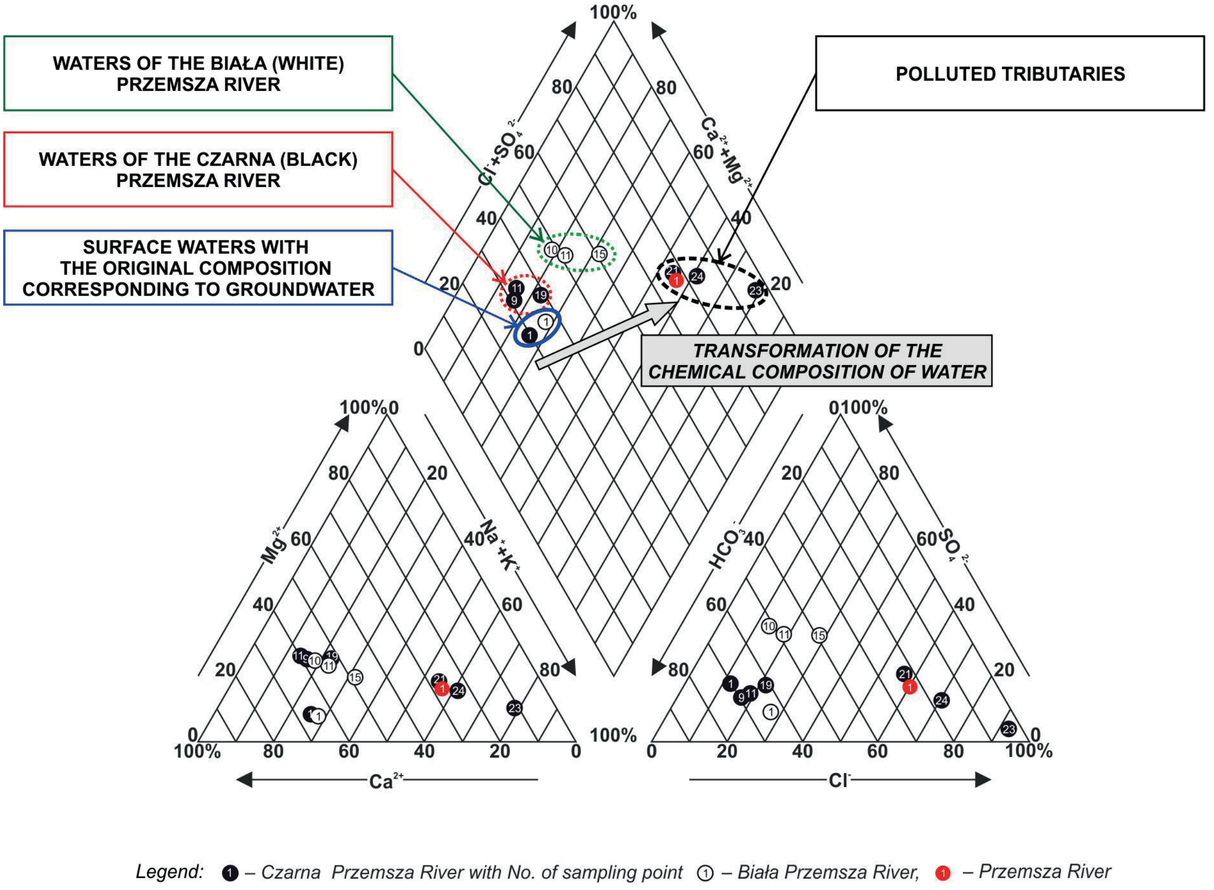

Fig. 2. Piper diagram of chemical characteristics of the Przemsza River surface water

Whereas arsenic is practically absent in the studied waters of the Przemsza River, silver, mercury and antimony, exhibit almost identical spatial distribution pattern. These metals show the highest concentrations in the springs and in the upper river course (the exception is silver in the Czarna Przemsza River, with the highest concentration in the Brynica River, a right-bank tributary). For the Biała Przemsza the maximum concentrations are 8 μg/L (avg. 2.8 μg/L) for silver, 1.2 μg/L (avg. 0.3 μg/L) for mercury and 5 μg/L (avg. 2.3 μg/L) for antimony (all max. values at point BP-1). For the Czarna Przemsza, they are 2.1 μg/L (avg. 1.5 μg/L) for mercury and 19 μg/L (avg. 9 μg/L) for antimony (max. at point CP-1).

DISCUSSION

The chemical composition of the waters reflects anthropogenic activity in a geochemically rich catchment, e.g., Triassic dolomites bearing sulfidic Zn-Pb ore deposits and Holocene fluvial sandy sediments filling most of the valley bottom (Szarek-Gwiazda & Ciszewski 2017). Regardless of the general chemical composition of the main ions determined in the waters, the presence of tree groups of metals and metalloids strongly related to the metalliferous associations of zinc and lead ores in the Upper Silesia region was found independently.

Ore association Zn-Pb-Cd (association in surface water Zn-Pb-Cd-(Tl))

After entering the environment, heavy metals are transported and may cross-react with other substances (Pachana et al. 2010, Pietrucin 2013). Transformation processes in the environment involve photo-and chemical degradation or biodegradation. Heavy metals may also be transformed within organisms by biotransformation (Boonsaner 2006, Pachana et al. 2010). Individual components of the environment, in particular soil, ground, and water, show an increase in the concentrations of Zn, Pb, and Cd metals, typical for zinc and lead ores in this region of Poland (Lis & Pasieczna 1997). A general ore association is type Zn-Pb-Cd and these metals are dispersed in the investigated area in the form of a halo around the zone of mineralization. In the surface water of the Czarna and Biała Przemsza the concentrations of these elements (together with Tl) increase along their courses. The corresponding association in surface water is Zn-Pb-Cd-(Tl) (Fig. 3A, B).

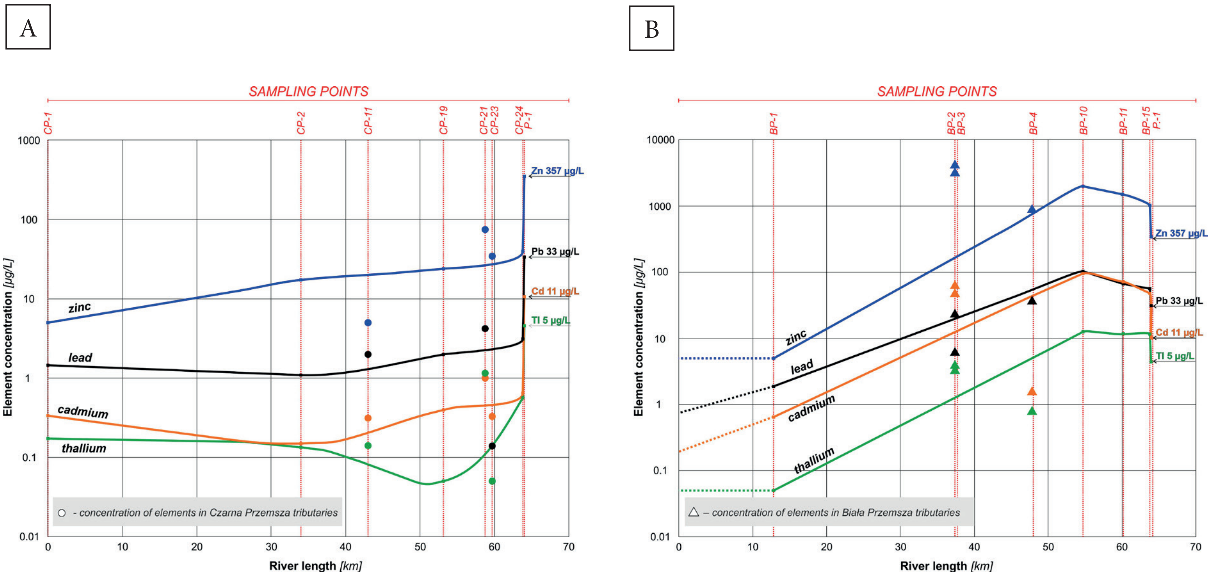

Fig. 3. *Change of concentrations of Zn, Pb, Cd and Tl metals with the course of the Czarna Przemsza River (A) and the Biała Przemsza River (B)*

The main natural process of enriching surface waters with Zn-Pb-Cd-(Tl) metals is the inflow of groundwater into the river bed. The origin of shallow groundwater in the zone of the extensive depression cone is mainly related to the infiltration of precipitation. The groundwater circulating in a rock matrix rich in metals becomes saturated with them, and then drained by the river. The metals are likely to be leached from soil and ground enriched in Zn, Pb, Cd, and Tl in the area. The share of Zn-Pb-Cd-(Tl) in surface waters and the ore is proportional (Fig. 4). The linear correlation of metal concentrations relative to zinc is in the range $R^2 = 0.94$ to 0.99. This is also confirmed by the fact that the highest concentrations of pollutants flowing into the Przemsza River with surface waters come from the tributaries flowing through the deposit zones, i.e., the Sztoła, Brynica and Biała. Mine discharges of groundwaters are an indisputable anthropogenic source of metals in the river waters.

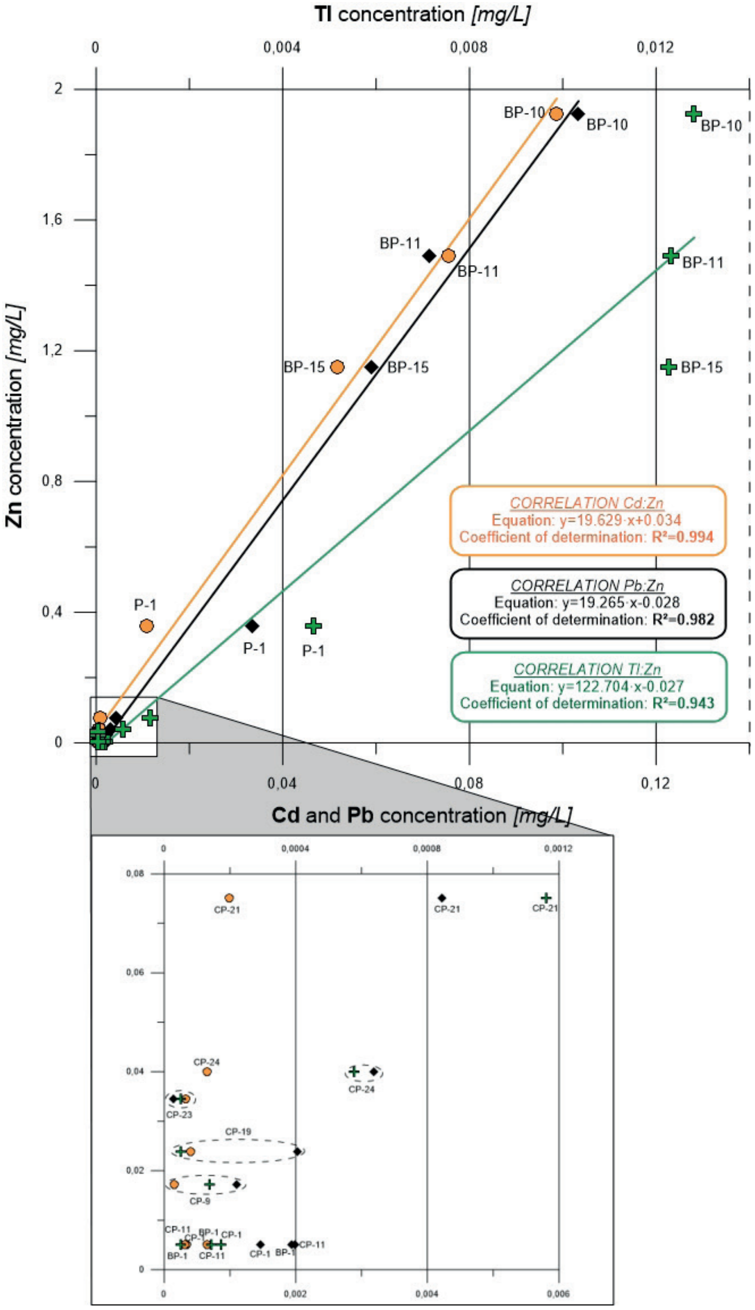

Fig. 4. *The concentration ratio of Cd, Pb and Tl metals to Zn*

Typical association of elements Pb-Zn-Ag-As-Sb-Hg (association in surface water Ag-Sb-Hg)

A typical association for zinc and lead in ore mining area of Upper Silesia is Pb-Zn-Ag-As-Sb-Hg, and the contamination of individual environmental components with these metals is significant, including soil and ground, surface and groundwaters, as well as plants (Xiangdong & Thornton 1993, Lis & Pasieczna 1997, Poulin & Gibb 2008). Silver, antimony, and mercury Ag-Sb-Hg association, exhibit an opposite behavior to the above-discussed ones Zn-Pb-Cd-(Tl) (Fig. 5). The concentrations of silver, mercury, and antimony association decrease logarithmically with the increase of zinc in surface waters. While the concentrations of Zn-Pb-Cd-(Tl) increase along the river course, the concentrations of Ag-Sb-Hg elements gradually decrease. In reference to previous research under oxidizing conditions (Eh 272 mV) and slightly alkaline conditions (pH 8.4), these metals incorporated into the chemical compounds in the suspension may, when the physicochemical parameters of the waters change, be adsorbed and/or precipitated (Niedzielski et al. 2001, Malicka 2007). This phenomenon is especially frequent in river zones with a reduced flow or water stagnation, where redox conditions change toward reducible conditions. The coefficient of determination of metal concentrations relative to zinc ranges from $R^2 = 0.60$ for silver and $R^2 = 0.68$ for antimony to $R^2 = 0.82$ for mercury (Fig. 6). Early petrographic characteristics from the 1980 s indicate that "cadmium and silver are the more important of the associated metals. Cadmium correlates with zinc with relative ratios of 0.005 Cd to 1 Zn, and silver with zinc and lead, with an average ratio of 0.0001 Ag to 1 Zn + Pb" (Gałkiewicz & Śliwiński 1983).

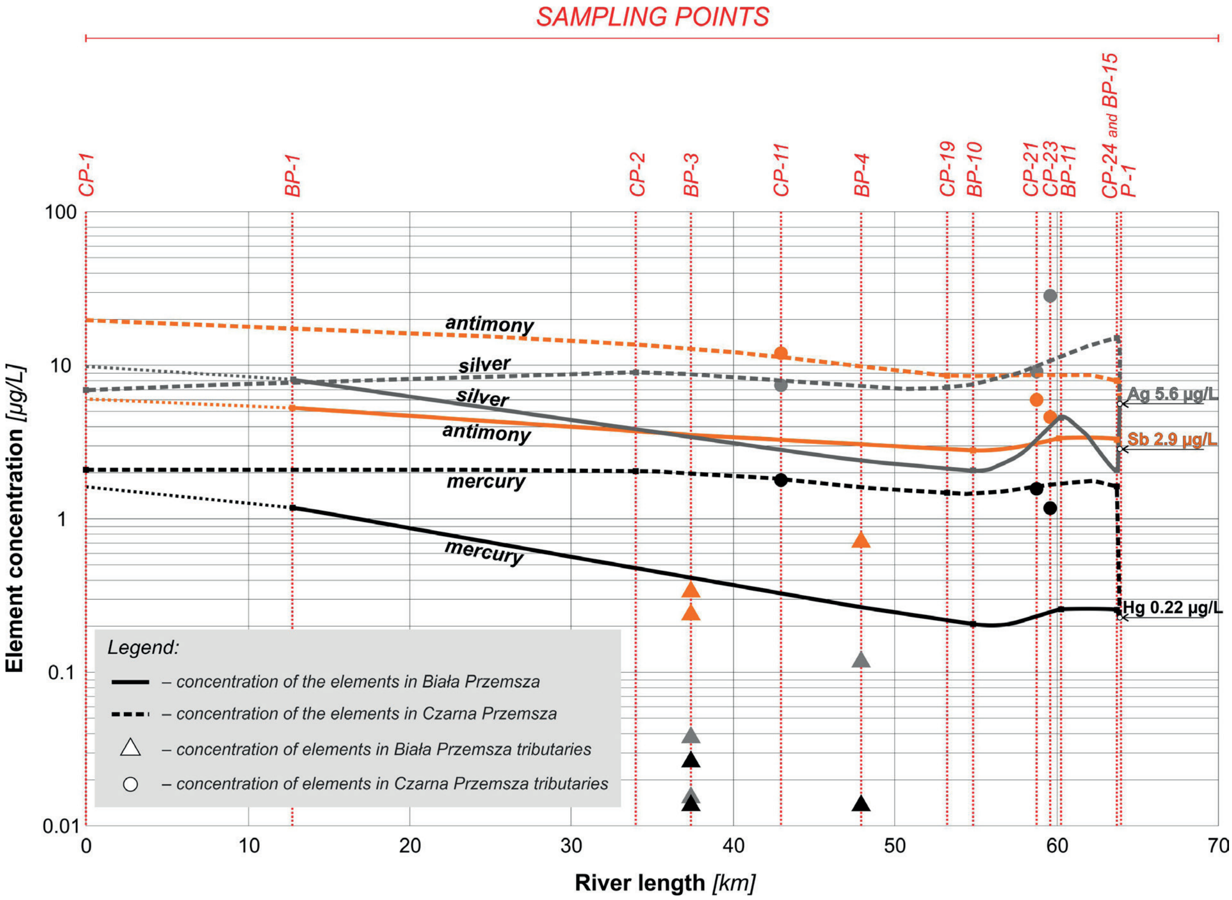

Fig. 5. *Change of concentrations of Ag, Sb and Hg metals with the course of the river*

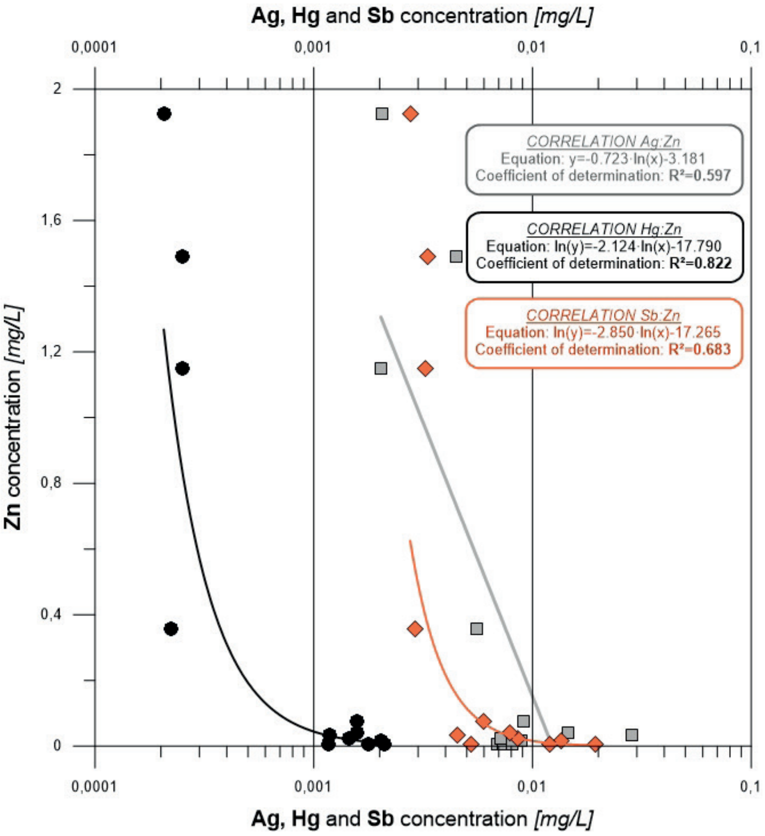

Fig. 6. *The concentration ratio of Ag, Hg and Sb metals to Zn*

Typical admixtures (association in surface water Co-Ni-Mo-Mn)

Common and typical admixtures in the zinc and lead ores of Upper Silesia are, inter alia, cobalt, manganese, molybdenum, and nickel Co-Ni-Mo-Mn. Their presence and the ratio of concentrations with respect to zinc are almost identical (Fig. 7), differing only in the size of the concentrations. The lowest values were measured for cobalt (max. 3.7 μg/L, avg. 1.5 μg/L), nickel (max. 16 μg/L, avg. 9 μg/L) and molybdenum (max. 39 μg/L, avg. 10 μg/L). For these elements, a coefficient of determination $R^2 = 0.91$ for cobalt, $R^2 = 0.60$ for nickel, and $R^2 = 0.74$ for molybdenum is observed, respectively. Manganese reaches the highest concentrations in the studied waters of the Przemsza River (max. 490 μg/L (point BP-11), avg. 231 μg/L). The coefficient of determination level was obtained to match the concentrations of manganese and zinc $R^2 = 0.80$.

Additionally, two pairs of elements showed a strong relationship in the surface waters of the zinc-lead region. The first is the Hg-Sb pair, which is the typical association accompanying mineralization. These elements are commonly found in the soils, ground, groundwater, and surface waters of this region (Pasieczna 2014). The coefficient of the determination for mercury and antimony concentrations is $R^2 = 0.90$ (Fig. 8). This points to the fact that both metals have the same source of origin and enter groundwater in similar proportions. Both mercury and antimony showed the highest concentrations in the spring and upper course of the river.

The second pair of metals that are closely related to each other is Br-Sr, with a linear correlation at the level of $R^2 = 0.98$ (Fig. 8). However, the origin of these elements is due to the strong anthropopressure of this area, particularly the discharge of industrial and municipal wastewaters. High concentrations of bromine (max. 13 mg/L) and strontium (max. 10 mg/L) occur in the Czarna Przemsza River. These metals are around the limit of determination in spring waters.

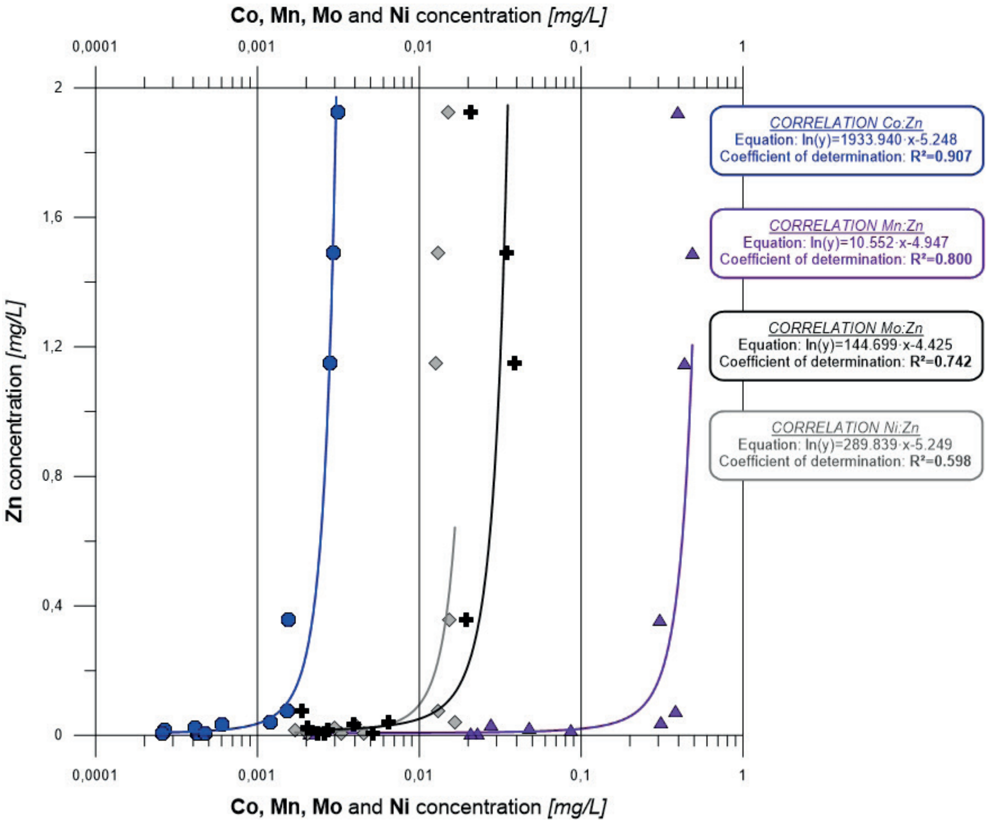

Fig. 7. *The concentration ratio of Co, Mn, Mo and Ni metals to Zn*

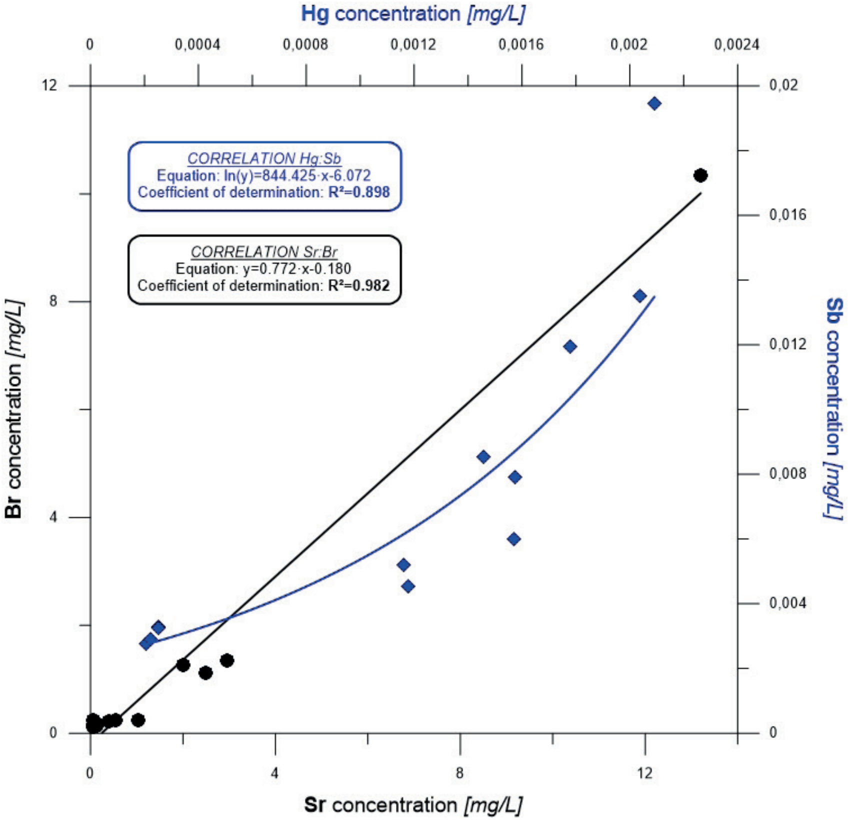

Fig. 8. *[Br:Sr] and [Hg:Sb] concentrations ratio in the Przemsza River surface water*

CONCLUSIONS

In Upper Silesia, the Przemsza River flows through an area enriched with zinc and lead ores, as well as hard coal deposits. Despite the clear influence of anthropopressure on surface waters in the form of mine waters and industrial wastewater discharge, it is possible to analyze the chemical composition of the waters, which is shaped by strong interference with the structure of the Zn-Pb ores. The presence of an ore association in the form of Pb-Zn-Ag-As-Sb-Hg has a strong correlation with the metals and metalloids determined in the water.

In environmental studies, four genetic types of surface waters were identified: (i) uncontaminated spring waters with a chemical composition similar to the Ca-HCO_3 groundwaters, (ii) characteristics of the Czarna and (iii) Biała Przemsza waters Ca-SO_4, and (iv) heavily polluted waters from the tributaries, resulting from the discharge of sewage and mine waters composed of Na-Cl. Regardless of the general chemical composition, the presence of three genetic groups of metals and metalloids strongly related to the metalliferous association of zinc and lead ores in the Upper Silesia region was found independently:

$$\begin{bmatrix} \text{Ca} & \text{HCO}_3 \text{ or SO}_4 \\ \uparrow\downarrow + & \uparrow\downarrow \\ \text{Na} & \text{Cl} \end{bmatrix} + \Big[\big[\text{Zn}-\text{Pb}-\text{Cd}-(\text{Tl})\big] +$$

$$+\big[\text{Ag}-\text{Sb}-\text{Hg}\big]+\big[\text{Co}-\text{Ni}-\text{Mo}-\text{Mn}\big]\Big].$$

The main natural process of enriching surface waters with Zn-Pb-Cd-(Tl) metals is when water circulates in a rock matrix naturally rich in the metals, becomes saturated with them, and then, due to the draining force of the river, flows to the surface. The origin of shallow groundwater in the zone of the extensive depression cone is mainly related to the infiltration of precipitation. The share of Zn-Pb-Cd-(Tl) in surface waters is proportional and increases along with the river course.

As the concentrations of Zn-Pb-Cd-(Tl) ore association elements increase, the concentrations of Ag-Sb-Hg elements gradually decrease. Under oxidizing and slightly alkaline conditions, these metals incorporated into the chemical compounds in the suspension may, when the physicochemical parameters of the waters change, be adsorbed and/or precipitated. The presence and ratio of concentrations of typical admixtures Co-Ni-Mo-Mn with respect to zinc are almost identical. They differ only in the size of the concentrations.

When analyzing the results, the geogenic and anthropogenic origin of metals was noticed additionally: (i) Hg-Sb, which is part of the typical association accompanying mineralization. These metals are found in individual components of the environment, i.e., in soils, grounds, groundwater, and surface waters of this region. Therefore, their presence in surface waters is strongly dependent on the deposits in the Upper Silesia region; (ii) and Br-Sr, however, the origin of these elements is due to the strong anthropopressure of this area, in particular the discharge of industrial and municipal wastewaters.

Metals and metalloids in the environment, due to the presence of zinc and lead deposits, undergo a series of complex hydrogeochemical reactions that cross over. Despite the overlapping of the geogenic condition of the mining activity, it is possible to demonstrate a strong relationship between the chemical composition of surface waters and the mineralogical structure of the ore-bearing rocks.

The presented results are preliminary, and the research will be continued because the work presents the results of the first series of tests which should be verified by subsequent investigations.

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Table 1a. Results of chemical analyzes of minor and major elements from 15 main measuring points on the Przemsza River.