

Spatial Diversity Characterising Certain Chemical Substances in Sediments of Besko Reservoir

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ABSTRACT

The article reports the conducted analyses of certain chemical parameters characterising the sediments of Poland's Besko Reservoir. Specifically, determinations concerned the pH value, percentage organic matter (OM), total organic carbon (TOC), total nitrogen (TN), carbonates (CO₃²⁻), total phosphorus (TP) and its fractions, as well as heavy metals (Fe, Al, Cr, Cu, Ni, Cd, Zn, Mn). The sediments have a slight alkaline reaction, with pH values correlating positively with the high content of carbonates. The sediments have low organic matter content, while organic carbon accounts for about 30% of OM. The values for the C:N ratio point to an allochthonous origin for organic matter. The analysis of phosphorus fractionation showed that inorganic phosphorus (IP) is predominant at every research station. The lowest percentage for a fraction was in turn obtained for NAIP. This testifies to a slight anthropogenic impact of the catchment area. The sediments can be classified as of the 2nd purity class (according to PIG), due to their highest concentration of chromium. According to Müller's classification, the sediments can be classified as purity class 3 (i.e. with moderate contamination). The values noted for the EF coefficient confirm a very strong enrichment by chromium ions. In addition, chromium, copper, nickel and cadmium have a negative effect on aquatic organisms. The results show that the sediments can be used for example in building and maintaining hydraulic structures.

Keywords: sediments, organic matter, phosphorus, heavy metals

INTRODUCTION

Bottom sediments are among the most important components of aquatic ecosystems. They participate in the circulation of matter, being places in which the chemical transformation, deactivation and decomposition of chemical substances occur. The products of these processes reach the water, while sediments store diverse chemical contaminants, including toxic ones. Under favourable conditions, the latter may also be released into the water, with the result being the so-called secondary pollution of aquatic ecosystems. Nevertheless, the content of hazardous substances is many times higher in sediments than in water. It is possible to detect and observe the changes in the quantity of contaminants, while the chemical composition of the sediment proves to be a better indicator of

water pollution than the chemical composition of water itself. The chemical composition of water proves to be variable over time [Szarek-Gwiazda 2013], with reservoirs being particularly exposed to various types of contaminants. The latter reach the aquatic environment, given the low-point locations of reservoirs, a fact that also ensures that sediments can provide the necessary knowledge on the impact of human activity on the aquatic environment. The knowledge of the physical and chemical properties of sediments is an essential source of information that can be used to assess the degree of degradation in reservoirs. It is also necessary if a concept regarding potential reclamation activities is to be developed.

The aim of the work described here has thus been to analyse selected chemical parameters in sediments in the case of Besko Reservoir.

RESEARCH AREA AND METHODOLOGY

Research area

Besko (or Sieniawski) Reservoir is an artificial body of water located in Sieniawa in Poland's Podkarpackie Voivodeship (Province-Region). It was established in 1978 along the River Wisłok, by means of a dam which is 174 m long, 38 m high and 7.5 m wide. Thanks to the dam, the waters of the Wisłok are impounded to a height of 30 m [<http://www.krakow.rzgw.gov.pl>].

The purpose of the construction was to supply drinking water to the nearby towns of Rymanów, Iwonicz, Krosno and Brzozów. However,

the reservoir is also used to generate energy, while helping to safeguard against flooding in the Wisłok Valley and in general evening out flows along the part of that river below the dam [<http://www.krakow.rzgw.gov.pl>].

Research methodology

In July 2016, sediments samples were collected using a gravity sampler (KC Kajak), at four research stations the locations of which are given, along with morphometric parameters of the Reservoir, in Figure 1.

The uppermost 5 cm layer of sediment was collected for analysis. The sampled sediments

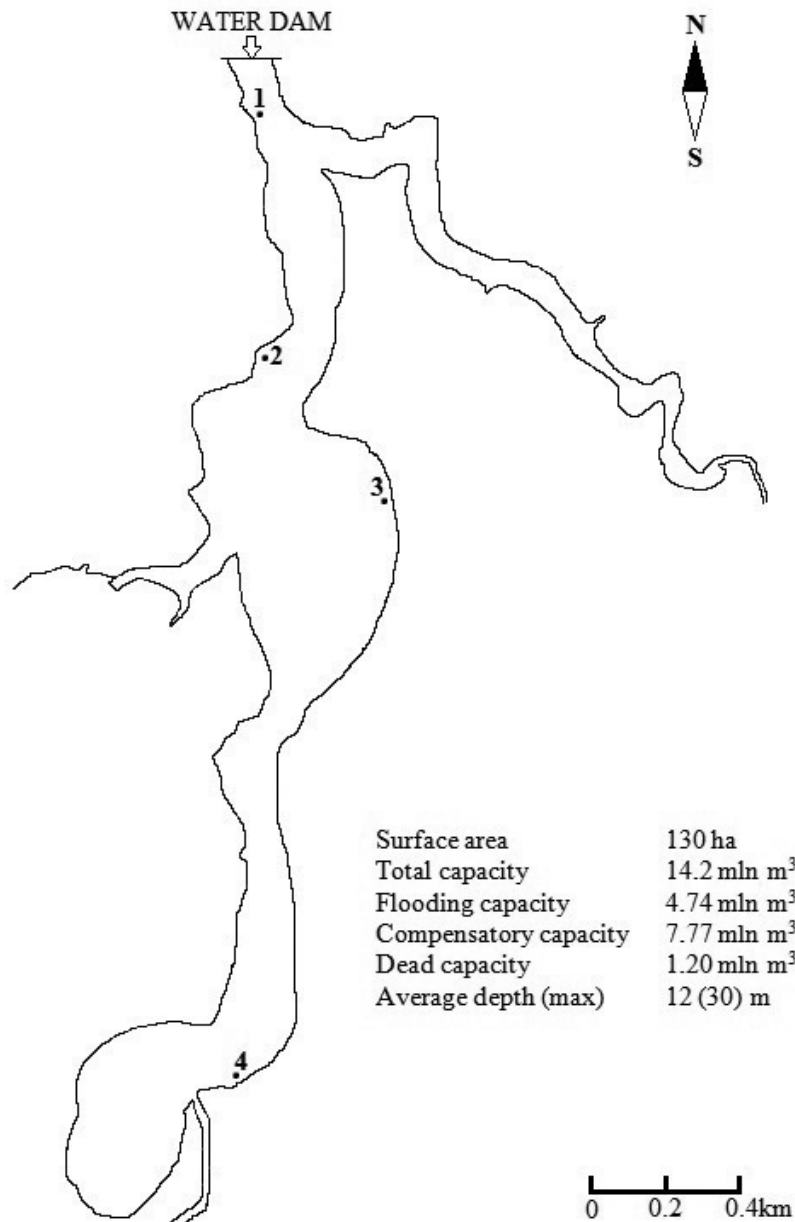


Figure 1. Besko Reservoir – research stations (1, 2, 3, 4), morphometric parameters of the Reservoir

then dried to a constant weight at room temperature, and subsequently at 60°C. The sediments were milled, prior to determinations being made for such parameters as pH, percentage of organic matter (OM), total organic carbon (TOC), total nitrogen (TN), carbonates (CO_3^{2-}) and total phosphorus (TP), as well as the metals Fe, Al, Cr, Cu, Ni, Cd, Zn and Mn.

The OM content was determined as the loss after drying of sediments within 4 h at 550°C. The reaction was determined potentiometrically (MultiLine P4, WTW, Germany) in slurry with 1N KCl [Ostrowska et al. 1991]. The carbonate content was measured by volume using a Scheibler apparatus, while the contents of TOC and TN were determined at 1020°C using a CN elemental analyzer (Flash EA 1112, ThermoQuest). The quality analysis made use of the standard samples of known amounts of carbon and nitrogen (sulfanilamide – $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$). Prior to determination of TOC content, the dried and grinded sediment samples were placed in a desiccator with concentrated HCl vapor [Zimmermann et al. 1997] for 72 h, to ensure the removal of carbonates. Prior to analysis, the sediment sample was again dried to constant weight at 60°C.

Sediment was mineralised for the determinations involving TP and heavy metals. For this purpose, 0.5 g of sediment was placed into each Teflon vessel, with 10 cm³ of concentrated, spectrally pure nitric acid added afterwards. The samples were placed into a MARS 6 Microwave Digestion System, and mineralised using microwave energy at 1600 watts for 40 min. (temperature rise time – 15 minutes, soaking time – 25 minutes), at 180°C. After cooling, mineralisates were filtered through quantitative paper filters, and additionally by syringe filters. TP was obtained using the spectrophotometric method (Thermo Spectronic spectrometer, United Kingdom), whereas heavy

metals were determined using a plasma emission spectrometer (ICP-OES GBC Quantima E 1330).

Phosphorus fractionation analysis was carried out in line with the Standards Measurements and Testing (SMT) protocol. Thus, an appropriate distinction between organic and inorganic forms of phosphorus can be drawn. The fractions obtained are inorganic phosphorus, organic phosphorus (OP), apatite phosphate (AP, calcium-bound forms) and non-apatite inorganic phosphorus (NAIP; Al, Fe and Mn oxides and hydroxides forms) [Ruban et al. 2001]. The analysis of phosphorus forms was performed spectrophotometrically, the determinations were made with Aquamate spectrophotometer.

Criteria used in assessing contamination of sediments with heavy metals

The criteria available in the literature were used to evaluate the degree to which reservoir sediments are contaminated with heavy metals. The geochemical classification of river and lake sediments devised by the Polish Geological Institute distinguishes three classes of sediment quality in line with the contents of individual elements. In order to qualify for purity class 1, the concentrations of heavy metals in sediments may only be 2–5 times the geochemical background level. In turn, assignment to purity classes 2 and 3 entails values 10–20, or 20–100, times higher, respectively [Bojakowska and Sokołowska 1998].

Table 1 relates to the selected heavy metals used to assess the degree of contamination of Besko Reservoir sediments.

Contamination with heavy metals was also determined by reference to the criterion from Müller [1981], as based on the values for the geoaccumulation index (I_{geo}) again detailing the concentrations of heavy metals in sediments against

Table 1. The geochemical classification of river and lake sediments devised by the Polish Geological Institute [Bojakowska and Sokołowska 1998]

Heavy metal	Geochemical background	Class 1 – small contamination	Class 2 – medium contamination	Class 3 – large contamination
	mg·kg ⁻¹ d.m.			
Chromium (Cr)	5.0	<20	<100	<500
Copper (Cu)	6.0	<20	<100	<200
Nickel (Ni)	5.0	<30	<50	<100
Cadmium (Cd)	<0.5	<1	<5	<20
Zinc (Zn)	48.0	<200	<1000	<2000

the geochemical background levels. I_{geo} is calculated from the formula:

$$I_{geo} = \log_2 \frac{c_n}{1.5B_n} \quad (1)$$

where: c_n is the concentration of the heavy metal in sediment,

B_n is the geochemical background value for the area under analysis,

1.5 is a factor determined for lithogenesis in the catchment area, taking into account fluctuations in the content of an element in an ecosystem subject to slight anthropogenic transformation.

Table 2 shows the sediment contamination levels in line with I_{geo} values. The geochemical backgrounds were taken from Bojakowska and Sokołowska [1998].

The level of accumulation of heavy metals in sediments was also expressed by reference to the sediment enrichment factor (EF) used in depicting the anthropogenic contribution to heavy metals in sediments [Salomons and Förstner 1984; Wiejaczka et al. 2017]. The EF factor is calculated using the formula:

$$EF = \frac{c_n B_b}{c_b B_n} \quad (2)$$

where: c_n is the concentration of an element in a sample,

B_n is the geochemical background for that element,

c_b is the reference sample content,

B_b is the geochemical background for the reference element.

An enrichment factor was also calculated in regard to aluminium, while the geochemical background in the case of this element ($17500 \text{ mg} \cdot \text{kg}^{-1}$) was that for soil, given the lack of geochemical background data relating to sediments [Szalińska et al. 2010].

The results, interpreted in line with the guidelines of Birch and Olmos [2008], are presented in Table 3.

Sediments have also been evaluated toxicologically, in line with two Canadian guidelines involving three levels of ecotoxicity. The first criterion is based on threshold values, i.e. NEL (No Effect Level), LEL (Lowest Effect Level) and SEL (Severe Effect Level). The values for heavy metals at the NEL level are taken to indicate no toxicity for aquatic organisms, while the values

below LEL relate to a level of pollution non-toxic to most organisms living in sediments. In contrast, where the SEL threshold is exceeded, there is a visible toxic effect of heavy metals on organisms, and sediment is considered highly contaminated [Persaud et al., 1993]. Another toxicological method has criteria of TEL (Threshold Effect Level) and PEL (Probable Effect Level). Exceeding TEL values for a given element implies a possible toxic effect on the living organisms, while exceeding the PEL indicates marked toxicity. The precise toxicity levels and threshold values are as shown in Table 4.

RESULTS AND DISCUSSION

The research results for the Besko Reservoir sediments are presented in Table 5.

The sediments sampled at all research stations were slightly alkaline, with pH values in the narrow range 7.96–8.24. The lowest pH value characterised the sediments at Station 2, while the highest one was noted for Station 1, located near the dam. The contents of carbonate in the sediment were relatively high, in the range 6.12% at Station 2 to 13.23% at Station 1. The pH values and carbonate contents were correlated ($R^2 = 0.864$). For comparison, the carbonate contents in sediments of Chańcza Reservoir were in the

Table 2. Sediment contamination levels in line with I_{geo} values [Müller 1981]

Class	Value	Sediment quality
0	$I_{geo} \leq 0$	practically not contaminated
1	$0 < I_{geo} < 1$	poorly contaminated
2	$1 < I_{geo} < 2$	moderately contaminated
3	$2 < I_{geo} < 3$	moderately to heavily contaminated
4	$3 < I_{geo} < 4$	heavily contaminated
5	$4 < I_{geo} < 5$	heavily to extremely contaminated
6	$5 < I_{geo}$	extremely contaminated

Table 3. The sediment enrichment factor (EF) in line with the guidelines of Birch and Olmos [2008]

EF value	Heavy metal enrichment of sediments
$EF < 1.50$	lack of enrichment
$1.50 < EF < 3.00$	little enrichment
$3.00 < EF < 5.00$	moderate enrichment
$5.00 < EF < 10.00$	significant enrichment
$EF > 10.00$	very strong enrichment

Table 4. Precise toxicity levels and threshold values [Persaud et al. 1993; MacDonald et al. 2000]

Heavy metal	Unit	NEL	LEL	SEL	TEL	PEL
Chromium (Cr)	mg·kg ⁻¹ d.m.	–	26	110	37	90
Copper (Cu)		–	16	110	36	197
Nickel (Ni)		–	16	75	16	42
Cadmium (Cd)		–	0.6	10	0.7	3.5
Zinc (Zn)		–	120	820	–	315
Manganese (Mn)		–	460	1100	37	90

Table 5. Research results for the Besko Reservoir sediments

Parameter	Unit	Research station 1	Research station 2	Research station 3	Research station 4
pH	–	8.24	7.96	8.00	8.01
CO ₃ ²⁻	%	13.23	6.12	7.03	9.76
OM		5.93	4.26	4.07	3.88
TOC		1.81	1.22	1.11	1.09
TN		0.12	0.07	0.05	0.06
C:N		–	15	17	21
Fe	%	1.94	2.23	2.20	1.88
Al		1.85	1.76	1.77	1.34
TP	mg·g ⁻¹ d.m.	0.832	0.795	0.773	0.533
IP	%	55.49	69.22	73.26	67.35
NAIP		14.34	8.74	5.01	18.92
AP		45.87	63.66	67.07	53.34
OP		24.39	13.91	7.25	21.60
P _{MOB}		38.70	22.70	12.30	40.50

2.10–3.20% range [Tarnawski et al. 2012], while the figures obtained for Solina and Rzeszów Reservoirs were 0.33–6.28% and 3.47–7.56%, respectively [unpublished materials]. In turn, the figures for Dobczyce Reservoir were in the 0.42–3.18% range [Wójcik 1991].

Organic matter (OM) is a key component of sediment, but was present at the rather low level of ca. 6% d.m. at Besko. Along the length of the Reservoir, the OM contents were found to be progressively higher. Thus, the lowest OM value (3.88%) characterised the upper part of the reservoir (Station 4), while the highest (5.93%) was noted close to the dam (at Station 1). The organic carbon content (TOC) was found to correlate with that of OM ($R^2 = 0.996$). The figure for TOC was at approximately 30% of the OM value.

Sediments were also characterised by low total nitrogen (TN) contents – in the range 0.05% (Station 3) to 0.12% (Station 1). The correlations between OM and TN ($R^2 = 0.947$); as well as TOC and TN ($R^2 = 0.972$), indicate that the main component of TN is organic nitrogen. The OM and TOC contents are rather typical for Polish reservoirs. For example, the sediments in Dobczyce Res-

ervoir have the OM contents in the 1.76–3.13% range, as well as TOC values of 1.02–1.82% [Wójcik 1991]. In the sediments of Rożnów Reservoir, the OM values ranged from 1–3% [Gwóźdź and Grodecki 2011], while corresponding values elsewhere are: Sulejów 9.9–21.8% OM and 5.2–10.3% TOC [Bednarek and Zalewski 2007]; Czorsztyn 2.3–11.9% OM [Haziak et al. 2013]; Solina 8.72–10.11% OM and 1.94–2.92% TOC; Myczkowce 10.78–11.94% OM and 3.95–4.08% TOC [Koszelnik 2009]; and Włocławek 11.5% OM, on average [Trojanowska et al. 2009].

In fact, TOC is the main component of OM, while the quality of the latter can be expressed in terms of the TOC/TN ratio (C:N). Land plants and algae differ in their C:N ratios, in that the values for the protein-rich algae are in the range of 4–10, while that for cellulose-rich land plants is at or above 20 [Meyers 1997]. It is thus assumed that the C:N ratios exceeding 12 indicate OM originating on land, while autochthonous organic matter has C:N values below 8 [Martinotti et al. 1997; Hellings et al. 1999]. The C:N ratio also relates to the rate at which OM is mineralised; thus, the lower the value of the ratio, the higher the rate

of mineralisation [Trojanowska and Antonowicz 2005; Piwińska and Gruca-Rokosz 2017]. An optimum C:N ratio for microorganisms is 17, with the lower values indicating nitrogen release into the water table as microbial decomposition of organic matter is taking place [Sobczyński et al. 1996]. In the present study, C:N ratios are in the range of 5–22, albeit with lower values observed in the sediments further along the reservoir. The lowest C:N value was thus recorded in the sediments at Station 1.

The results show that OM (and especially that in sediments of Besko Reservoir's upper parts) is mainly supplied from the catchment area. Sources include macrophytes and plants rich in cellulose. In turn, lower C:N values at Stations 1 and 2 indicate a greater share of autochthonous matter in sediments.

Besko Reservoir also features the contents of iron and aluminium in the ranges of 1.88–2.23% and 1.34–1.85% respectively. The sediment contents of these heavy metals are lowest at Station 4, while the peak for aluminium is at Station 1. In turn, the highest iron content characterised the sediments from Station 2. These values are similar to one obtained in the sediments of other Polish reservoirs [Czerwieniec et al. 2003; GIOŚ 2016].

In contrast, the Besko sediments have contents of total phosphorus slightly above those in other reservoirs. Their values were in the range from 0.533 mg·g⁻¹ d.m. at Station 4 to 0.832 mg·g⁻¹ d.m. at Station 1 (Table 5). These values also conform an upward trend when the backwater of the Reservoir is compared with the site near the water dam. Elsewhere, the values for phosphorus in reservoir sediments expressed in mg·g⁻¹ d.m. were 0.22–0.44 at Krempna; 0.37–0.40 mg·g⁻¹ d.m. at Zesławice and 0.34 at Dobczyce [Tarnawski et al. 2012]. The analysis of phosphorus fractionation showed the dominant contribution of the inorganic form (IP) in the sediments at all Stations (albeit with the values ranging from 55.49% at Station 1 to 73.26% at Station 3). No similar trends

have been observed. Organic phosphorus (OP) was present at the percentages of total P between 7.25% (at Station 3) and 24.39% (at Station 1). In turn, inorganic phosphorus consists of NAIP and AP fractions, the respective contributions of which are 5.01–18.92% and 45.87–67.07%. The smallest NAIP and highest AP characterised the sediments at Station 3. The proportion of IP was evidently affected by apatite phosphorus (AP) ($R^2 = 0.860$). The lowest share of the NAIP fraction is taken to indicate a limited anthropogenic influence in the catchment area, including the inflows of wastewater. In the sediments of the Bort-Les-Orgues Reservoir (France), the percentages noted for the OP; NAIP and AP fractions were 25%; 59% and 16% respectively [Ruban et al. 1999]. In turn, the sediments of the Solina Reservoir were found to have ca. 63% IP; 34% OP; 24% NAIP and 39% AP [Bartoszek and Tomaszek 2011].

At Besko, the highest percentage noted for mobile phosphorus (i.e. NAIP+OP) was 40.5% at Station 4. Correspondingly, the lowest percentage characterised the sediments at Station 3. The content of mobile phosphorus is important, given that it determines the bioavailability of phosphorus forms. In fact, the sediments of Besko Reservoir look poor in mobile phosphorus when compared with other reservoirs. Here, the internal supply of phosphates is impossible due to the low content of total phosphorus, mobile phosphorus and organic matter.

The qualitative analysis of heavy-metal contamination in the Besko Reservoir sediments is useful in helping to determine the distribution of these elements, potentially even with the sediments being put to use once extracted. As far as heavy metals are concerned, the results of the analysis are in Table 6.

In practice, each heavy metal was found to be present at rather similar levels in sediments at the different research stations. The contents of chromium were highest vis-à-vis the geochemical background (at 38.42–46.28 mg·kg⁻¹ d.m.).

Table 6. The results of the analysis pertaining to heavy metals

Heavy metal	Unit	Research station 1	Research station 2	Research station 3	Research station 4
Chromium (Cr)	mg·kg ⁻¹ d.m.	38.42	44.43	46.28	40.24
Copper (Cu)		31.78	24.82	25.53	24.48
Nickel (Ni)		29.16	30.49	31.19	35.28
Cadmium (Cd)		0.42	0.67	0.65	1.25
Zinc (Zn)		79.76	81.85	75.75	78.61
Manganese (Mn)		311.58	337.20	383.90	438.29

Similar values for chromium and copper were recorded in sediments of Zesławice Reservoir (29.9 mg Cr·kg⁻¹d.m.; 7.7 mg Cu·kg⁻¹d.m.), Majdan Sopocki Reservoir (34.8 mg Cr·kg⁻¹d.m.; 11.8 mg Cu·kg⁻¹d.m.) [Madeyski and Tarnawski 2006] and Rzeszów Reservoir (41.74 mg Cr·kg⁻¹d.m.; 29.54 mg Cu·kg⁻¹d.m.) [unpublished materials]. The catchment areas of all these reservoirs are agricultural and forested [WIOŚ 2017; www.pzw.org.pl]. In contrast, significantly higher concentrations of chromium and copper were observed in the sediments of Włocławek Reservoir (330 mg Cr·kg⁻¹d.m.; 55.8 mg Cu·kg⁻¹d.m.) [Gierszewski 2008] and Rybnik Reservoir (140 mg Cr·kg⁻¹d.m.; 1000 mg Cu·kg⁻¹d.m.) [Madeyski and Tarnawski 2006].

The sediments of Besko Reservoir are seen to support relatively high concentrations of nickel. Only Rybnik Reservoir has reported a higher value (55.0 mgNi·kg⁻¹d.m.). In contrast, the concentrations of cadmium and zinc at Besko are such as to suggest only slight sediment contamination as compared with what can be noted in other reservoirs. For example, the respective concentrations of cadmium are 10 and 25 times higher in the sediments of Włocławek and Rybnik Reservoirs than in those at Besko [Gierszewski 2008; Madeyski and Tarnawski 2006]. In turn, Zesławice Reservoir reported a lower content of zinc (72.6 mg Zn·kg⁻¹ d.m.) [Madeyski and Tarnawski 2006].

In line with the classification of sediments prepared at the Polish Geological Institute, those at Besko can be categorised as 2nd-class purity. In turn, applying the Müller criterion, only 3rd-class purity is achieved, which is to say that sediments are moderately to heavily contaminated. This is particularly the case given the observed values for the geoaccumulation index related to chromium and nickel (Table 7).

Heavy-metal enrichment of sediments expressed using factor EF is as presented in Table 8.

Metal-ion enrichment was in the order Cr>Ni>Cu>Zn>Cd>Mn in the sediments at Stations 1–3. In turn, Station 4 was characterised by the order Cr>Ni>Cu>Cd>Zn>Mn. The highest EF value (of 10.29) was noted in the case of chromium in sediments at Station 4.

In line with the ecotoxicological criteria, chromium, nickel and cadmium may all prove potentially toxic to the living organisms (>LEL, TEL). Copper (>TEL) and zinc (<PEL) also exhibit toxicity.

Under the Regulation of the Minister of the Environment of the Republic of Poland of 11th May 2015 on the recovery of waste beyond installations, sediments should not be seen as contaminated in terms of the contents of some heavy metals studied. This ensures a potential use for these sediments, for example in the building and maintenance of hydraulic structures like wharves, embankments, etc.; or in surface hardening.

Table 7. Purity classes in line with I_{geo} values

Heavy metal	Geochemical background [mg·kg ⁻¹ d.m.]	Research station 1	Research station 2	Research station 3	Research station 4
Chromium (Cr)	5.0	3	3	3	3
Copper (Cu)	6.0	2	2	2	2
Nickel (Ni)	5.0	2	3	3	3
Cadmium (Cd)	<0.5	0	0	0	1
Zinc (Zn)	48.0	1	1	1	1
Manganese (Mn)	850.0	0	0	0	0

Table 8. Heavy-metal enrichment of sediments expressed using factor EF

Heavy metal	Research station 1	Research station 2	Research station 3	Research station 4
Chromium (Cr)	7.29	8.81	9.17	10.49
Copper (Cu)	5.02	4.10	4.21	5.32
Nickel (Ni)	5.53	6.05	6.17	9.19
Cadmium (Cd)	0.80	1.33	1.29	3.26
Zinc (Zn)	1.58	1.69	1.56	2.13
Manganese (Mn)	0.34	0.39	0.45	0.67

CONCLUSIONS

The conclusions to be drawn from analysis of the sediments in Poland's Besko Reservoir are as follows:

- the sediment reaction is slightly alkaline, with pH values in the range of 7.96–8.24, as correlated with a high 6.12–13.23% carbonate content ($R^2 = 0.864$);
- sediments are of low (approx. 6%) organic matter content, with C:N ratios of 15–22, indicative of an allochthonous origin of organic matter, and with lower values towards the dam associated with progressively higher OM content;
- the IP fraction is the dominant phosphorus fraction in sediments, while the lowest values within total P characterise the NAIP fraction (perhaps on account of the resuspension of sediments and a zero or limited inflow from anthropogenic sources);
- in line with the PIG criterion, sediments at Besko are of 2nd-class purity; while under the Müller classification they are in 3rd class (suggesting moderately or heavily contaminated sediment); in turn, EF coefficient values show very strong enrichment of chromium ions; while ecotoxicity criteria suggest that the contents of chromium, copper, nickel and cadmium are sufficient to indicate potential toxicity to the living organisms;
- sediments are nonetheless utilisable, due to their limited contents of heavy metals, for example in the construction and maintenance of hydraulic structures or else in surface hardening.

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