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# Hydrochemical characteristics and pollution of the River Biała Przemsza catchment basin

# Hydrochemiczna charakterystyka i zanieczyszczenie dorzecza Białej Przemszy

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Abstract — The basic chemical composition and the concentration of Zn, Fe, Cu, Pb, Cd, Ni in the drainage area of the Biała Przemsza in the region of occurrence of natural deposits of zinc and lead were described. The water and sediments samples taken monthly from sixteen stations during 1977 were analysed. The character of the introduced pollutions and their sources were discussed. Upon chemical analysis it has been possible to distinguish sectors considerably differing in their level of pollution.

In the water system of the Kraków-Wieluń Upland the River Biała Przemsza catchment basin is a natural receiver of various wastes from the Upper Silesia industrial region. As early as 1939 Starmach reported some pollution of the Biała Przemsza, due to the wastes from a paper mill at Klucze. In later investigations considerable pollution of the middle and upper river course by organic compounds and haevy metals was found by Bombówna and Wróbel (1966), and Pasternak (1973, 1974).

The aim of the present work was to investigate the range of variability in the chemical composition of water and sediments in the River Biała Przemsza and its main tributaries within a yearly cycle and to determine the character and level of pollution found in the river basin. The work was part of group investigations carried out by the Laboratory of Hydrobiology of the Jagellonian University Institute of Environmental Biology.

* Praca wykonana w ramach problemu węzłowego 10.2. 07.05.01.

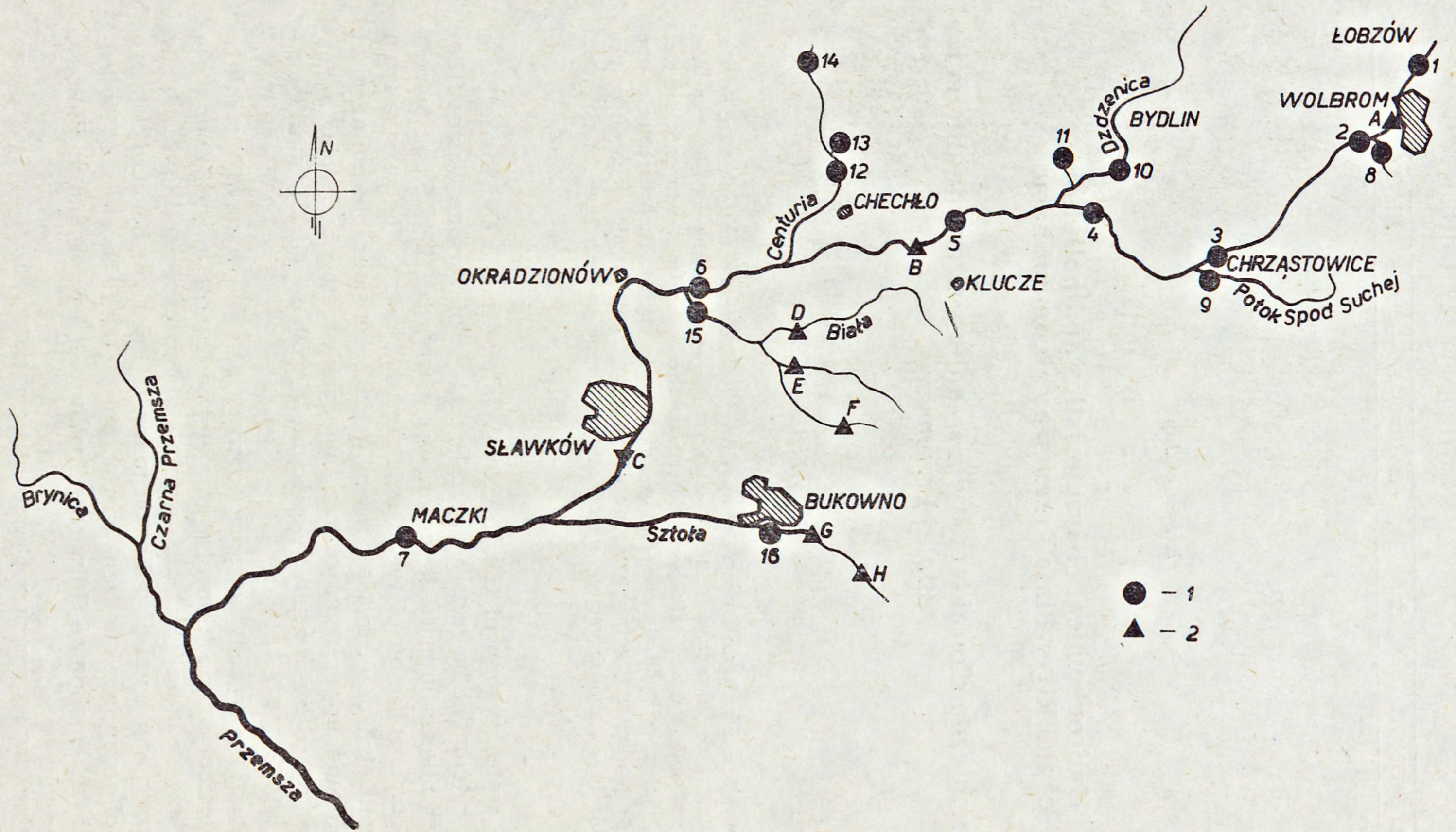


Fig. 1. Distribution of measurement stations in the Biała Przemsza catchement basin: 1 — stations (1—16); 2 — inflow of wastes (A—H)

Ryc. 1. Rozmieszczenie punktów pomiarowych dorzecza Białej Przemszy z zaznaczeniem wpływu zanieczyszczeń: 1 — stanowiska (1—16); 2 — punkt ujścia ścieków (A—H)

The research also included the macro- and microfauna and algae of this catchment basin.

Chemical investigations covered a 50-kilometre sector of the Biała Przemsza, from its springs near Wolbrom to Maczki, and its main tributaries: the Stream Potok spod Suchej, Dzdzenica, Centuria, Biała, and Sztoła streams (fig. 1).

## Description of the investigation area

### Hydrography

The Biała Przemsza basin lies within the Kraków-Wieluń Upland. The area belongs to the climatic regions of the central uplands with an average annual rainfall of 700 mm (Kleczkowski 1972).

Biała Przemsza

The River Biała Przemsza flows out of a peat bog 377 m above sea level, near the town of Wolbrom. At first it flows southwest, at a gradient of 3.34—3.57‰, through a wide valley with sandy substratum; then, at Chrząstkowice it winds northwest, its gradient increasing to 5‰. In this sector two left bank tributaries feed the river at Kaliś and Chrząstowice (the Potok spod Suchej). Below the mouth of the Baba valley, the River Biała Przemsza receives a left side tributary: the Dzdzenica. Below Golczowice the river winds west, flowing through a valley 8—12 m deep and 200—300 m wide. Near Klucze the river flows in an area covered with diluvial sands, the Błędowska desert constituting its central part. The River Biała Przemsza flows through the desert from east to west at a gradient of 1.62—1.66. From Okradzionów the Biała Przemsza begins to flow south, crossing a belt of calcium-dolomite rocks. In this sector it is fed by the Centuria stream from the right and by Biała from the left. A few kilometres below Sławków the river winds west and southwest. Near Mysłowice it merges with the River Czarna Przemsza and in this sector it receives a left bank affluent, the Sztoła stream. From Sławków to the mouth of the river its gradient distinctly diminishes, being from 1.23—1.29‰. The total lenght of the river is 62 kilometres, its catchment area covering 873 sq. kilometres (Zaczyński 1957).

At Chrząstowice the mean yield of the River Biała Przemsza is 2.5 cu. metre/sec, while at Golczowice and Sławków it increases to 7.1 and 11.6 cu.metre/sec respectively (Punzet 1959).

The geological substratum of the River Biała Przemsza is mainly composed of Triassic calcium rocks and ore-bearing dolomites with zinc and lead ores. The surface of calcium rocks and Triassic dolomites is partly covered by a layer of postglacial sands (Kozłowski 1972).

### Main tributaries

The Potok spod Suchej stream. In the stream's upper sector its bed is a drainage ditch. At Cieplice the stream flows into a natural river bed, to the river's mouth deeply cut in sand formations. The stream is 8.1 kilometres in length with a catchment basin of 59.6 kilometres and a multi-annual average yield of 0.27 cu.metre/sec in the mouth sector.

The Dzdzenica stream. This stream begins from 7 karstic springs flowing out of the Grodzisko Mountain. The river bed is 5—8 m in width; the river itself is 9.5 kilometres in length. The substratum of the catchment basin is mainly composed of Jurassic calcium rocks.

The Biała stream flows out at the outskirt of the Błędowska desert at the foot of the Jurassic cuesta. The river starts flowing from a number of springs occurring in two funnel sinks. Two streams merge together forming a river 5 metres in width, with a sandy bottom.

At Lasek the River Biała Przemsza receives waters from the Sztolnia Ponikowska stream whose springs lie in a drift of ore-bearing dolomites. The Biała is 11 kilometres in lenght, with a mean gradient of 2.36‰.

The Centuria stream. The spring area of this stream lies in a sandy plain. Its regular river bed is cut in stratified sands. The Centuria stream is 8.9 kilometres in lenght with an average gradient of 4.1‰.

The Sztoła stream flows out of a rise at an altitude of 350 m. The stream bed is cut in sands. The substratum of the river basin is chiefly composed of dolomites. The river is 12.5 kilometres in length, with a mean gradient of 4.0‰.

### Sources of pollution

The most severe threat for the water resources of the River Biała Przemsza occurs in the upper and central part of the river basin. The upper sector of the Biała Przemsza is polluted with municipal wastes from a tannery in Wolbrom, fed into the Pokrzywianka stream which flows into the Biała Przemsza below the town of Wolbrom, and by 360 cu. metre/day of industrial wastes from „Stomil" rubber plant.

Highly noxious wastes from the cellulose and paper mill at Klucze are discharged into the river in its middle course. These wastes amount to about 45.000 cu. metre/day and contain great quantities of waste sulfite liquors. In this part of the river basin great amounts of industrial wastes from the „Bolesław" mone — and metallurgic plant are discharged through 6 channels. 51.000 cu. metre/day of wastes, chiefly flotation waters from a zinc and lead ore dressing plant are fed to the River Biała through the channel D. Near the mouth of this channel the Biała joins the Sztolnia Ponikowska stream fed by two discharge channels (E and F) one from the Olkusz-Południe and the other from the „Bolesław" zinc and lead mines. Another channel (C) drains 30.000 cu.metre/day of wastes from metallurgic plants directly into the Biała Przemsza in the vicinity of Sławków, while two other channels (G and H) feed about 26.000 cu. metre/day of wastes from zinc and lead mines to the Sztoła stream. As reported by Pasternak (1973), in the years 1971—1972 the flotation and metallurgic waste waters were characterized by a marked total hardness of 30—45n°, mainly caused by a large content of magnesium, sodium (90—110 mg Na/l), and potassium (10 mg K/l) and also by a strongly alkaline reaction with pH 8.0—9.5. In addition, metallurgic waste waters brought in enormous quantities of sulphates (400—600 mg $SO_4$/l), while mine waste waters showed a lower alkaline reaction (pH 8.1) and a low content of sodium, potassium, and chlorides with a constant high content of dissolved oxygen.

In the water of all these channels the level of zinc and lead was very high although there were periodical fluctuations. Mean concentrations of these metals amounted to 1250 and 568 ppb in flotation waters, to 6850 and 220 ppb in metallurgic waters, and to 250-and 35 ppb in mine waste waters, respectively.

## Method

Sixten investigation stations were designated (fig. 1): seven on the River Biała Przemsza (1—7), and one at the mouth sector of a left bank tributary of the Biała Przemsza at Kaliś (8), and the Potok spod Suchej stream (9), two on the Dzdzenica (10 and 11), three on the Centuria (12—14), and one in the middle sectors of the Biała (15) and the Sztoła (16).

The investigation was carried out on the following dates: January 17, February 3, March 18, May 10, June 14, July 20, September 26, October 24, and November 28, 1977.

Water samples were collected with a modified Żukrowski sampler (Żadin 1966) at a depth of 15—20 cm below water surface, and kept in

1 and 2-litre plastic containers. The water temperature and ionic reaction were measured at the station, using a sampler thermometre and N-511 battery operated pH-metre, which was standardized with pH 4.0 and pH 6.8 buffers before measurements. The analyses of the remaining chemical factors were carried out on the sampling day or in a period of time not exceeding 48 hrs after the samples were transported to the laboratory. Electrolytic conductivity was masured in the laboratory using an „Oxytester". Macroelements were determined according to Standard Methods (1971) or to those given by Golterman (1969) and Hermanowicz (1976). Microelement content in water was determined by spectral emission analysis, according to the method described by Pasternak (1973). Microelement content in sediments was found by the Mathis and Cummings method (1973).

## Results

A comparison of temperature changes at the successive stations showed that the highest thermal differences occurred in summer months (June-September). In July the highest temperature was observed at all stations, although it did not exceed 21° (Table I). In summer months water temperature in the tributaries was always lower by 1—2°C than that of the Biała Przemsza water; a reverse relationship was observed in winter months. Thermal relations in the springs of the investigated region, characterized by slight seasonal variation and a temperature not exceeding 10°C, were typical of Jurassic waters, which were also observed in the area of the Ojców National Park (Oleksynowa 1966).

In the whole investigation period the River Biała Przemsza water was very turbid. The load of suspension was chiefly related to the amount of wastes released from the paper mill at Klucze and, to a lesser degree, to differences in water yield. The greatest water turbidity was always observed at the stations of Okradzionów (183—235 mg $SiO_2$/l) and Maczki (36—94 mg $SiO_2$/l). The water reaction was slightly alkaline, ranging from 6.7—8.0. A general tendency towards a decreased pH value, related to increased carbonate hardness, was noted. Probably, it was related to a high $CO_2$ content in these waters.

In polluted sectors the basic chemical composition of the Biała Przemsza water markedly differed from that of all its tributaries. The proportions of macroelements in the water of the tributaries showed, with respect to anions, the highest percent of carbonates (23.6—41.5%), while the content of sulphates and chlorides was lower (20.6—31.1% and 04.4—5.0% respectively). Among cations, calcium distinctly dominated (33.5—47.7%): next came mangesium (1.8—14.1%), sodium (1.0—3.9%) and potassium (0.2—0.8%). Quantitative relations of macrolements indicated

Table I. Physical and chemical properties of water in the River Biała Przemsza and some of its tributaries for the investigated stations - average values for the period of investigations (1977). For five main stations (2,3,4,6,7) the standard deviation was also given (±SD)

Tabela I. Fizyko-chemiczne właściwości wody Białej Przemszy i niektórych jej dopływów na badanych stanowiskach. Wartości średnie z okresu badań w 1977 roku. Dla pięciu głównych stanowisk (2,3,4,6,7) podane także wartości odchylenia standartowego (±SD)

| Factors / Czynniki | | | Stations - Stanowiska | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| Water temperature / Temperatura wody | | °C | 9.00 | 8.70 | 8.40 | 8.70 | 8.40 | 10.90 | 9.20 | 8.80 | 8.00 | 3.60 | 8.90 | 4.30 | 9.10 | 8.20 | 9.00 | 11.10 |
| | | ±SD | | 4.10 | 4.10 | 5.00 | | 6.80 | 5.40 | | | | | | | | | |
| pH | | | 7.10 | 7.20 | 7.40 | 7.50 | 7.80 | 7.20 | 7.50 | 7.20 | 7.90 | 7.70 | 7.20 | 7.30 | 7.30 | 6.80 | 7.60 | 7.60 |
| | | ±SD | | 0.10 | 0.20 | 0.20 | | 0.10 | 0.20 | | | | | | | | | |
| Colour / Barwa | | °Pt | 7 | 34 | 28 | 22 | 22 | 77 | 49 | 19 | 10 | 12 | 5 | 20 | 3 | 6 | 16 | 17 |
| | | ±SD | | 2.60 | 2.00 | 3.10 | | 8.80 | 18.10 | | | | | | | | | |
| Turbidity / Mętność | $SiO_2$ | $mg/dm^3$ | 12 | 47 | 30 | 25 | 12 | 198 | 61 | 12 | 15 | 5 | 2 | 21 | 0 | 6 | 15 | 35 |
| | | ±SD | | 8.80 | 6.60 | 6.50 | | 18.60 | 22.90 | | | | | | | | | |
| Conductance of electrolytes / Przewodnictwo | µS | 20°C | 398 | 506 | 449 | 394 | 410 | 475 | 472 | 389 | 321 | 392 | 479 | 273 | 403 | 211 | 462 | 399 |
| | | ±SD | | 19.70 | 18.60 | 32.00 | | 71.70 | 12.00 | | | | | | | | | |
| Total number of electrolytes / Suma elektrolitów | | $me/dm^3$ | 12.00 | 13.00 | 11.10 | 9.90 | 9.60 | 12.60 | 12.30 | 9.60 | 8.00 | 8.40 | 12.70 | 8.20 | 10.10 | 4.40 | 9.90 | 11.00 |
| | | ±SD | | 0.40 | 0.30 | 0.20 | | 0.70 | 0.40 | | | | | | | | | |
| Total hardness / Twardość ogólna | °G | °n | 15.80 | 15.50 | 14.50 | 13.40 | 13.40 | 16.50 | 17.20 | 12.60 | 10.90 | 11.80 | 17.40 | 11.40 | 13.90 | 6.40 | 13.50 | 14.90 |
| | | ±SD | | 1.40 | 0.60 | 0.60 | | 1.20 | 0.50 | | | | | | | | | |
| Carbonate hardness / Twardość węglanowa | °G | °n | 8.70 | 11.60 | 10.30 | 9.90 | 9.70 | 7.70 | 9.00 | 8.40 | 8.50 | 9.80 | 13.40 | 7.80 | 9.40 | 2.90 | 10.00 | 10.70 |
| | | ±SD | | 0.80 | 0.60 | 0.40 | | 0.80 | 0.70 | | | | | | | | | |
| Chloride / Chlorki | Cl | $mg/dm^3$ | 20.20 | 26.20 | 19.00 | 11.40 | 11.00 | 34.50 | 17.80 | 17.20 | 4.00 | 4.60 | 15.00 | 4.60 | 9.40 | 0.80 | 9.00 | 7.20 |
| | | ±SD | | 4.30 | 2.60 | 2.80 | | 7.70 | 2.10 | | | | | | | | | |
| Sulphate / Siarczany | $S-SO_4$ | $mg/dm^3$ | 33.50 | 19.70 | 16.70 | 13.20 | 10.00 | 40.30 | 35.80 | 19.40 | 8.50 | 4.20 | 12.70 | 13.20 | 20.00 | 14.80 | 11.60 | 20.40 |
| | | ±SD | | 3.40 | 4.20 | 2.80 | | 7.20 | 4.00 | | | | | | | | | |
| Silica / Krzemiany | $SiO_2$ | $mg/dm^3$ | 2.41 | 4.76 | 3.63 | 3.10 | 3.84 | 3.27 | 2.70 | 3.85 | 2.87 | 3.56 | 3.21 | 3.44 | 2.87 | 3.18 | 2.69 | 3.05 |
| | | ±SD | | 0.60 | 0.60 | 0.70 | | 0.50 | 0.50 | | | | | | | | | |
| Calcium / Wapń | Ca | $mg/dm^3$ | 97.40 | 93.80 | 88.20 | 83.80 | 83.60 | 103.30 | 84.60 | 81.60 | 72.80 | 80.60 | 115.30 | 75.90 | 93.70 | 33.80 | 70.30 | 74.60 |
| | | ±SD | | 4.60 | 3.20 | 4.70 | | 7.10 | 5.40 | | | | | | | | | |
| Magnesium / Magnez | Mg | $mg/dm^3$ | 9.54 | 9.62 | 6.46 | 5.72 | 4.65 | 7.58 | 18.60 | 4.20 | 3.40 | 0.40 | 5.42 | 3.24 | 2.25 | 5.06 | 15.28 | 19.10 |
| | | ±SD | | 1.00 | 1.20 | 0.80 | | 1.50 | 2.40 | | | | | | | | | |
| Potasium / Potas | K | $mg/dm^3$ | 2.31 | 5.73 | 3.46 | 2.15 | 2.28 | 1.81 | 1.70 | 3.00 | 0.80 | 2.30 | 1.66 | 0.70 | 0.98 | 1.27 | 2.09 | 0.90 |
| | | ±SD | | 1.20 | 0.90 | 1.10 | | 1.10 | 0.90 | | | | | | | | | |
| Sodium / Sód | Na | $mg/dm^3$ | 8.25 | 15.50 | 9.35 | 6.56 | 6.11 | 6.36 | 7.07 | 5.50 | 3.25 | 3.75 | 3.00 | 3.60 | 3.80 | 2.88 | 9.00 | 6.10 |
| | | ±SD | | 1.20 | 3.40 | 2.60 | | 2.70 | 2.50 | | | | | | | | | |
| Ammonia / Amoniak | $N-NH_4$ | $mg/dm^3$ | 0.31 | 3.93 | 1.50 | 0.68 | 0.67 | 1.93 | 0.68 | 0.28 | 0.31 | 0.31 | 0.40 | 0.12 | 0.12 | 0.22 | 0.38 | 0.24 |
| | | ±SD | | 1.00 | 0.90 | 0.40 | | 0.80 | 0.30 | | | | | | | | | |
| Nitrite / Azotyny | $N-NO_2$ | $mg/dm^3$ | 0.02 | 0.17 | 0.07 | 0.05 | 0.02 | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | | ±SD | | 0.07 | 0.05 | 0.03 | | 0.01 | 0.00 | | | | | | | | | |
| Nitrate / Azotany | $N-NO_3$ | $mg/dm^3$ | 3.18 | 1.26 | 2.50 | 2.40 | 2.46 | 0.73 | 0.44 | 2.59 | 1.51 | 2.83 | 4.90 | 1.25 | 3.28 | 0.45 | 0.62 | 1.07 |
| | | ±SD | | 0.60 | 0.70 | 0.60 | | 0.10 | 0.10 | | | | | | | | | |
| Organic nitrogen / Azot organiczny | N | $mg/dm^3$ | 1.12 | 6.52 | 2.89 | 2.30 | 1.82 | 1.47 | 1.85 | 0.93 | 1.16 | 1.08 | 1.12 | 1.68 | 0.52 | 0.45 | 0.61 | 1.02 |
| | | ±SD | | 2.78 | 0.53 | 0.80 | | 0.60 | 0.90 | | | | | | | | | |
| Phosphate / Fosforany | $PO_4$ | $mg/dm^3$ | 0.09 | 0.40 | 0.26 | 0.14 | 0.11 | 0.04 | 0.06 | 0.06 | 0.02 | 0.03 | 0.03 | 0.02 | 0.01 | 0.04 | 0.08 | 0.03 |
| | | ±SD | | 0.20 | 0.14 | 0.06 | | 0.02 | 0.03 | | | | | | | | | |
| Total phosphorus / Fosfor ogólny | P | $mg/dm^3$ | 0.11 | 0.60 | 0.42 | 0.27 | 0.20 | 0.17 | 0.19 | 0.10 | 0.14 | 0.04 | 0.06 | 0.08 | 0.02 | 0.09 | 0.28 | 0.45 |
| | | ±SD | | 0.24 | 0.18 | 0.16 | | 0.13 | 0.09 | | | | | | | | | |
| $CO_2$ free / wolny | | $mg/dm^3$ | 8.80 | 9.80 | 6.60 | 5.00 | 2.60 | 5.70 | 7.80 | 3.90 | 3.30 | 4.00 | 6.80 | 3.10 | 5.10 | 4.20 | 3.90 | 2.30 |
| | | ±SD | | 1.80 | 2.30 | 2.20 | | 2.10 | 3.90 | | | | | | | | | |
| Dissolved oxygen / Tlen rozpuszczony | $O_2$ | $mg/dm^3$ | 8.64 | 4.82 | 9.16 | 10.70 | 10.70 | 3.32 | 9.68 | 9.04 | 11.80 | 9.60 | 9.60 | 11.00 | 9.28 | 11.40 | 8.72 | 10.90 |
| | | ±SD | | 2.60 | 1.90 | 1.70 | | 2.80 | 2.50 | | | | | | | | | |
| Saturation oxygen / Nasycenie tlenem | $O_2$ | % | 77.20 | 41.10 | 78.40 | 93.90 | 80.70 | 28.00 | 87.00 | 79.50 | 103.20 | 74.70 | 85.70 | 87.60 | 83.10 | 99.60 | 76.80 | 102.00 |
| | | ±SD | | 18.80 | 14.50 | 12.00 | | 19.60 | 14.00 | | | | | | | | | |
| $BOD_5$ / $BZT_5$ | $O_2$ | $mg/dm^3$ | 2.24 | 15.40 | 5.66 | 4.50 | 3.86 | 48.90 | 5.50 | 3.84 | 4.32 | 3.68 | 2.24 | 3.68 | 1.92 | 1.02 | 0.71 | 4.00 |
| | | ±SD | | 9.60 | 0.90 | 1.00 | | 33.70 | 1.70 | | | | | | | | | |
| Oxidability / Utlenialność | $O_2$ | $mg/dm^3$ | 3.68 | 11.00 | 6.11 | 4.51 | 4.18 | 46.60 | 18.00 | 6.30 | 2.36 | 2.20 | 1.72 | 7.84 | 1.80 | 3.04 | 4.56 | 4.70 |
| | | ±SD | | 3.90 | 1.30 | 0.70 | | 9.70 | 7.20 | | | | | | | | | |
| Dry residue / Sucha pozostałość | | $mg/dm^3$ | 386 | 413 | 366 | 315 | 222 | 487 | 456 | 345 | - | 249 | 384 | 105 | 222 | 148 | 404 | 310 |
| | | ±SD | | 41.20 | 37.40 | 43.30 | | 76.80 | 42.80 | | | | | | | | | |
| Loss on ignition / Strata przy prażeniu | | $mg/dm^3$ | 133 | 128 | 141 | 107 | 130 | 198 | 183 | 88 | - | 87 | 134 | 34 | 62 | 38 | 175 | 115 |
| | | ±SD | | 47.70 | 26.90 | 20.10 | | 52.50 | 37.20 | | | | | | | | | |
| Remains after ignition / Pozostałość po prażeniu | | $mg/dm^3$ | 253 | 284 | 224 | 199 | 92 | 288 | 273 | 256 | - | 161 | 250 | 71 | 222 | 109 | 229 | 195 |
| | | ±SD | | | | | | | | | | | | | | | | |

that the waters of the tributaries could be classified as pure waters with calcium carbonates as the main components (A l e k i n 1956). The equivalent Ca : Mg ratio suggested the occurrence of two markedly related to the different character of the geological structure of the substratum in the upper and central part of the catchment basin. In the differing types of water in the affluents of the River Biała Przemsza, tributaries of the upper catchment basin this ration was 20.2 at Kaliś, 21.4 in the Potok spod Suchej stream, 23.4 in the Centuria, and 15.0 in the Dzdzenica. A markedly lower value of the Ca : Mg ratio, 3.9—5.0, was noted in the water of two other affluents, the Sztoła and Biała streams, which flow into the Biała Przemsza in the central part of the river basin.

The ionic composition of the Biała Przemsza water, affected by the inflow of wastes, was characterized by an increased per cent of sulphates (6.5—19.8%), chlorides (3.2—7.7%), and sodium (2.3—5.2%), and, as a result, by a decreased percentage of calcium carbonates (34.4—41.8%). In view of the varying composition of wastes, the ionic composition of the Biała Przemsza water distinctly changed at the successive stations (Table I). The greatest load of organic pollution was found in the Biała Przemsza at Kaliś below Wolbrom, and at Okradzionów. In Kaliś great quantities of organic nitrogen, mineral nitrogen and phosphoric

Table II. Content of heavy metals in water (w) and in bottom sediments (o) of the River Biała Przemsza and some of its tributaries. Average values for the period of investigations were calculated in ppb for water, and in ppm for sediments

Tabela II. Zawartość metali ciężkich w wodzie (w) i osadach dennych (o) Białej Przemszy i niektórych jej dopływów. Wartości średnie z okresu badań zmierzone w wodzie wyrażono w ppb, natomiast w osadzie w ppm

| Station Stanowisko | Metal | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cd | | Pb | | Cu | | Ni | | Zn | | Fe |
| | w | o | w | o | w | o | w | o | w | o | w |
| 1 | 0.0 | 0.0 | 15 | 2 | 4 | 16 | 15 | 12 | 330 | 185 | 140 |
| 2 | 0.5 | 3.0 | 16 | 153 | 17.5 | 51 | 10 | 29 | 432 | 504 | 418 |
| 3 | 1.0 | 7.1 | 23 | 177 | 20 | 60 | 12 | 33 | 588 | 810 | 259 |
| 4 | 0.0 | 7.7 | 12.5 | 160 | 15 | 34 | 3 | 29 | 598 | 857 | 213 |
| 5 | 2.5 | 0.0 | 75 | 1052 | 27.5 | 24 | 12.5 | 15 | 120 | 87.5 | 512 |
| 6 | 0.0 | 6.3 | 39 | 354 | 32 | 131 | 18 | 17 | 827 | 675 | 747 |
| 7 | 2.0 | 11.3 | 25 | 147 | 28 | 227 | 16 | 43 | 965 | 729 | 1528 |
| 8 | 0.0 | 3.0 | 20 | 162 | 34.5 | 186 | 12.5 | 30.5 | 102 | 881 | 635 |
| 9 | 0.0 | 0.0 | 20 | 5 | 6 | 11 | 7 | 10 | 200 | 143 | 130 |
| 10 | 0.0 | 3.0 | 30 | 263 | 48 | 55 | 12.5 | 20 | 95 | 15.5 | 170 |
| 11 | 0.0 | 1.5 | 15 | 23 | 51 | 16 | 12.5 | 44 | 100 | 57 | 105 |
| 12 | 0.0 | 0.0 | 20 | 14 | 22 | 31 | 15 | 14 | 120 | 65 | 170 |
| 13 | 0.0 | 0.0 | 0.0 | 20 | 3 | 21 | 7.5 | 22 | 95 | 93 | 110 |
| 14 | 0.0 | 0.0 | 0.0 | 15 | 19 | 13 | 0.0 | 8 | 135 | 9 | 127 |
| 15 | 0.0 | 9.0 | 38 | 2441 | 35 | 107 | 10 | 70 | 358 | 945.5 | 221 |
| 16 | 1.5 | 79.2 | 78 | 1092 | 5 | 49 | 6 | 18 | 786.5 | 1273 | 325 |
| Canal Kanał F | 0.0 | 129 | 568 | 950 | 0.0 | 516 | 1 | 13 | 1250 | 968 | 67 |

compounds were brought in with municipal wastes. Below the point of sewage discharge, intense processes of the biochemical decomposition of organic matter occurred for several kilometres. These processes could be clearly seen at station 2 where there were increased values of the biochemical oxygen demand and a low content dissolved oxygen.

From station 3 at Chrząstowice to station 5 at Klucze, i.e. along a 15-kilometre sector, a constant decrease in the concentration of both organic matter and all investigated macroelements and, simultaneously, a constant increase in water oxygenation were observed (Table I). Owing to the self-purification processes occurring in this river sector and to the changing physico-chemical conditions, heavy metals were precipitated from water, forming compounds, chiefly with ferric hydroxides. At Jaroszowiec and Klucze their level was already very low (Table I). In this sector water properties, i.e. good oxygenation and increasing alkaline reaction, promoted this proces. The pure water of the Potok spod Suchej and Dzdzenica streams accelerated the self-purification process in this sector. In spite of a considerable improvement, however, it could not be claimed that the water from the stations at Jaroszowiec and Klucze, was pure, as the content of ammonium, organic nitrogen and total phosphorus was high there. An increased content of heavy metals found in sediments also indicated high periodical concentrations of metals reaching these stations (Table II). The same process occurred at the last investigated sector of the Biała Przemsza, though in the water from the station 7, at Maczki, most of the investigated microelements did not reach levels usually noted in pure rivers (Pasternak, Antonowicz 1970).

Below Klucze these conditions undergo a striking change caused by an enormous amount of wastes discharged into the Biała Przemsza. Hard-decomposable wastes with a large content of sulphates and sulphonate compounds from the Klucze paper mill were discharged into the most polluted station at Okradzionów. In this sector of the Biała Przemsza water the content of sulphates and chlorides as well as the oxidability and the biochemical oxygen demand greatly increased with a simultaneous constant oxygen deficit. A low content of dissolved oxygen and high average concentrations of heavy metals, particularly of lead (40 ppb), copper (32 ppb), and zinc (827 ppb) in water of this sector inhibited the final stage of the nitrification process, as it was shown by the constantly low level of nitrate nitrogen, which ranged from 0,39—0,83 mg $N—NO_3$/l. Organic compounds, chiefly in the form of ethyl-sodium xanthate (Pasternak 1973) used in the flotation of zinc and lead ores, get into the strongly polluted sector of the Biała Przemsza at Sławków together with waste waters. The decomposition of this compound releases carbon sulphide whose toxic effect on aquatic organisms greatly increased in an environment of high chloride content (Solski et al. 1972), such as was observed in this river sector.

Not until station 7 (Maczki) did the quality of water begin to improve owing to the influence of a left bank tributary, the Sztoła stream, as was proved by the similar Ca : Mg ratios for these two rivers.

The content of most heavy metals in water and in bottom sediments of the Biała Przemsza and its affluents greatly changed in the successive seasons of the year. The least variation was observed in the content of cadmium and nickel while the concentration of the other elements considerably differed on each sampling date (Table II). Of the investigated elements, zinc and lead appeared in the greatest amounts both in water and in sediments. These metals precipitated from water with various speed rates. In the first kilometres below the inflow of wastes, the precipitation of lead mainly occurred while the zinc content in sediments increased with the course of the river. These results support earlier reports on the migration of heavy metals in aquatic enviroments brought in with industrial and mine wastes (Alekseenko 1973, Gale 1973, Pasternak 1973).

The obtained results allowed for an identification of three types of water in the Biała Przemsza catchment basin, considerably differing from each other in the content of the investigated microelements. The concentration of heavy metals in water of pure sectors amounted to 0.0 ppb cadmium, 0—30 ppb lead, 0—51 ppb copper, 0—15 ppb nickel, 93—330 ppb zinc, and 105—215 ppb iron, while in bottom sediments of these sectors 0—3 ppm cadmium, 20—263 ppm lead, 16—55 ppm copper, 16—44 ppm nickel, and 9—93 ppm zinc were recorded. These values were found for the spring area of the Biała Przemsza and its affluents the Potok spod Suchej, Dzdzenica, and Centuria streams (stations 1,9,10,11,12,13 and 14). This area, set apart from the Biała Przemsza catchment basin can be a point of reference for the other part of the basin, where the content of heavy metals in water and bottom sediments was much higher. As compared with the pure area which can be accepted as the basic level, waters of the other type in the Biała Przemsza sector from Wolbrom to Klucze with an inflow at Kaliś (stations 2,3,4,5 and 8) contained five times more cadmium, and three times more lead, nickel, zinc, and iron on the average. Still greater differences were found in sediments, where the average quantities of metals were four times higher for cadmium, six times higher for lead, five times higher for copper, two times higher for nickel, and sixteen times higher for zinc as compared with the pure sector. In waters of the third type, including the Biała Przemsza sector from Okradzionów to Maczki with two affluents, the Biała and the Sztoła (stations 6, 7, 15 and 16), most strongly polluted with heavy metals, the content of the investigated elements ranged from 0—5 ppb cadmium, 340—1572 ppb zinc, to 107—3095 ppb iron, while in bottom sediments at these stations the respective values were: 0—89 ppm Cd, 93—3367 ppm Pb, 25—931 ppm Cu, 2—152 ppm Ni, and 123—1448 ppm Zn (Table II).

## Discussion

The results of chemical investigations showed a constant rise in the pollution level of the Biała Przemsza water. As compared with data quoted by Pasternak (1973) for 1971—1972 the content of heavy metals in Biała Przemsza waters distinctly increased, except for cadmium whose concentration was the same as in the previous period. The mean concentrations of the investigated metals were twice as high as those for the years 1971—1972. In spite of these great quantities of heavy metals in the aquatic environment of the Biała Przemsza, their toxicity decreased due to the high content of carbonates which formed insoluble compounds with metals (Mc Kee, Wolf 1963). The toxicity of metals was also decreased by the slightly alkaline water reaction, which to a certain degree inhibited the transition of metals from molecule to free forms (Hartung 1976). However, at some stations, where an increased content of heavy metals and specific conditions such as the occurrence of carbon sulphide at a high content of chlorides, were simultaneously observed, the constant oxygen deficits could harmfully affect organisms of the whole trophic system. As Leland et al. (1974) claimed the amounts of heavy metals deposited on the bottom were related to the quality of the water layer above the deposit and to the time of sediment accumulation. Similarly, in the most polluted sectors of the Biała Przemsza particularly harmful living conditions for animals were found even in the upper layer of bottom sediments. Hence, to protect the Biała Przemsza biocenosis from the injurious effects of heavy metals a more effective treatment of industrial and domestic wastes should be applied and the inflow of metallurgic waters containing mineral compounds which greatly decrease the percent of carbonates in the chemical composition of these waters should be stopped.


## STRESZCZENIE

W pracy przedstawiono ogólną charakterystykę hydrochemiczną i stopień zanieczyszczenia środowiska wodnego dorzecza Białej Przemszy na podstawie badań przeprowadzonych w 1977 roku. Biała Przemsza jest naturalnym odbiornikiem różnorodnych zanieczyszczeń dochodzących głównie z ośrodka górniczo-hutniczego rud cynku i ołowiu, przez co skład jonowy jej wody ulega znacznemu odkształceniu.

Wybrano szesnaście stanowisk badawczych (Ryc. 1): z tego siedem na Białej Przemszy, trzy na Centurii, dwa na Dzdzenicy oraz po jednym w przyujściowych odcinkach lewobrzeżnego dopływu Białej Przemszy w Kalisiu, Potoku spod Suchej, Białej i Sztoły.

Najsilniej zanieczyszczone zarówno organicznie jak i metalami ciężkimi były odcinki Białej Przemszy od Wolbromia do Chrząstowic oraz od Klucz do Maczek (tabela I). Koncentracja metali ciężkich w wodzie i osadach dennych Białej Przemszy i jej dopływów wykazywała duże wahania sezonowe (tabela II). Pomimo dużego odkształcenia prawie całego środowiska wodnego dorzecza Białej Przemszy można jeszcze na obszarze

tym wyznaczyć odcinki czyste. Do takich należy obszar źródliskowy Białej Przemszy do Wolbromia a także jej niektóre dopływy: Potok spod Suchej, Dzdzenica i Centuria.

Proces samooczyszczania zachodzący poniżej Wolbromia pomimo znacznego spadku zarówno wskaźników zawartości materii organicznej jak również wszystkich badanych makro- i mikroelementów nie doprowadza stężeń niektórych analizowanych czynników na stanowisku w Jaroszowcu i Kluczach do poziomu właściwego dla rzeki czystej.

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