

BASIC COMPONENTS AND TRACE ELEMENTS IN SEDIMENTS IN THE INACTIVE CHANNEL OF THE DUNAJEC RIVER (PIENINY MTS.) AND THEIR GEO-ECOLOGICAL SIGNIFICANCE

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Abstract: Geochemical tests of sediments were conducted in isolated water bodies in the river channel located in the Szczawnica reach of the inactive branch of the Dunajec River in the Pieniny Mountains. Basic composition and contents of trace elements as indicators of anthropogenic pollution were determined. It was found that the components included in the basic composition of the sediments examined exhibited typical quantitative variation in their average amounts (SiO_2 – 57.02%, loss on ignition – 11.72%, Al_2O_3 – 14.17%, Fe_2O_3 – 5.74%, CaO – 4.83%, K_2O – 2.46%, MgO – 2.05% and Na_2O – 1.13%, TiO_2 – 0.87%, P_2O_5 – 0.18%, MnO – 0.11%, S – 0.25%), showing little variability when individual samples were compared. It was found that the content of trace elements in sediments of the inactive branch of the Dunajec River channel meets the geochemical background criteria in the case of Ag, Be, Cd, Hg and is slightly higher than the geochemical background in the case of Pb and Zn while for As, Ba, Co, Cr, Cu, Ni, S, Sr and V the geochemical background is exceeded a few times (As, Ba, Co, Cu, S, Sr), around a dozen times (Ni and V) or several dozen times (Cr); for many elements, the comparison to the geochemical background was not made for the lack of data. The geoaccumulation index (I_{geo}) indicates that the sediments are uncontaminated, moderately contaminated or heavily contaminated with some elements. The contamination factor indicates moderate sediment contamination with arsenic and chromium while Hg, PCBs, Pb, Cd, Cu and Zn are absent. The degree of sediment contamination ($C_d=5.2$) is low. The content of some trace elements found in sediments of the inactive channel of the Dunajec River branch is higher than the ranges in which these elements are found in the aquatic sediments of the hydrologically active channel of the same river. The enrichment ratio of sediments in the inactive river channel with respect to microelements ranges from unity (Zn, Pb) to around a dozen – Cu ($I_{\text{AP}} = 2.7$), Co ($I_{\text{AP}} = 3.0$), As and Sr ($I_{\text{AP}} = 3.2$), Ni ($I_{\text{AP}} = 3.7$), Ba ($I_{\text{AP}} = 6.8$), Cr ($I_{\text{AP}} = 7.6$), S ($I_{\text{AP}} = 9.6$) and V ($I_{\text{AP}} = 11.6$). Sediments in inactive river channels (oxbow lakes) contain a wealth of geoenvironmental information whose significance is completely different from that which can be read from sediments in hydrologically active river channels.

Keywords: chemical composition, trace elements, heavy metals, inactive river channel, Dunajec, Pieniny.

1. INTRODUCTION

All depressions filled with water are places where the material forming bottom sediments accumulates and thus serve as sedimentation basins of sorts that are shaped in the environment conditioned by the local erosion base. Thus bottom sediments are a good indicator of environmental characteristics in the vicinity (Rzętała et al., 2013). They can be considered an excellent “recorder” of the phenomena and processes that take part in the geographical environment of the catchment and in the vicinity of water bodies. This also underlines the role of bottom

sediments as an indicator of environmental changes and a factor reflecting the dynamic evolution of aquatic ecosystems (Rzętała, 2014).

Geoenvironmental significance can be attributed to basic components of bottom sediments, including particularly trace elements in bottom sediments of inland water bodies. The concentration of these substances documents the role of natural and anthropogenic factors in shaping the chemical composition and physico-chemical properties of aquatic sediments (Ciszewski, 1998, 2003, 2004; Ciszewski et al., 2004; Jabłońska-Czapla et al., 2014; Aytmukhanovich et al., 2014; Skorbillowicz, 2014; Ilie et al., 2014). It is also

important in the context of the economic use of bottom sediments (Rzętała et al., 2013, 2015).

Particular attention is paid to documenting human impact on areas that enjoy special protection owing to e.g. their natural value, curative properties and spas operating there, attractive landscape and the presence of mineral waters. The Pieniny Mountains meet such criteria and the new study area is the periodically inactive channel of the Dunajec River branch at the mouth of the Pieniny reach of the river.

The aim of the study was to determine the basic composition and trace element content in sediments of isolated water bodies in the Szczawnica reach of the inactive branch of the Dunajec River. An additional contribution of this study is the assessment of the content of trace elements in sediments in isolated water bodies in the inactive channel of the Dunajec River branch as an indicator of anthropogenic pollution.

2. STUDY AREA

The Dunajec River is a right tributary of the Vistula River that begins around the city of Nowy Targ at the confluence of the Biały Dunajec and Czarny Dunajec Rivers. The most important tributaries of the Dunajec River include the Białka, Grajcarek, Kamienica, Ochotnicki Potok, Poprad and Biała Rivers. The Dunajec River together with the Czarny Dunajec River has a length of ca. 247 km and a basin area of 6804.0 km² (Jaguś & Rzętała, 2002). The catchment area of the Dunajec River down to Szczawnica is 1,487.1 km² and when the catchment area of the Grajcarek Stream (84.9 km²) is included, it is 1,572 km² (Hydrographic division..., 1983).

The Dunajec River, which flows through the Pieniny Mountains, is an example of a mountain river. At the gauging station at the Krościenko nad Dunajcem village (i.e. 3.2 km below the mouth of the Grajcarek Stream, 149.2 km from the beginning of the Dunajec River), which marks the end of the 1,580 km² Dunajec River catchment (Hydrographic division..., 1983), water levels ranged from 143 cm to 545 cm from 1971 to 1990 (Jaguś & Rzętała, 2001). The absolute minimum was 125 cm (25 March 1918), while the absolute maximum (714 cm) was reached during the catastrophic flood of 17 July 1934. Low flows in hydrological years from 1971 to 1990 ranged from 3.5 m³/s to 7.9 m³/s (LLQ – 3.5 m³/s, MLQ – 5.8 m³/s, HLQ – 7.9 m³/s), and mean flows ranged from 23.6 m³/s to 42.8 m³/s (LMQ – 23.6 m³/s, MMQ – 31.4 m³/s, HMQ – 42.8 m³/s), while high flows were as follows: LHQ – 177.0 m³/s, MHQ – 478.3 m³/s, HHQ – 1,290.0 m³/s (Jaguś & Rzętała, 2001). Absolute minimum flows are 3.45 m³/s (14–27 December 1987), while the absolute

maximum flow (2,260 m³/s) was recorded during the flood wave of 17 July 1934 (Jaguś & Rzętała, 2002).

At low and medium stages the water flows in the river channel, but during high water stages it also flows on the floodplain, which is virtually absent in the gorge reach of the Dunajec River. The river channel is constantly changing due to the continuity of water flow, debris transport and human activities (Zawiejska & Wyzga, 2010). In the Pieniny reach of the Dunajec River, various land forms can be found that reflect the morphological activity of the river. The most significant manifestation of the river's morphological activity is the Dunajec River gorge in the Pieniny Mountains. In many places, there are visible erosion undercuts on the edges of the river channel. There are also numerous gravel banks, which are the cause of river branching in many places. Some water-filled depressions in the vicinity of the river can be considered oxbow lakes (Jaguś & Rzętała, 2002).

Several reaches of inactive Dunajec River channels date from the time of the great Dunajec River flood of 1934. They include the right channel branch that was then created; an island also formed at the time, separated from the Sromowce Średnie village by the old river channel. A similar branch of the river that is a temporarily inactive river channel is present in the Szczawnica reach of the Dunajec River (between the Polish-Slovak border and the mouth of the Grajcarek Stream).

The southern and northern parts of the inactive Szczawnica branch of the Dunajec River (Fig. 1) were the sites where sediment samples were collected along a longitudinal profile parallel to the flow of the main channel of the river in this reach. Sediments in the usually inactive channel are intensively washed only episodically during high water stages (as the channel is periodically active), while during low and mean flows of the Dunajec River, the inactive channel is an isolated body of water.

3. MATERIALS AND STUDY METHODS

Five samples of bottom sediments from isolated water bodies in the temporarily inactive channel of the Dunajec River branch were collected on 30 August 2011 (Fig. 1). Sediment samples were collected directly into a polystyrene container by sinking it into surface sediments. The study concerned the top layer (0-1 cm) of uniform sediments accumulated since the last high water stage. The material collected was dried at a temperature of 105°C in laboratory conditions. After they had been dried, the samples were homogenised using a mill. The samples prepared in this manner were then subjected to analyses at Activation Laboratories Ltd. (Canada).

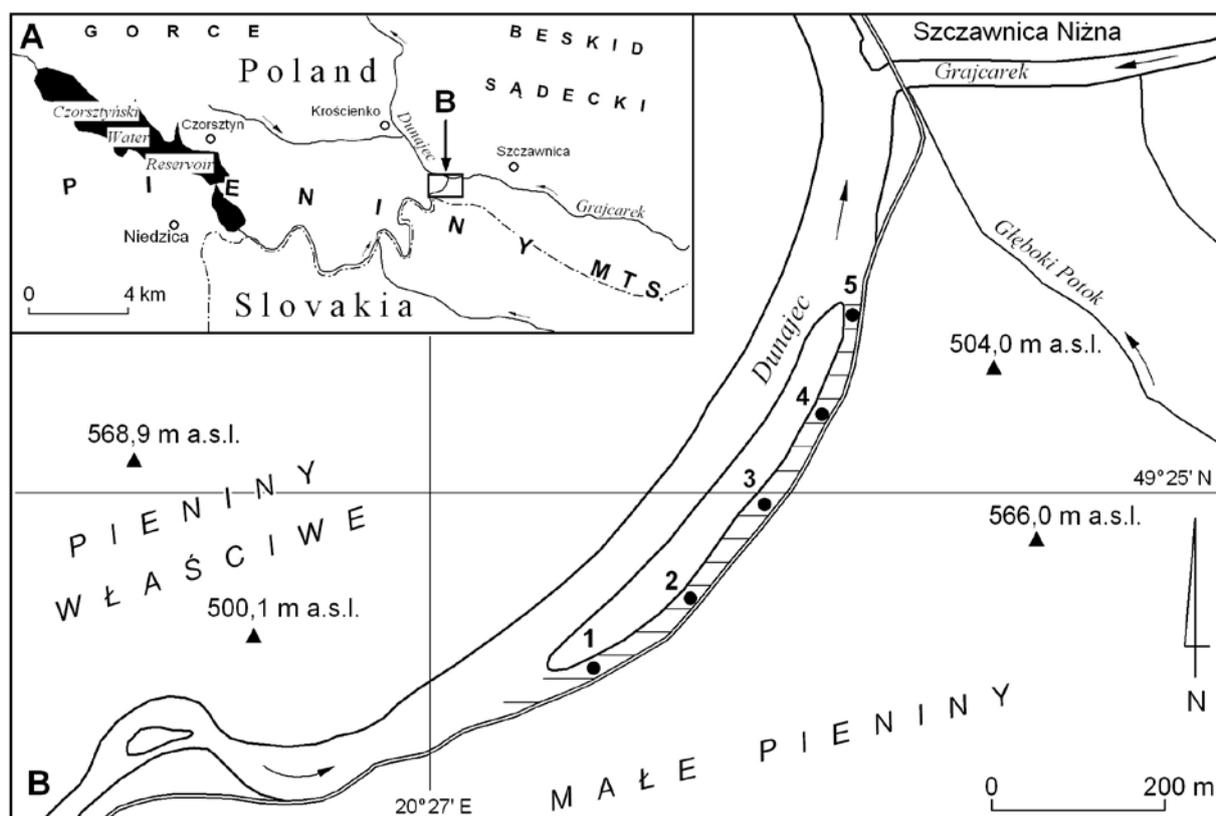


Figure 1. The location of the temporarily inactive channel of the Dunajec River branch in the Pieniny Mountains (sediment sampling sites within isolated water bodies are marked – samples 1–5).

Concentrations of the following oxides were determined in the samples using the ICP method: SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 . Moreover, loss on ignition was measured and sulphur content was determined. The same method was used to determine the content of the following elements: Ba, Sr, Y, Zr, Be, C, Cu, Pb and Zn. Concentrations of the following elements were determined using the INAA method: Ag, Ni, Cd, Bi, Au, As, Br, Co, Cr, Cs, Hf, Ir, Mo, Rb, Sb, Se, Ta, W, La, Ce, Nd, Sm, Eu, Sc, U and Th. Mercury content was determined in sediment samples of 0.5 g each using the Cold Vapour FIMS (Perkins Elmer FIMS 100) method. Detection limits were as follows: for SiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 – 0.01%; for TiO_2 – 0.005%, and for S – 0.001%. In the case of trace elements, the lower quantification limit varied and was as follows: 5 ppb (Au), 0.1 ppm (Sm, Eu, Sc), 0.2 ppm (Sb, La), 0.5 ppm (Ag, Cd, Cs, Hf), 1.0 ppm (Y, Be, Cu, Zn, Ni, Br, Co, Cr, Ta), 2.0 ppm (Sr, Zr, Bi, As, Mo), 3.0 ppm (Ba, Se, W, Ce), 5.0 ppm (V, Pb, Au, Ir, Nd), 20.0 ppm (Rb) and 5 ppb (Hg). In order to calculate one of the indicators, the PCB level was estimated on the basis of the results of monitoring of aqueous sediments in the upper section of the Dunajec River basin (conducted by the Regional In-

spectorate of Environmental Protection in Kraków) and the Cd concentration was assumed at the lower quantification limit, i.e. the maximum level that could be present in the sediment samples tested.

In the examination of the geoenvironmental significance of the content of trace elements in sediments in isolated water bodies in the inactive channel of the Dunajec River branch, five simple indicators were used. The assessment of the degree to which bottom sediments in isolated water bodies in the inactive channel of the Dunajec River branch are contaminated with trace elements was conducted using the geoaccumulation index (Eq. 1) developed by Förstner & Müller, (1981), the degree of contamination and the contamination factor (Eq. 2) developed by Håkanson (1980), the ratio of the actual content of these elements to the regional geochemical background (Eq. 3), and the anthropogenic enrichment factor for bottom sediments (Eq. 4) (Rzętała, 2015a,b).

The geoaccumulation index (Eq. 1) includes a few classes depending on sediment quality (Förstner & Müller, 1981): practically uncontaminated ($I_{\text{geo}} \leq 0.0$), uncontaminated to moderately contaminated ($0.0 < I_{\text{geo}} < 1.0$), moderately contaminated ($1.0 < I_{\text{geo}} < 2.0$), moderately to heavily contaminated ($2.0 < I_{\text{geo}} < 3.0$), heavily contaminated ($3.0 < I_{\text{geo}} < 4.0$),

heavily to extremely contaminated ($4,0 < I_{geo} < 5,0$) and extremely contaminated ($5.0 < I_{geo}$).

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad (\text{Eq. 1}),$$

where:

I_{geo} – geoaccumulation index;

C_n – concentration of the element in question in bottom sediments;

B_n – geochemical background for the element in question;

1.5 – coefficient expressing natural variation in the content of the element in question in the environment.

The degree of sediment contamination (C_d) resulting from the contamination factor (C_f^i) was determined on the basis of the formula developed by Håkanson (1980).

$$C_d = \sum_{i=1}^8 C_f^i = \sum_{i=1}^8 \frac{\bar{C}_{0-1}^i}{C_n^i} \quad (\text{Eq. 2})$$

where:

C_d – the degree of contamination;

C_f^i – the contamination factor;

\bar{C}_{0-1}^i – the mean content of the substance in question (i) from superficial sediments (0–1 cm) from accumulation areas (at least 5 samples, which provide an even area cover of the lake or basin should be taken);

C_n^i – the standard preindustrial reference level;

determined from various European and American lakes to be (in ppm): PCB = 0.01, Hg = 0.25, Cd = 1.0, As = 15.0, Cu = 50.0, Pb = 70.0, Cr = 90.0 and Zn = 175.0).

The contamination factors calculated for individual elements can be interpreted depending on the C_f^i value. If the content of substances present in the 0–1 cm layer of surface sediments is greater than or equal to the pre-industrial content of this substance in the sediments, these sediments are considered to be contaminated or enriched ($1 \leq C_f^i < 3$ – moderate contamination, $3 \leq C_f^i < 6$ significant contamination, $C_f^i > 6$ – very high contamination). Accordingly, $C_f^i < 1$ means low sediment contamination. On the other hand, the degree of contamination depends on the C_d value: $C_d < 8$ – low degree of contamination, $8 \leq C_d < 16$ – moderate degree of sediment contamination, $16 \leq C_d < 32$ – significant degree of contamination, $C_d > 32$ – very high degree of anthropogenic sediment contamination.

The ratio of the value measured to the regional geochemical background it explicitly states the number of times the regional geochemical back-

ground is exceeded and is expressed as follows (Rzetalá, 2015a,b):

$$I_{RE} = \frac{C_{BS}}{C_{GB}} \quad (\text{Eq. 3}),$$

where:

I_{RE} – the ratio of the value measured to the regional geochemical background,

C_{BS} – the average concentration of the element in question in bottom sediments,

C_{GB} – the regional geochemical background level for the element in question in bottom sediments.

The ratio of the value measured to the regional geochemical background (I_{RE}) exceeds unity if the concentration of the element is higher than the regional geochemical background (the higher the concentration the higher the ratio) and is below unity when this level is not reached.

In comparing sediments in isolated water bodies in the inactive channel of the river branch with aquatic sediments in the hydrologically active channel of the Dunajec River with respect to the concentrations of trace elements, the sediment enrichment ratio was used (Eq. 4) (Rzetalá, 2015a,b), which in this case simply points to the similarity or difference in concentrations of the elements analysed in the sediments from the water bodies included in the comparison. The anthropogenic enrichment factor of bottom sediments (I_{AP}) has a value below unity if the concentration of the element in sediments is lower than its concentration in the formations in the vicinity of the basin and above unity if the concentration of the element in bottom sediments is higher than that in the vicinity of the basin.

$$I_{AP} = \frac{C_{BS}}{C_{SR}} \quad (\text{Eq. 4})$$

where:

I_{AP} – the anthropogenic enrichment factor for bottom sediments (dimensionless number);

C_{BS} – the average concentration of the element in question in bottom sediments of the water body;

C_{SR} – the average concentration of the element in question in substrate sediments and in the vicinity of the basin.

4. RESULTS

Individual components included in the basic composition of the sediments tested in isolated water bodies in the inactive channel of the Dunajec River branch exhibited typical quantitative variation in their average amounts, showing little variability when individual samples were compared. As con-

cerns the basic composition of sediments, they are dominated by silica (54.23%–60.70%), with loss on ignition ranging from 9.58% to 16.55% (Table 1). Al₂O₃ content ranges from 12.10% to 16.81% depending on the sample. Several components account for lower shares: Fe₂O₃ (4.98–6.46%), CaO (4.23–5.62%), K₂O (2.02–2.77%), MgO (1.88–2.23%) and Na₂O (1.01–1.42%). The following components account for tenths of a percent: TiO₂ (0.83–0.92%), P₂O₅ (0.16–0.21%), MnO (0.10–0.12%). The average sulphur content determined was 0.25% (Table 2).

Among the microelements determined, the following account for the largest shares on average: Ba (474 ppm), Zr (255 ppm), Cr (160 ppm), Sr (146 ppm), V (139 ppm), Rb (120 ppm), Zn (101 ppm), Ni (73 ppm), Ce (70 ppm), La (38,6 ppm), Cu (35 ppm), Y and Nd (28 ppm), and Pb (22 ppm). The following elements are present at levels of around a dozen ppm: Co (18 ppm), As (16 ppm) and Sc (14.4 ppm). The remaining trace elements are present in average amounts of up to a few ppm: Th (9.8 ppm), Cs and Hf (7.1 ppm), Br (7 ppm), Sm (6.4 ppm), U (3.2 ppm), Sb (2.7 ppm), Be and Ta (2 ppm) and Eu (1.4 ppm). Mercury is present at the level of 50 ppb average. Gold is present at the level of 18 ppb on average.

Several elements were present in amounts below the lower limit of detection of the method used: Ir (<5.0 ppm), Bi and Mo (<2.0 ppm), Se and W (<3.0 ppm) and Ag and Cd (<0.5 ppm).

5. DISCUSSION OF STUDY RESULTS

As concerns overall composition, SiO₂ prevailed in all samples and loss on ignition was inversely proportional to SiO₂ content, which is reflected by the negative correlation coefficient (-0.63). Generally, the high SiO₂ content present where loss on ignition is

lower is a relationship that results from catchment conditions and human impact. The dominant factor in shaping the relationship between SiO₂ content and loss on ignition appears to be the supply to the inactive channel of the Dunajec River of suspensions from its catchment area, which occurs after continuous and torrential rainfall. On the other hand, the organic matter found in the sediments is mainly autochthonous. Almost the entire length of the banks of the temporarily inactive channel of the Dunajec River branch is colonised by compact rush and willow stands. They exhibit high bioproductivity and the plant fall originating there has a significant impact on the chemical composition of sediments as autochthonous matter (Rzętała et al., 2013).

Apart from organic matter and silica as their primary building materials, bottom sediments also include the following primary minerals or their components: Al₂O₃ and Fe₂O₃ as well as manganese, magnesium, calcium, sodium, potassium, titanium and phosphorus compounds. Their percentage shares are also dependent on catchment lithology and the nature of human impact. Al₂O₃ accounts for a high proportion of the sediment samples tested. The CaO found in sediment samples indicates a significant amount of calcium in their composition. This is probably a result of the presence of carbonate formations in the geological structure of the catchment, but may also be partially caused by human impact from agriculture and fertiliser load, since fertilisers include this element. Similarly, the phosphorus present in the sediments may be attributed to natural processes (e.g. the leaching of bioelements from the rocks present within the catchment) as well as to anthropogenic sources (e.g. run-off from agricultural land).

In addition to the macroelements present in the sediments of the inactive channel of the Dunajec River branch, many so-called trace elements were found as well.

Table 1. Basic chemical composition of bottom sediments from isolated water bodies in the temporarily inactive channel of the Dunajec River branch at Szczawnica.

Component	Unit	Characteristics related to the presence of main sediment components		
		minimums	maximums	arithmetic means
SiO ₂	%	54.23	60.70	57.02
Al ₂ O ₃	%	12.10	16.81	14.17
Fe ₂ O ₃	%	4.98	6.46	5.74
MnO	%	0.10	0.12	0.11
MgO	%	1.88	2.23	2.05
CaO	%	4.23	5.62	4.83
Na ₂ O	%	1.01	1.42	1.13
K ₂ O	%	2.02	2.77	2.46
TiO ₂	%	0.83	0.92	0.87
P ₂ O ₅	%	0.16	0.21	0.18
Loss of ignition	%	9.58	16.55	11.72

Table 2. Trace elements in sediments of the temporarily inactive channel of the Dunajec River branch at Szczawnica.

Component	Unit	The presence of elements in sediments of the temporarily inactive channel of the Dunajec River branch at Szczawnica (Pieniny Mountains)			The range of element content in Dunajec River aquatic sediments ¹⁾			Geochemical background for Poland ¹⁾	Range of content in sedimentary rocks ²⁾
		min.	max.	arithmetic means	min.	max.	arithmetic means		
Ag	ppm	below the lower limit of detection			<1.0	1.0	<1.0	<1.0	0.05-0.25
As	ppm	13.0	20.0	16.0	<5.0	7.0	<5.0	<5.0	1.0-13.0
Au	ppb	15.0	22.0	18.0	no data			no data	2.0-7.0
Ba	ppm	425.0	508.0	474.0	19.0	125.0	70.0	54.0	50.0-800.0
Be	ppm	1.0	3.0	2.0	<0.5	0.7	<0.5	<0.5	0.2-6.0
Bi	ppm	below the lower limit of detection			no data			no data	no data
Br	ppm	5.0	9.0	6.0	no data			no data	1.0-10.0
Cd	ppm	below the lower limit of detection			<0.5	1.5	0.5	<0.5	0.05-0.35
Ce	ppm	66.0	74.0	70.0	no data			no data	7.0-90.0
Co	ppm	15.0	23.0	18.0	3.0	11.0	6.0	3.0	0.1-20.0
Cr	ppm	140.0	165.0	160.0	6.0	49.0	21.0	5.0	5.0-120.0
Cs	ppm	5.3	8.9	7.1	no data			no data	0.5-10.0
Cu	ppm	30.0	42.0	35.0	5.0	28.0	13.0	7.0	2.0-60.0
Eu	ppm	1.0	1.8	1.4	no data			no data	0.2-2.0
Hf	ppm	6.3	8.3	7.1	no data			no data	no data
Hg	ppm	0.005	0.122	0.050	<0.050	0.560	0.070	0.050	no data
Ir	ppb	below the lower limit of detection			no data			no data	no data
La	ppm	33.8	45.4	38.6	no data			no data	4.0-90.0
Mo	ppm	below the lower limit of detection			no data			no data	no data
Nd	ppm	26.0	30.0	28.0	no data			no data	4.7-41.0
Ni	ppm	67.0	85.0	73.0	9.0	42.0	20.0	6.0	5.0-90.0
Pb	ppm	17.0	32.0	22.0	6.0	29.0	13.0	13.0	3.0-40.0
Rb	ppm	100.0	130.0	120.0	no data			no data	5.0-200.0
S	%	0.18	0.32	0.25	0.005	0.079	0.026	0.04	no data
Sb	ppm	1.9	3.2	2.7	no data			no data	0.03-2.0
Sc	ppm	12.5	16.0	14.4	no data			no data	0.5-15.0
Se	ppm	below the lower limit of detection			no data			no data	no data
Sm	ppm	5.8	7.2	6.4	no data			no data	1.3-22.1
Sr	ppm	131.0	162.0	146.0	13.0	103.0	45.0	20.0	20.0-600.0
Ta	ppm	2.0	2.0	2.0	no data			no data	no data
Th	ppm	9.1	11	9.8	no data			no data	1.7-12.0
U	ppm	3.0	3.4	3.2	no data			no data	0.45-4.00
V	ppm	133.0	142.0	139.0	6.0	23.0	12.0	7.0	10.0-130.0
W	ppm	below the lower limit of detection			no data			no data	no data
Y	ppm	22.0	32.0	28.0	no data			no data	4.0-50.0
Zn	ppm	83.0	110.0	101.0	44.0	151.0	78.0	62.0	10.0-120.0
Zr	ppm	242.0	269.0	255.0	no data			b.d	20.0-220.0

Explanation: ¹⁾ according to: Lis & Pasieczna (1995); ²⁾ according to: Kabata-Pendias & Pendias (1993).

The presence of microelements in the environment is determined both by natural processes (e.g. the weathering of rocks) and by their supply from anthropogenic sources (e.g. industrial processes, traffic). Some trace elements (e.g. zinc, copper) are considered necessary for organisms to thrive as microelements, while others (e.g. lead, cadmium, chromium, nickel) are considered unnecessary and even harmful. In general, heavy metals and particularly lead, cadmium and copper are considered danger-

ous to humans due to their toxic effects (Kabata-Pendias & Pendias, 1979).

Some trace elements are present in the sediments of the inactive channel of the Dunajec River in amounts similar to the geochemical background for Poland as determined by Lis & Pasieczna (1995) (e.g. Ag, Be, Cd, Hg) or in only slightly higher amounts (e.g. Pb, Zn).

The variation in the sediments in the periodically active branch of the Dunajec River channel is

reflected by the geoaccumulation index values determined for: Hg ($I_{geo} = -0.58$), Zn ($I_{geo} = 0.12$), Pb ($I_{geo} = 0.17$), As ($I_{geo} = 1.09$), Cu ($I_{geo} = 1.74$), Co ($I_{geo} = 2.00$), S ($I_{geo} = 2.06$), Sr ($I_{geo} = 2.28$), Ba ($I_{geo} = 2.55$), Ni ($I_{geo} = 3.02$), V ($I_{geo} = 3.73$), Cr ($I_{geo} = 4.42$). I_{geo} values indicate that these sediments are uncontaminated ($I_{geo} \leq 0.0$), uncontaminated to moderately contaminated ($0.0 < I_{geo} < 1.0$), moderately contaminated ($1.0 < I_{geo} < 2.0$), moderately to heavily contaminated ($2.0 < I_{geo} < 3.0$), heavily contaminated ($3.0 < I_{geo} < 4.0$) or heavily to extremely contaminated ($4.0 < I_{geo} < 5.0$) with certain elements.

The contamination factor (C_f^i) indicates moderate sediment contamination with chromium ($C_f = 1.8$) and arsenic ($C_f = 1.1$) while Hg, PCBs, Pb, Cd, Cu and Zn are absent. The degree of sediment contamination ($C_d=5.2$) is low.

The ratio of the value measured to the geochemical background reflects the concentration of substances in bottom sediments in relation to the levels considered natural and also indirectly indicates the contamination level. For the aforementioned elements it is as follows: $I_{RE} = 1.0$ (Hg), $I_{RE} = 1.6$ (Zn), $I_{RE} = 1.7$ (Pb), $I_{RE} = 3.2$ (As), $I_{RE} = 5.0$ (Cu), $I_{RE} = 6.0$ (Co), $I_{RE} = 6.3$ (S), $I_{RE} = 7.3$ (Sr), $I_{RE} = 8.8$ (Ba), $I_{RE} = 12.2$ (Ni), $I_{RE} = 19.9$ (V), $I_{RE} = 32.0$ (Cr). These values indicate contamination with virtually all of the elements listed (excluding Hg).

Concentrations of some microelements are similar to the range in which they occur naturally in sedimentary rocks (stated by Kabat-Pendias & Pendias, 1993); these are e.g. Br, Cd, Ce, Co, Cs, Cu, Eu, La, Nd, Ni, Pb, Rb, Sb, Sc, Sm, Th, U, Y, Zn.

In many cases, the content of trace elements found in sediments of the inactive channel of the Dunajec River is higher than the ranges in which these elements are found in the aquatic sediments of the river; the latter ranges were examined along the entire river length by Lis & Pasieczna (1995). This is particularly true of the following elements: As, Ba, Co, Cr, Ni, S, Sr and V. For these elements, the geochemical background is exceeded. This points to the enrichment of sediments in the inactive channel of the Dunajec River branch with trace elements when compared to the hydrologically active main channel of the river. On the basis of sediment enrichment ratio values, it can be stated that average concentrations of Hg ($I_{AP} = 0.7$), Zn ($I_{AP} = 1.3$) and Pb ($I_{AP} = 1.7$) are similar. For several other elements, I_{AP} values indicated that average concentrations of analysed elements in sediments in the water bodies compared differed by at least several times – Cu ($I_{AP} = 2.7$), Co ($I_{AP} = 3.0$), As and Sr ($I_{AP} = 3.2$), Ni ($I_{AP} = 3.7$), Ba ($I_{AP} = 6.8$), Cr ($I_{AP} = 7.6$), S ($I_{AP} = 9.6$) and V ($I_{AP} = 11.6$).

The concentration of copper in sediments of the inactive channel of the Dunajec River branch is several times higher than the geochemical background for this element in Poland and also significantly higher than the content found in the aquatic sediments of the hydrologically active channel of the same river (Table 2). Although copper is common in the Earth's crust (the average is 15 mg/kg) and the areas most vulnerable to contamination are those where it is mined and those adjacent to copper smelters, in the case of the sediments analysed wastewater may be an important source of contamination (Kabata-Pendias & Pendias, 1979). Copper accumulation in sediments of the inactive river channel is favoured by its easy and fast adsorption on suspension particles. Copper is highly toxic for vegetation. Consuming food and water contaminated with copper may be harmful to the human body (Bennet-Chambers et al., 1999). Increased content of this element in the diet may lead to poisoning, a decrease in haemoglobin content, adverse metabolic changes and also to liver and kidney damage (Kabata-Pendias & Pendias, 1993).

Cobalt was detected in sediments of the inactive channel of the Dunajec River branch in concentrations ranging from 15 to 23 ppm. The Co concentrations determined are in each case higher than the geochemical background for Poland and are also higher than the amounts found by Lis & Pasieczna (1995) in the Dunajec River channel (Table 2). In Polish river bottom sediments, cobalt is normally present in somewhat higher amounts, i.e. from 25 to 78 mg/kg (Dojlido, 1995). Although cobalt is present in the lithosphere in amounts of around 40 mg/kg, in closed water bodies it is subject to intense bioaccumulation, as a result of which it enters the food chain and may be toxic to aquatic organisms, especially at high concentrations (Kabata-Pendias & Pendias, 1979). Cobalt is easily oxidised and migrates in aqueous solutions and is intensely sorbed (Kabata-Pendias & Pendias, 1979). The presence of cobalt in aquatic ecosystems may be caused to a large extent by the denudation of the natural rock and soil environment (Świdorska-Bróz, 1993).

Arsenic is a metalloid with properties that are intermediate to metals and non-metals. Its presence in sediments has different environmental contexts because anthropogenic sources of arsenic include the mining and metallurgy of non-ferrous metal ores as well as combustion processes. In examined bottom sediments, the arsenic content determined ranged from 13.0 ppm to 20 ppm while its natural content in the lithosphere is up to 18 mg/kg (Kabata-Pendias & Pendias, 1979). The fact that geochemical background for Poland has been exceeded and the arsenic content in the sediment of the inactive channel of the

Dunajec River branch that is three times higher compared to the active channel of the same river can be explained by the greater ability of this element to accumulate in the limnic environment.

Barium and strontium are elements included in the alkaline earth metal group whose content in the Earth's crust is lower than that of calcium and magnesium, which are the most common among this group of elements. The natural barium content in crustal rocks is estimated at 240 ppm and that of strontium at 150 ppm (Kabata-Pendias & Pendias, 1979). Strontium, which is widely used in industry, is present in sediments of the inactive Dunajec River channel in amounts ranging from 131 ppm to 162 ppm while barium concentrations range from 425 ppm to 508 ppm. In this case there are also clear differences in the accumulation potential of pollutants between the inactive channel of the Dunajec River branch and the hydrologically active channel.

Nickel is present in sediments in the inactive Dunajec River branch in amounts ranging from 133 to 142 ppm, which corresponds to the highest concentration of this metal in the bottom sediments of anthropogenic water bodies in urban and industrial areas of the Silesian Upland (Rzętała, 2015b). This means ten times the geochemical background for Poland and twice the level determined in the hydrologically active channel of the Dunajec River (Table 2). Although nickel is present in the Earth's crust in concentrations averaging 100 mg/kg, it easily bioaccumulates and in an acidic environment its solubility and concentrations are high, which is harmful to plants (Kabata-Pendias & Pendias, 1979). The toxicity of nickel results from its high mobility and its tendency to accumulate both in soil and in plants (Wilk & Gworek, 2009). It appears that this is the origin of the accumulation of the element in question in the analysed inactive channel of the Dunajec River branch. The fact that excess exposure to nickel results in its accumulation in lymph nodes and may disrupt the structure of nucleic acids and cause changes in the bone marrow as well as resulting in eczema and leading to cancer (Kabata-Pendias & Pendias, 1993) is of less importance in view of the negligible economic use of the sediments in question.

In sediments of the inactive channel of the Dunajec River, chromium is present in amounts ranging from 140.0 to 165.0 ppm, i.e. many times higher than the concentration considered natural and also than concentrations in the hydrologically active river channel. This is an element that migrates primarily in highly acidic and reducing environments or in alkaline and oxidising ones and does not bioaccumulate strongly (Kabata-Pendias & Pendias, 1979). Geochemical background for chromium in various sedi-

mentary rocks ranges from 5 to 120 mg/kg (Kabata-Pendias & Pendias, 1993). In general, chromium is particularly toxic neither to aquatic organisms nor to humans and it is not accumulated in tissues, but hexavalent chromium, which is easily soluble, is toxic both to plants and humans (Wilk & Gworek, 2009). The presence of chromium in Dunajec River waters and sediments, which is related to the anthropogenic supply of this element, certainly contributes to the contamination of sediments of the inactive channel of the branch of that river (Pawlikowski et al., 2006).

The sulphur content of the sediments tested ranges from 0.18% to 0.32%. This amount should be seen on the one hand as the result of the biochemical processes that take place in the sediments of the inactive Dunajec River channel and on the other hand as the reflection of the intensity of the human-caused acidification of the environment in the vicinity of the inactive channel. This is especially true since Dunajec River aquatic sediments exhibit only a fraction of the sulphur content with geochemical background at the level of 0.04%. This element, although it does not cause severe poisoning, is considered toxic in many compounds; at the same time, however, it is essential for living organisms.

Vanadium is a metal used in industry whose natural concentration in the Earth's crust is estimated at 140 ppm (Kabata-Pendias & Pendias, 1979); a similar amount has been found in the sediments tested, but the concentration is many times lower in the sediments of the active main Dunajec River channel and geochemical background is lower as well. This demonstrates the high ability of this metal to accumulate in isolated water bodies, oxbow lakes and inactive branches of river channels.

6. CONCLUSIONS

Individual components included in the basic composition of the sediments tested in isolated water bodies in the inactive channel of the Dunajec River branch exhibited typical quantitative variation in their average amounts, showing little variability when individual samples were compared. On average the most important component in basic composition is silica (SiO_2 – 57.02%), with loss on ignition at 11.72%. Al_2O_3 content averages 14.17%. Several components account for lower shares: Fe_2O_3 – 5.74%, CaO – 4.83%, K_2O – 2.46%, MgO – 2.05% and Na_2O – 1.13%. The following components account for tenths of a percent: TiO_2 (0.87%), P_2O_5 (0.18%), MnO (0.11%). The average sulphur content determined was 0.25%.

The content of trace elements in sediments of the inactive branch of the Dunajec River channel meets

the geochemical background criteria in the case of Ag, Be, Cd, Hg and is slightly higher than the geochemical background in the case of Pb and Zn while for As, Ba, Co, Cr, Cu, Ni, S, Sr, V the geochemical background is exceeded a few times (As, Ba, Co, Cu, S, Sr), around a dozen times (Ni and V) and several dozen times for Cr; for many (Au, Bi, Br, Ce, Cs, Eu, Hf, Ir, La, Mo, Nd, Rb, Sb, Sc, Se, Sm, Ta, Th, U, W, Y, Zr) elements the comparison to the geochemical background was not made for the lack of data.

The geoaccumulation index (I_{geo}) indicates that the sediments are uncontaminated, moderately contaminated or heavily contaminated with some elements. The contamination factor indicates moderate sediment contamination with arsenic and chromium while Hg, PCBs, Pb, Cd, Cu and Zn are absent. The degree of sediment contamination ($C_d=5.2$) is low.

The content of such trace elements as As, Ba, Co, Cr, Ni, S, Sr and V found in sediments of the inactive channel of the Dunajec River branch is higher than the ranges in which these elements are found in the aquatic sediments of the hydrologically active channel of the same river. The enrichment ratio of sediments in the inactive river channel with respect to microelements ranges from unity (Zn, Pb) to around a dozen – Cu ($I_{AP} = 2.7$), Co ($I_{AP} = 3.0$), As and Sr ($I_{AP} = 3.2$), Ni ($I_{AP} = 3.7$), Ba ($I_{AP} = 6.8$), Cr ($I_{AP} = 7.6$), S ($I_{AP} = 9.6$) and V ($I_{AP} = 11.6$). This means a rapidly progressing accumulation of contaminants in sediments of isolated water bodies during periods when the channel is hydrologically inactive.

Sediments in inactive river channels (oxbow lakes) contain a wealth of geoenvironmental information whose significance is completely different from that which can be read from sediments in hydrologically active river channels. Even in the case of oxbow lakes that are periodically drained during high water stages, thoroughness is required in interpreting the record of sediment contamination given the existing differences in the concentration of trace elements.

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Received at: 29. 04. 2015

Revised at: 20. 07. 2015

Accepted for publication at: 14. 08. 2015

Published online at: 19. 08. 2015