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Research Article

Background Concentrations of Nickel in the Sediments of the Carpathian Dam Reservoirs (Southern Poland)

The background nickel (Ni) concentrations in the sediments of two sub-mountain reservoirs (Dobczyce and Czorsztyn) situated in the Carpathian Flysh (southern Poland) were evaluated. Ni concentrations ($15.6\text{--}83.1\ \mu\text{g g}^{-1}$ dry wt.) in both reservoir sediments were affected mainly by the high background content of Ni in the surrounding watershed. Distribution of elevated Ni concentrations mostly revealed an impact of long-range transport influenced by the flow of the main tributary. Ni spatial pattern was mainly influenced by mineral compounds of Fe, Mn, and Al, and to a lesser degree by organic matter content and silt and clay fractions of the sediments of both investigated reservoirs. Spatial distribution was additionally modified by hydrological conditions (flood events and course of the old river-bed). In both reservoirs, substantial portions of Ni were bound to potentially immobile phases, i.e., moderately reducible and residual phases (64–82% in total). Laboratory experiments showed that changes in pH affected Ni leaching from the sediment to a small degree (at pH ~ 3 up to 19.9%). Our results indicated that Ni in these reservoirs has low mobility and, therefore, poses a low toxicological risk to aquatic organisms.

Keywords: Dam reservoirs; Nickel; Sediments

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1 Introduction

Spatial distribution of trace metals may show considerable variability within sediments of particular water bodies. This is mainly related to the sediment properties, i.e., amount of organic matter, Fe and Mn oxides/hydroxides, pH, and grain size [1]. It is well known that similar contents of trace metals deposited in sediments are to a different degree available and toxic to organisms [2]. Analyses of operationally defined binding forms of toxic elements in sediments are of primary importance in recognizing their potential mobility and bioavailability. However, the content of the leachable fraction of trace elements does not necessarily correspond to the amount available to biota [3]. Metal remobilization is influenced by physicochemical conditions in the water–sediment interface, microbial activity, and hydrological factors [3–7].

Nickel is potentially hazardous and toxic to aquatic organisms [8, 9] and is included in the list of priority substances in the field of water quality within the Water Framework Directive of the European Union (2000/60/EC). The main sources of Ni in dam reservoirs are: metallurgical industries, burning of fossil fuels, municipal wastewater, and geological weathering [10]. Elevated Ni concen-

trations of natural origin have been previously detected in the fluvial sediment of European rivers, notably in the Po watershed [11, 12] and in North America, in the pre-industrial sediments of the St. Lawrence River [13]. It has been demonstrated that nickel of natural origin deposited in sediments, also in very high concentrations, has low potential mobility and low ecological risk [12–15], whereas, Ni of anthropogenic origin has higher potential mobility [12, 16].

The Carpathian Flysh (southern Poland) has elevated background concentrations of Ni [17, 18]. As there is little information about the distribution and potential mobility of Ni deposited in sediments of aquatic ecosystems in this area [19, 20], this paper aims to fill this knowledge gap. The goal of the present study was to determine the factors (Fe, Mn, and Al concentrations, grain size, and organic matter content) influencing the spatial distribution of Ni in sediments of sub-mountain dam reservoirs (Dobczyce and Czorsztyn, southern Poland) situated in the Carpathian Flysh. An additional aim was to evaluate the chemical forms of Ni in these sediments, which will influence its potential mobility, and to quantify the fraction of Ni released from the sediments under decreasing pH.

2 Materials and methods

2.1 Study area

This study was conducted in two sub-mountain reservoirs, the Dobczyce Reservoir (DR) and Czorsztyn Reservoir (CR), both situated in the Carpathian Flysh (southern Poland) and having catchment

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Abbreviations: CR, Czorsztyn Reservoir; DR, Dobczyce Reservoir; LOI, loss of ignition

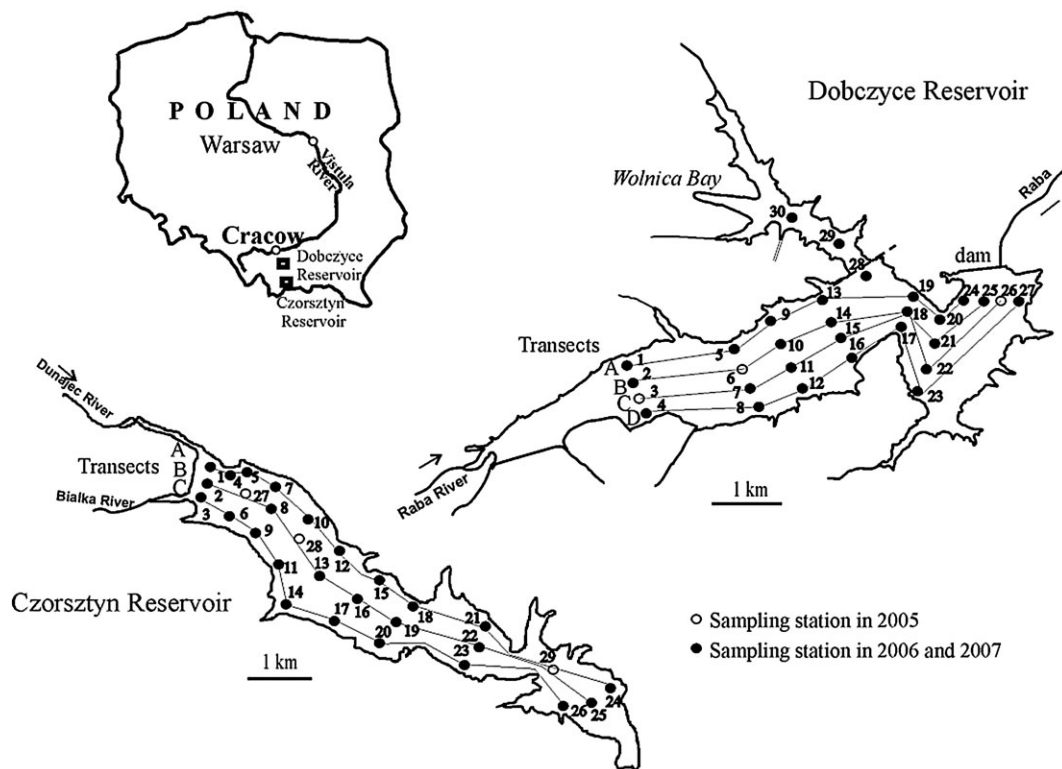


Figure 1. Location of the study area and the sampling stations at the Dobczyce and Czorsztyn.

basins of similar natural conditions. The DR is located on the Raba River, while CR is located on the Dunajec River (Carpathian tributaries of the Vistula River, Fig. 1). Both reservoirs are characterized by considerable capacity and depth and have limnetic character (Tab. 1). Constructed in 1986, the DR supplies the Krakow agglomeration with drinking water. Built in 1997, the CR is one of the youngest and the highest located reservoirs in Poland [21]. Its main functions are to reduce flood flow rates, expand available resources of the Dunajec River, and to increase minimum flows of the river downstream from the reservoir. A hydroelectric power plant also operates on this reservoir.

The DR and CR catchment basins have areas of 768 and 1147 km², respectively. Sandstone-shale rocks of medium to high calcium and

magnesium content dominate in the majority of both catchment basins [22]. The mountain part of the DR catchment basin is mainly covered with brown acid soils with a texture of silt loams, or silty clay loams and occasionally with leached brown soils. The CR catchment basin is mostly covered with skeletal soils, rendzinas, loams, and alluvial soils with a small portion covered with peat soils [23]. The eastern part of this catchment basin is mostly covered with loams and skeletal soils. Fields, pastures, meadows, and orchards occupy about 50% of the DR and CR catchment basins [21].

The geochemistry and acid leachability of the sediments containing Ni were investigated in 2005. Chemical forms of Ni were analyzed in the sediment samples (layer 0–5 cm) collected from stations situated along the long axis of the DR (stations 3, 6, and 26 at depths of 5, 10, and 25 m, respectively), and the CR (stations 27–29 at depths of 5, 10, and 40 m, respectively; Fig. 1). In collected samples (three in total from each reservoir) pH, organic matter content, Ni content, and its chemical forms were determined. The acidic leaching test was performed on the sediment samples from stations 3 and 26 in the DR and stations 27 and 29 in the CR (two sediment samples in total from each reservoir).

Spatial distribution of Ni and factors influencing its distribution were studied in the sediments collected from the DR in May and November (after a flood event in September) 2007 and from the CR in May 2006. The DR stations were situated in lengthwise (A–D) transects along the long axis of the reservoir and additionally three stations were situated in the shallow Wolnica Bay (30 stations in total; Fig. 1). The CR stations (26 in total) were situated in lengthwise (A–C) transects (Fig. 1). The concentrations of Ni, Mn, Fe, and Al, pH, organic matter content, and grain size fractions were determined in

Table 1. Characteristic features of the Dobczyce and Czorsztyn Reservoirs according to Mazurkiewicz-Boroń [21]

	Czorsztyn Reservoir	Dobczyce Reservoir
Start exploitation	1997	1986
Standard damming ordinate (m)	529	269.9
Surface area (km ²)	10.5	9.5
Capacity (mln m ³)	181.2	99.2
Mean depth (m)	19	11
Max depth (m)	46	28
Length (km)	11	10
Water exchange (times year ⁻¹)	3.3	3.4

Data presented in this table concern the standard damming level.

the collected sediment samples (in total 60 samples from the DR and 26 samples from the CR).

2.2 Analytical Methods

The pH of the wet sediments was measured in situ with an Elmetron pH meter (CX-742). The content of organic matter was determined by loss of ignition (LOI) at 550°C. The grain size fractions (sand: 1–0.05 mm, clay silty: 0.05–0.002 mm, and clay: <0.002 mm) were analyzed according to the aerometric method [24].

Sediment samples were dried at 105°C for 24 h and then sieved through a 0.200-mm sieve. In order to determine the content of Ni, Mn, Fe, and Al sediment samples (2–3 sub-samples from each station) were extracted with 65% HNO₃ using microwave Speed Wave (Berghof). Chemical forms of the Ni were analyzed using the operationally defined procedure of Förstner and Calmano [25]. This procedure allows the fractionation of metals into six operationally defined phases: (F1) exchangeable, (F2) carbonates, (F3) easily reducible, i.e., Mn oxides and amorphous Fe hydroxides, (F4) moderately reducible, i.e., mainly poorly crystalline oxy-hydroxides Mn/Fe, (F5) organic/sulfides, and (F6) residuals. The acidic leaching test was conducted according to Helios-Rybicka et al. [26] method. Sediment samples (1.5 g dry wt.) were shaken with the solutions of 0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, and 0.12 M HNO₃ for 24 h, and then Ni concentration and solution pH were measured.

Manganese, iron, and aluminum concentrations were determined by flame atomic absorption spectroscopy (AAS). Nickel concentrations were determined using both flame and graphite furnace AAS (Varian Spektra AA-20). Detection limits for those elements determined by flame were (in µg dm⁻³) as follows: Ni 10, Mn 2, Fe 6, and Al 30. The detection limit for Ni using the graphite furnace method was 0.24 µg dm⁻³. The sum of the Ni contents obtained with the six-step selective leaching method was compared with Ni content (extracted with 65% HNO₃), and a good agreement (87–98% of the total amount) was found. Accuracy of the analytical method was assessed using the Sediment Reference Materials (NCS DC 73308, river sediment). Measured content of Ni in the analytical standard was 31 ± 0.3 µg g⁻¹, while in the certified Ni content was 30 ± 2 µg g⁻¹.

The Mann-Whitney *U*-test was used to determine the differences in Ni content in the bottom sediments between both reservoirs and also among transects. To establish contamination status of the DR and CR sediments the geochemical index (*I*_{geo}) was calculated [27]. The concentration of Ni in the sediment of the Vistula River (near Kraków, southern Poland) was considered to represent the geochemical background concentration of Ni [28]. The dated sediment sample was taken from a depth of 2 m from the old river-bed of Vistula River. It was silt rich in organic debris with a very low heavy metal contents in fraction with <60 µm. According to Helios-Rybicka [28] the origin and grain and mineral composition of the sample are similar to the average composition of the river sediments of the Vistula River and some of its tributaries. Therefore, the sediment Ni concentration of [28] can serve as a local geochemical background for the river sediments.

Taking into consideration *I*_{geo}, Müller [27] described seven classes of sediment contamination, where class 0 (*I*_{geo} < 0) means unpolluted and class 6 (*I*_{geo} > 5) extremely polluted sediments. According to Chapman [29] the word “contaminated” rather than “polluted” should be used when no biological effect has been determined.

Table 2. Physicochemical parameters of sediments in the Dobczyce and Czorsztyn Reservoirs

Parameters	Unit	Czorsztyn Reservoir	Dobczyce Reservoir
pH		6.9–7.7	6.9–7.9
Ni	µg g ⁻¹ dry wt	15.6–68.3	17–83.1
Mn	µg g ⁻¹ dry wt	237–3372	155–2355
Fe	mg g ⁻¹ dry wt	8.1–34.1	10.3–42
Al	mg g ⁻¹ dry wt	2–12.1	3.9–21.2
LOI	%	1.7–11.2	0.7–15.1
Grain size (mm)			
1–0.05	%	0.4–82.6	0–48
0.05–0.002	%	14.1–84.2	42–82
<0.002	%	3.3–40.6	7–52

However, the original *I*_{geo} terminology was retained in comparing our results to the *I*_{geo} classification scheme.

3 Results

3.1 Parameters influencing Ni spatial distribution

The pH, organic matter content, grain size, and Mn, Fe, and Al concentrations of the DR and CR sediments are presented in Tab. 2. The sediments were characterized by pH ranging from neutral to slightly alkaline (6.9–7.9). At most stations silty clay and clays dominated, with a small amount (below 15%) of organic matter (express as LOI). Higher amounts of sand were occasionally found at stations situated in the upper part of the reservoirs and the near shore sections. Mn, Fe, and Al occurred in the investigated sediments in a wide range of concentrations.

3.2 Ni content

Concentrations of Ni in the sediments of the DR were in the range of 17–83.1 µg g⁻¹ dry wt. In May lower Ni concentrations occurred on the northern and southern banks of this reservoir (including the Wolnica Bay, Fig. 2). Higher contents of Ni (70–82.7 µg g⁻¹ dry wt.) were found in the middle part of the reservoir along its long axis (from stations 6 and 7). In November, after storm flow, an increase of Ni content was mainly found in the middle and northern bank portions of the reservoir (except the Wolnica Bay). The highest Ni content (83.1 µg g⁻¹ dry wt.) was detected in the sediment from the deepest part of the DR (station 25). Contents of Ni in the Wolnica Bay were similar in May and November. According to the geoaccumulation index (*I*_{geo}), the DR sediments were low polluted with Ni (class 1) at 50% of the stations in May and at 60% of the stations in November; the remaining stations were unpolluted (class 0).

In May, mean Ni concentrations in the sediments of the northern and southern bank parts (Transects A and D) of the DR were lower, but were characterized by higher variability compared to the middle part (Transects B and C; Tab. 3). In November, Ni contents in the sediment of the southern part (forested bank, Transect A) were lower compared to the middle and northern sides (Transects B–D). These differences were statistically significant (Tab. 4). The mean Ni contents were ca. 1.6 times higher in Transect A in November than in May, while similar in Transects B–D, despite slight changes at selected stations.

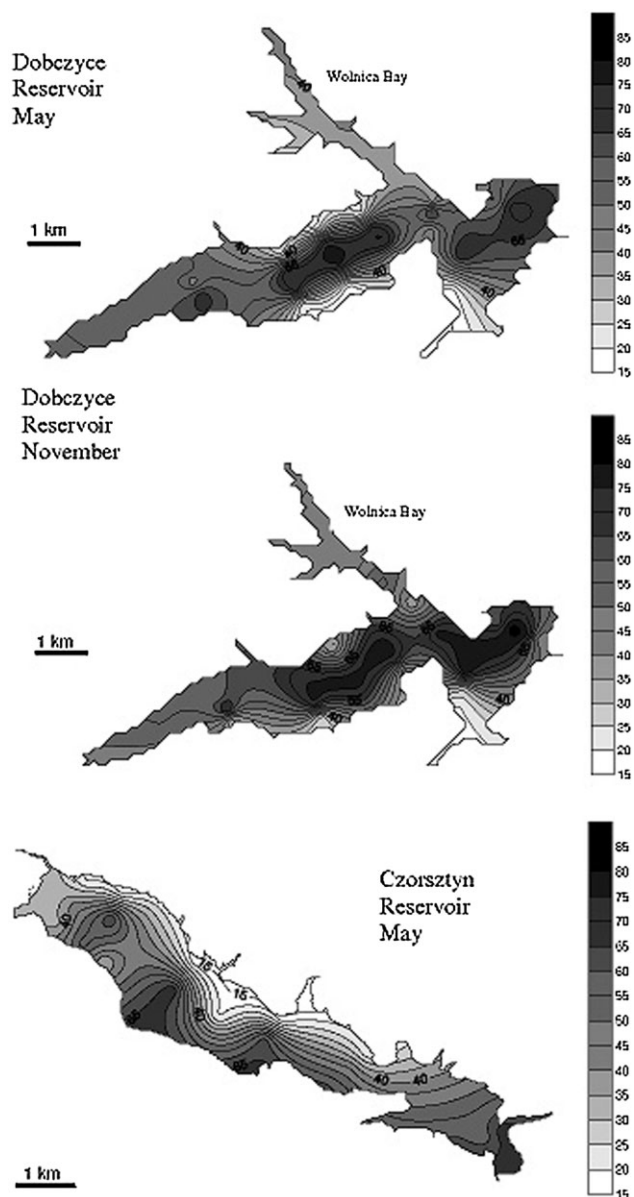


Figure 2. Spatial distribution of Ni ($\mu\text{g g}^{-1}$ dry wt.) in the sediments of the Dobczyce (May and November) and Czorsztyn (May).

Statistical analysis showed that Ni contents in the sediments of the DR (both in May and November) were significantly higher than in the CR (in May $N_1 = 30$, $N_2 = 26$, $Z = -2.62$, $p = 0.009$ and November $N_1 = 30$, $N_2 = 26$, $Z = -3.57$, $p < 0.001$).

According to the correlation coefficients, Ni was strongly correlated with Fe ($r = 0.91$), Mn ($r = 0.82$), and Al ($r = 0.93$) compounds in the DR in May. A weaker correlation was found with the LOI content ($r = 0.71$) and the clay fraction ($r = 0.69$), and with the morphometric features of the reservoir, i.e., depth ($r = 0.51$; Tab. 5). In November, after storm flow, accumulation of Ni in the DR sediments was mainly related with Mn and Al compounds, and to a lower degree with Fe compounds, clay fraction, and reservoir depth (Tab. 5).

The contents of Ni in the sediments of the CR were characterized by considerable variability ($15.6\text{--}68.3 \mu\text{g g}^{-1}$, Tab. 2). The mean Ni contents for particular transects were lower in the northern side of

the reservoir (Transect A) compared to the middle (Transect B) and southern side (Transect C; Tab. 3). These differences were statistically significant (Tab. 4). The content of Ni in the northern side of the CR (Transect A) was characterized by the highest variability. The elevated Ni content was detected in the vicinity of the dam of this reservoir (Fig. 2). According to the I_{geo} values, the CR sediments had low Ni pollution (class 1) at 35% of the stations and were unpolluted (class 0) at the remaining stations.

According to the correlation coefficients, accumulation of Ni in the CR sediments was mainly related to Fe compounds ($r = 0.97$), and to a lower degree to Mn compounds ($r = 0.70$), LOI ($r = 0.80$), silty clay ($r = 0.74$), and clay fractions ($r = 0.61$; Tab. 5).

3.3 Chemical forms of Ni in the sediments

In the DR sediments nickel was mainly bound to the moderately reducible phase Mn/Fe (22.9–29.8%) and the residual phase (43–53.9%; Fig. 3). Given that these phases accounted for 65.9–82.2% of the total sediment Ni, this element showed potentially low mobility. Portions of Ni associated with the easily reducible phase ranged from 5.3 to 20.2%, with the highest amount detected in the sample collected from the deepest part of the reservoir (station 26). Portions of Ni associated with the exchangeable phase, carbonates, and organic/sulfides were low (up to 3.3, 7, and 5.9%, respectively). The chemical forms of Ni were similar in the sediments along the long axis of the DR.

In the CR sediments, Ni was also mainly bound to the moderately reducible phase Mn/Fe (21.4–31.6%) and the residual phase (37.2–45.6%; Fig. 3). However, amounts of Ni bound to these phases were slightly lower compared to those in the DR. About 10% of Ni was associated with the easily reducible phase. Portions of Ni associated with the exchangeable phase (<6%), carbonates (<10%), and organic/sulfides (<12.5%) were slightly higher compared to those in the DR. As in the DR, the chemical forms of Ni were similar in the sediments along the long axis of the CR.

3.4 Acidic leaching test

As mentioned above, sediment pH ranged from approximately neutral to slightly alkaline. The portions of Ni leached from the sediments of both reservoirs at pH ca. 6 were low (from 1.5 to 4.3%, Fig. 4). At a pH of approximately 3, higher amounts of Ni were leached out of the sediments (up to 17.8% in the DR and 19.7% in the CR). Although curves of Ni leaching were similar for both reservoirs, slightly higher amounts of Ni were leached from the CR sediments, especially at the lower pH values.

4 Discussion

Nickel concentrations in the sediments of the DR and CR ranged from below $20 \mu\text{g g}^{-1}$ up to the concentrations exceeding the guideline value for sediments contaminated by dredging activity ($75 \mu\text{g g}^{-1}$) [30]. Large spatial variability of Ni content has also been found in the sediments of other reservoirs [6, 14, 31–33]. Taking into consideration the sediment quality guidelines (SQGs) [34], the sediments of the DR and CR could be regarded as contaminated with Ni. Nickel concentrations exceeded the threshold effect concentration (TEC, $22.7 \mu\text{g g}^{-1}$) for 73 and 97% of the samples, and the probable effect concentration (PEC, $48.6 \mu\text{g g}^{-1}$) for 42 and 70% of the samples of the CR and DR sediments, respectively. However, Farkas et al. [12]

Table 3. Statistical parameters of Ni concentration in the sediments of the Dobczyce (Transects A–D) and Czorsztyn (Transects A–C) Reservoirs

Transects	Mean ($\mu\text{g g}^{-1}$ dry wt.)	Minimum ($\mu\text{g g}^{-1}$ dry wt.)	Maximum ($\mu\text{g g}^{-1}$ dry wt.)	SD	CV (%)
Dobczyce Reservoir					
May					
Transect A	39.9	18.5	63	17.6	44
Transect B	68.2	45.7	74.8	10.1	15
Transect C	68.8	47.1	75.6	9.9	14
Transect D	39.4	17	66.3	21.6	55
November					
Transect A	63.2	32.4	77.6	15.1	24
Transect B	73	57.3	83.1	10.8	15
Transect C	69.9	31.7	79.3	17	24
Transect D	41.8	19.8	66.3	18.6	45
Czorsztyn Reservoir					
Transect A	26.9	15.6	67.5	15.9	59
Transect B	51	19	68.3	17.4	34
Transect C	52.2	30.8	66.1	14.6	28

dw, dry weight.

Table 4. Significant differences in Ni concentrations among lengthwise transects in the Dobczyce (May and November 2007) and Czorsztyn (May 2006) Reservoirs

Transects	N_1	N_2	Z	p-value	Z	p-value
Dobczyce Reservoir						
A–B	7	7	–2.75	0.006	–1.47	ns
A–C	7	7	–2.75	0.006	–1.60	ns
A–D	7	7	0.19	ns	2.11	0.035
B–C	7	7	–0.71	ns	0.71	ns
B–D	7	7	2.75	0.006	2.62	0.009
C–D	7	7	2.75	0.006	2.62	0.009
Czorsztyn Reservoir						
A–B	10	7	–2.3	0.019	nd	nd
A–C	10	9	–2.8	0.006	nd	nd
B–C	7	9	0.2	ns	nd	nd

p-value, significance level; ns, statistically not significant; nd, not determined.

Table 5. Coefficients of correlation between Ni concentration and parameters affecting Ni distribution in the sediments of the Dobczyce and Czorsztyn Reservoirs

Parameters	Dobczyce Reservoir				Czorsztyn Reservoir	
	May		November		r	p-value
	r	p-value	r	p-value		
Mn	0.82	<0.001	0.86	<0.001	0.70	<0.001
Fe	0.91	<0.001	0.60	0.001	0.97	<0.001
Al	0.93	<0.001	0.89	<0.001	0.40	ns
LOI	0.71	<0.001	–0.23	ns	0.80	<0.001
Reservoir depth	0.51	0.004	0.51	0.004		
Grain size (mm)						
0.05–0.002	0.24	ns	0.31	ns	0.74	<0.001
<0.002	0.69	<0.001	0.62	<0.001	0.61	0.001

r, correlation coefficient; p-value, significance level; ns, statistically not significant.

suggested using SQGs together with regional background data to assess the risk of Ni in contaminated sediment. According to these authors, risk assessment may be overestimated if based on the SQGs only. The Carpathian Flysch region has high background Ni concentrations in both in soils and sediments [19, 20]. The Ni content in the

sedimentary rocks of the Carpathian Flysch may be considerable. In the Czeremosza River basin (Eastern Carpathians) the content of Ni in the shale sediments (marine sediments) reached up to 3.5% [17]. In the studied area, great portions of Ni are bound to the clay fraction of the sedimentary rock [18]. The amount of Ni bound in silicate

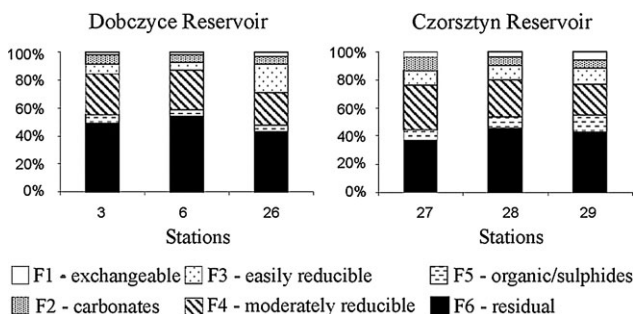


Figure 3. The chemical forms of Ni in the sediments of the Dobczyce and Czorsztyn.

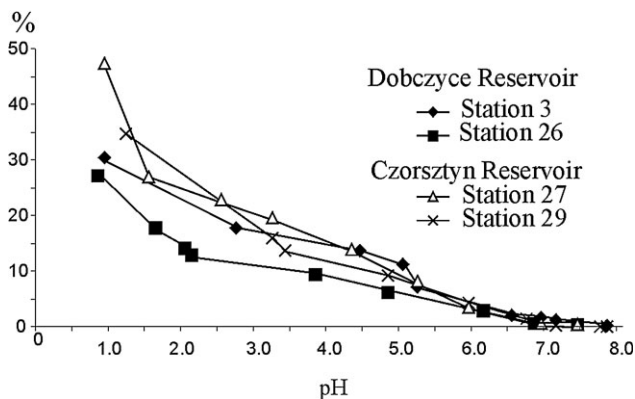


Figure 4. Relative (%) amount of Ni released from the sediments of the Dobczyce and Czorsztyn during acidic leaching test.

minerals ranged from 0.5 to 3% [18]. Taking into consideration the background Ni concentration in the sediment of the Vistula River (southern Poland, $40 \mu\text{g g}^{-1}$) [28], the DR and CR sediments can be classified as unpolluted to low polluted ($I_{\text{geo}} < 1$). The background Ni concentration determined for the Vistula River was higher compared to the geochemical background for freshwater sediments given by Wedepohl [35] (Tab. 6). Our findings confirm an earlier study of Ni distribution in the River Po (Italy), which found that river sediment was influenced by natural Ni sources (the presence of basic and ultrabasic rocks) and anthropogenic Ni sources [11, 12]. Although the Ni content (mean range $52.7\text{--}161 \mu\text{g g}^{-1}$) exceeded the PEC in 50% of the samples analyzed, it did not exceed the regional background levels and revealed a low-to-moderate pollution load of its middle stretch [36].

Moreover, the concentrations of Ni in the DR and CR sediments were in the range of those found in water bodies with the naturally elevated sediment concentrations (Tab. 6) [12, 37, 38]. They were higher compared to the sediment Ni concentrations found in uncontaminated water bodies [31, 39–43] and considerably lower compared to other contaminated system [32, 44–46]. For instance, Ni content in the sediments of the Goczałkowice and Rybnik Reservoirs, situated within or near the Upper Silesian Industrial Region (USIR, Poland), reached ca. $170 \mu\text{g g}^{-1}$ [32, 33]. In the Rybnik Reservoir (Russia), which was contaminated by wastewater from steel plant, mean Ni content reached $394 \mu\text{g g}^{-1}$ [45]. In the Keban Dam Lake (Turkey), which was contaminated by oil wastes from Diesel fuel, sediment Ni concentrations reached up to $700 \mu\text{g g}^{-1}$ [46].

The patterns of nickel distribution in the DR and CR sediments indicate the influence of the main tributaries and long-range trans-

Table 6. Nickel concentrations in the Dobczyce Reservoir, Czorsztyn Reservoir, and other water bodies

Water body	Mean ($\mu\text{g g}^{-1}$)	Range ($\mu\text{g g}^{-1}$)	References
Reservoirs			
Dobczyce (this study)	58	17–83.1	
Czorsztyn (this study)	43	15.6–68.3	
Rożnów, Poland	56.3	28.3–73.9	[37]
Goczałkowice, Poland	3	170	[32]
Solina, Poland		7.16–52.99	[31]
Rybnik, Poland			[33]
Włocławek, Poland	23.2	8.4–33.5	[39]
Rybnik, Russia	8.3–392		[45]
Guanting, China	37.1	14.7–56.7	[38]
Lake Waco, USA	25	7–36	[40]
Keban Dam Lake, Turkey	167.1	1–700	[46]
Kaunas, Lithuania	26–29		[41]
Rivers			
Odra, Poland	51.6	37–108	[55]
Odiel, Spain		14–47	[42]
Lakes			
11 lakes, Poland	17.1	4.5–28	[43]
Local geochemical background:	40		[28]
Fresh water sediments			

port. Elevated Ni contents were noted in the middle part and along the long axis of the DR, and in middle and southern parts of the CR. A similar phenomenon was observed in the sediments of other reservoirs [33, 47]. Nickel content at the banks of the reservoirs seems to be mainly affected by the geological background and the land use in the direct catchment basin, as well as morphological features. Higher Ni content was found in the northern side of the DR where cultivated areas prevail, whereas, lower Ni concentrations exist in the southern portion of the basin where forests prevail. Elevated Ni content in the CR sediments was observed along the old bed of the Dunajec River, where the high content of clay fraction was detected in previous studies [48]. Lower concentrations of sediment Ni in the northern part of the CR, compared to the southern part, may also be related to the small tributaries entering the reservoir and higher sand content in the sediments in the northern part [48].

Temporal sampling of the DR sediments (May and November 2007) facilitates the discussion of seasonal changes and impact of the hydrological events on Ni content. The obtained results showed an increase in the sediment Ni concentrations in November compared to May. This is possibly connected with seasonal changes of Ni content but also with the flood event which occurred in the Raba River in September 2007. Seasonal changes of Ni content in sediments have also been found in other reservoirs [14, 32, 49], however, the presented results are contradictory. Kwapuliński et al. [32] found high Ni concentrations in the Goczałkowice Reservoir sediments during the spring season, after the snow melting period, and again during the autumn circulation. Conversely, Ni content in the Kuibyshev Reservoir (Russia) sediments increased in summer and decreased in the period from autumn to spring [14]. In sediments of the Kozłowa Góra Reservoir (Poland), located near large urban-industrial centers (USIR), seasonal changes in Ni content were related to seasonal atmospheric emissions. During cold periods, dusts-contaminated emissions from heating plants contribute to the Ni content in reservoir sediments [49]. The increase in Ni content in the DR seems to be influenced by flood events. In September 2007, the water flow in the Raba River reached $430 \text{ m}^3 \text{ s}^{-1}$, and during a few days about $90 \text{ m}^3 \text{ m}^{-3}$ of water (81% of the total reservoir capacity) was dis-

charged into the DR [50]. The high load of suspended matter flushed by the storm water from the catchment basin to the DR increased the sediment Ni content. The phenomenon of decreasing trace metal content in the sediment of the River Po (Italy) during flood conditions was found by Vignati et al. [51]. The authors suggested that floods may flush a part of the contaminated sediments.

In general, the sediments of the middle parts of the sub-mountain DR and CR were characterized by potentially small Ni mobility. Nickel was mainly bound to the moderately reducible and residual phases. The moderately reducible phase included mainly poorly crystalline Fe oxyhydroxides and has little potential for mobility. The residual phase was mainly composed of detrital silicate minerals and resistant sulfides [52]. Ni bound to this phase is not reactive during sedimentation and diagenesis. Similar Ni speciation was found in sediments of the Kuibyshev Reservoir (Russia) [14] and Kolleru Lake (India) [15], and the slightly contaminated section of the River Po [12]. In the deepest part of the DR, a higher portion (ca. 20%) of Ni was associated with the easily reducible Fe and Mn oxides, which can be released under reductive conditions in the water-sediment interface layer [4]. A decrease in dissolved oxygen concentration (an increase of the reductive conditions) in the hypolimnion of both reservoirs occurs usually during summer stagnation [21].

In the studied reservoirs significantly smaller portions of Ni were bound to the potentially mobile phases: exchangeable, carbonate, and organic/sulfides. Higher amounts of Ni associated with the exchangeable phase were observed in the River Po (13–27%), especially in the more contaminated sections [12]. In more contaminated water bodies, a greater portion of Ni has been associated with carbonates [16, 32, 33]. Since mobilization of Ni bound to carbonates can occur when pH decreases [5], the acidic leaching test was performed on the sediment samples from both reservoirs. Laboratory experiments showed that under acidic condition (pH ca. 3) a relatively small amount of Ni was released from the sediments of the DR and CR (up to 17.8 and 19.7%, respectively). At this pH slightly higher amounts of Ni (25%) but much higher amounts of Zn and Mn (up to 60%) and Cd (up to 50%) were leached from the sediment of the Odra River [53].

As mentioned above, the Ni portion bound to the organic/sulfidic phase was rather low and probably related to the low amounts of organic matter in the sediments of the investigated reservoirs. Higher amounts of Ni bound to this phase were found in water bodies where sediments contained higher amounts of organic matter, i.e., in the Kolleru Lake [15], the anoxic sediments of the Rybnik Reservoir [33], or more contaminated water environments [12]. The organic/sulfidic phase is considered as moderately mobile and available. Ni may be released from this phase as a result of organic matter decomposition and oxidation of sulfides to SO_4^{2-} [5].

Despite the differences in the Ni content, the chemical forms of Ni in the sediments of the middle part of the DR were similar. The same phenomenon was observed in the CR. The high portion of Ni bound to stable geochemical phases suggests that there is a limited potential for Ni mobility. Therefore, Ni likely poses a low toxicological risk to aquatic organisms. These results confirm an earlier study by Saulnier and Gagnon [13], which found elevated natural concentrations of Ni in the pre-industrial sediments of the St. Lawrence River and low amounts of potentially bioavailable Ni [13].

The obtained correlations showed the significant role of the mineral phase (Fe, Mn, and Al compounds) in Ni accumulation in the sediments of both reservoirs. In May, chemical forms of Ni were dominated by the moderately reducible phase (including poorly

crystalline Fe hydroxides and Mn oxides) and the residual phase (including probable aluminum-silicate minerals), thus Ni concentration was probably affected by geological background and redox condition in the water-sediment interface. Fe and Al hydroxides play an important role in trace metal accumulation [6, 33, 47], therefore, such a phenomenon was expected in the DR and CR. Compared to May, weaker relationships between Ni and Fe (but not between Ni and Mn) in November indicated the effect of flood events on Ni accumulation rather than changes in redox conditions in the water-sediment interface. It is well known that under naturally occurring Eh conditions, Fe compounds are uniformly less soluble than Mn ones. Therefore, inorganic processes lead to the precipitation of Fe before Mn and the reduced species of Mn(II) appear in the water column much earlier than those of Fe(II) [54]. Results of element correlations and the chemical forms of Ni showed that organic matter has limited effect on Ni accumulation compared to mineral phases. A relationship between Ni content and organic matter content was not always observed in other reservoirs [33, 47] or rivers [11]. The clay fraction played a minor role in Ni accumulation in the DR and CR sediments, although it was an important factor of Ni accumulation in the River Po sediments [11].

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