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SEASONAL VARIATIONS IN NICKEL CONTAMINATION OF WATER AND SEDIMENTS OF SMALL DAM RESERVOIRS IN SOUTHERN POLAND

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Abstract: The paper presents the results of analyses of nickel content in bottom sediments of four small dam reservoirs, as well as nickel content in water of tributaries to these reservoirs. The analyzed reservoirs, with capacities ranging from 34 to 3860 thousand m^3, are located in southern Poland. Based on the results of analyses conducted over five years, i.e. in the periods 2005-2007 and 2012-2013, an attempt was made to determine the seasonal variation in the concentration of nickel in sediments along with the seasonal variation of nickel concentration in water flowing into these reservoirs. Additionally, an attempt was made to correlate the nickel concentration in water flowing into the reservoirs with nickel concentration of sediments. Also, nickel content in water and sediments was evaluated according to different criteria and standards. It was concluded that the concentration of nickel in sediments significantly exceeds the limits set for this element by the EQS. Significantly lower concentrations of nickel in water indicated that there is no risk of environmental contamination. The highest mean concentration of nickel in sediments was noted in samples collected in spring. On the other hand, the lowest mean Ni concentrations were observed in winter.

Keywords: nickel, seasonal variation, sediment quality guidelines, small reservoirs

1. INTRODUCTION

Small dam reservoirs, regardless of the world region, provide water for agriculture and economic/domestic purposes during periods of its scarcity. In the semi-arid regions these reservoirs collect water during rainy season, in order to use it in the dry season (Liebe et al., 2005, Sawunyama et al., 2006). Also in Europe, small reservoirs are used for storage of water, but - due to their small size, - in a full annual cycle. According to Neto et al. (2011), micro reservoirs are characterized by a capacity of less than 1 million m^3, while the capacity of small dam reservoirs ranges from 1 to 10 million m^3. In Poland and Romania the upper limit of capacity for a small reservoir is 5 million m^3, while in Great Britain it is 1 million m^3 (White et al. 1996). Due to their short period of operation, resulting from intense reduction of capacity, small reservoirs need to be frequently dredged. After being removed, the accumulated sediment - if it does not contain high levels of toxic elements - can be an important resource for agricultural purposes. Reservoir sediments may be a good quality material for reclamation of industrially degraded areas (Darmody & Marlin, 2008). Such use of chemically uncontrolled bottom sediments is associated with the risk of increasing content of harmful substances, including heavy metals, in the soil environment. Determination of the degree of sediment contamination, including the concentration of heavy metals, is important, not only because of the assessment of the possible use of dredged sediment, but also may be helpful in the assessment of the condition of the environment.

Seasonal differences in the concentration of nickel in sediments of two large reservoirs in southern Poland were observed by Szarek-Gwiazda et al., (2011). Also Reza & Singh (2010) reported seasonal variations in the concentration of nickel in Indian river waters. On the other hand, Rabee et al., (2009) showed seasonal variation in pollution with heavy metals (Ni, Cu, Pb, Mn and Cd) of sediments of the Tigris and Euphrates rivers. Research of Rabee et al., (2009) shows that there is a clear seasonal variation in the concentration of all metals in sediments, including nickel. Seasonal or temporal changes in the concentration of pollutants in water and sediments were demonstrated by many researchers, e.g. by Szarek-Gwiazda et al., (2011), Senze at al., (2010), Davutluoglu et al., (2011), Amegashie et al., (2011) or Petronio et al., (2012).

In the mid-nineties of the previous century, Foster & Charlesworth (1996) found that seasonal variations in heavy metal concentrations are also evident in many European rivers. The main aim of this study was to determine the seasonal variation in the nickel concentration in sediments of four small dam reservoirs in southern Poland, as well as to assess the seasonal changes in the concentration of nickel in water flowing into these reservoirs. Moreover, an attempt was made to correlate the concentration of nickel in water flowing into the reservoirs with the concentration of nickel in sediments, as well as to evaluate the nickel pollution of water and sediments according to different criteria and standards.

2. MATRIALS AND METHODS

2.1. Study area

The study was conducted in four reservoirs, located in the upper Vistula basin (Fig. 1). Samples of bottom sediments and water of tributaries to the Cierpisz, Maziarnia, Niedźwiadek and Narożniki reservoirs were analyzed over the period of five years, in 2005-2007 and 2012-2013. The sample collection was carried out during the volume measurements of excavated sediments (Michalec, 2015).

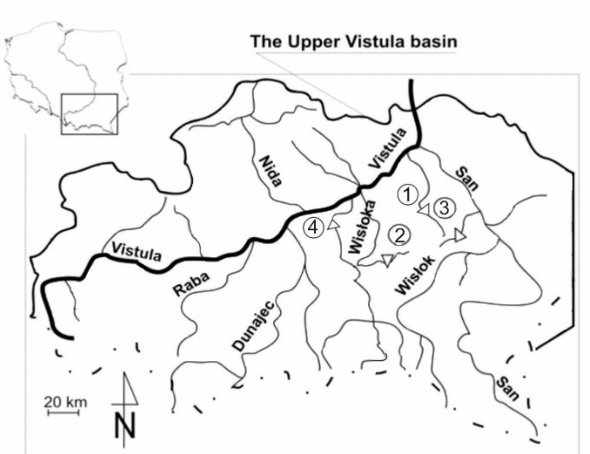

Figure 1. Location of the selected small dam reservoirs: 1) Maziarnia, 2) Cierpisz, 3) Niedźwiadek, 4) Narożniki

These measurements were conducted within two research projects, entitled "Development of new and validation of existing formulas to predict silting of small reservoirs" and "Determination of transport and sedimentation conditions of suspended sediment in a river and a small reservoir". The capacity of the tested reservoirs falls within the range from 34 to 3860 thousand m^3 (Table 1). A general feature of the reservoirs selected for the analysis is their rapid reduction of capacity, mainly resulting from retention of small-fraction debris with diameters smaller than 1 mm. The selected reservoirs have a single tributary (river or stream) with no side tributaries. They are characterized by relatively elongated shape, without coves or stagnant water zones. Catchments of the investigated reservoirs are mainly used for agricultural purposes.

Table 1. Selected basic parameters of the studied small dam reservoirs

Reservoir	Reservoir capacity [10^3 m^3]	Surface area [ha]	Mean depth [m]	Length of the reservoir [m]
Maziarnia	3 860.0	160.0	2.4	6510
Cierpisz	34.5	2.3	1.5	340
Niedźwiadek	124.5	8.1	1.5	550
Narożniki	283.0	28.0	1.0	2000

2.2. Analytical methods

Water samples from the tributaries to the reservoirs and samples of sediments from these reservoirs were collected once per month over five years of research. The samples of water were collected from the main stream in the cross section located approximately 100 m above the inlet to reservoirs. In order to determine the nickel concentration, three samples were collected at each sampling site. Mean concentrations of heavy metals were calculated based on the values determined in three water samples collected at each site in cross sections of tributaries to the reservoirs.

Core samples of reservoir sediments were collected by dividing the sample into three layers, i.e. surface layer (layer of 0-1 cm) and two layers from depths of 1-25 cm and 25-50 cm. The performed analyzes of seasonal variation of nickel concentration in sediments were based only on samples collected from the surface layer. All sediment samples were collected in cross sections of the investigated reservoirs, located at the inlet to each reservoir (point III in Fig. 2), in the center (point II in Fig. 2) and by the dam (point I in Fig. 2). In this way, a total of nine sediment samples were obtained during one sampling cycle in each reservoir, which then were subjected to the nickel concentration analyzes. The paper demonstrates the range of nickel concentrations, determined for individual samples collected at each site of the reservoir, i.e. from a depth of 0-50 cm. The samples were collected once per month. There was no fixed date of sampling in each month, due to technical difficulties, resulting from weather conditions in each season, as well as due to the organization of transport to the studied reservoirs. Thus, a data string from 60 months was collected for each reservoir, including the nickel concentration results in sediments.

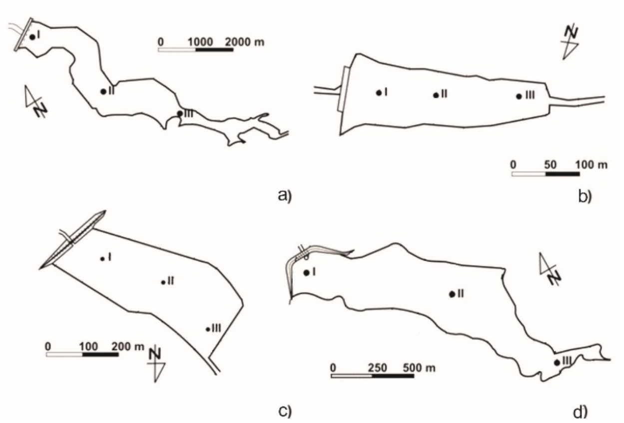

Figure 2. Investigated small dam reservoirs: a) Maziarnia, b) Cierpisz, c) Niedźwiadek, d) Narożniki, with marked points of the bottom sediment sampling (I, II, III)

Samples of sediments were collected with a standard Beeker sampler (Eijkelkamp), according to the methodology developed by Madeyski (1998). Sediment samples from reservoirs were subjected to the grain size and organic matter content analyzes. Grain composition of small-fraction mineral material was determined with Cassagrande method modified by Prószyński according to the polish standard (PN-R-04032, 1998). Specific weight was determined pictometrically, while volume weight was determined by a bulk method. Organic matter content (O_M) was determined by annealing (Lityński et al., 1976). The content of heavy metals in sediments, the same as in water, was assessed by Flame Atomic Absorption Spectrometry – (FAAS) with the use of the Solaar M6 spectrometer (Unicam). These analyses were preceded by the sample preparation through mineralization carried out using a mixture of $HClO_4$ and HNO_3 acids in a 1 to 3 ratio and dissolving the dry residue in hot HCl in a 1 to 1 ratio. The assessment was performed in a flame of the gas mixture of air-acetylene with deuterium background correction. The obtained total concentrations of heavy metals in sediments collected in the analyzed reservoirs allowed to determine the maximum, minimum and mean concentrations of each element. Reference material CRM 16-05 was used for the accuracy of the analyses of nickel - the percentage of recovery was between 95 and 106%.

The results of nickel concentrations in water and sediment samples were divided into four groups corresponding to meteorological seasons. Seasonal differences in nickel concentration in water and sediments were assessed for separate seasons: spring (months: March, April and May), summer (June, July and August), autumn (September, October and November) and winter (December, January and February). The obtained results were verified statistically using one way ANOVA and Tukey test at significance level $\alpha < 0.05$ using Statistica 11 software. The analysis of variance was performed to compare the mean nickel (Ni) content in water and sediment samples between seasons.

The nickel content in sediments was evaluated according to the environmental quality standards - EQS (Directive, 2013) and geoaccumulative index (I_{geo}) (Müller, 1981). The nickel content in water flowing into the investigated reservoirs was also assessed according to the EQS (Directive, 2013) and by the WHO standards (Guidelines, 2011). Following the guidelines of the EQS, the methodology proposed by Förstner (2007) was applied, by which the determination of harmful substances content in water, including heavy metals, should be performed according to one out of two standards. According to the first standard, determination of pollution level should be conducted based on the mean value from the measurements conducted over at least a year. Mean value of substances, determined in such way, should be compared with threshold values of the Environmental Quality Standards. However, according to the second standard, the maximum concentration recorded for each substance should be compared with threshold values of the Environmental Quality Standards. By using the geoaccumulative index (I_{geo}) (Müller, 1981), the concentration of heavy metals was determined in a separate fraction of sediment with grain size smaller than 2 μm and the total concentrations of trace metals were measured in <1 mm fraction of sediment. The background concentration in the shale sediment was adopted in accordance with Wedepohl (1995) as elemental concentrations in the continental crust.

3. RESULTS

3.1. General characteristics of sediments of the investigated reservoirs

Mean volumetric density of sediments (ρ_0), mean bulk density of sediment deposits (ρ_s) and organic matter content (O_M) were determined for the entire profile of sediments, i.e. for the entire sample of sediment collected with a tubular sampler from the 0-50 cm layer (Table 2). On the other hand, grain size and the concentration of Ni in dry weight were determined for the surface layers of sediments (Table 2). The volumetric density of sediments of the investigated reservoirs falls within the range of 0.79-1.71 $t \cdot m^{-3}$, while the mean bulk density of sediments ranges from 2.49 to 2.67 $t \cdot m^{-3}$. Grain size distribution corresponds to sandy loam, loam and silt loam. Organic matter content is low and does not exceed 10%.

3.2. Nickel content in the reservoir sediments

A total of 45 sediment samples were collected in each reservoir in different meteorological seasons over the five-year research period. For each analysis, a run included blank, certified reference materials (CRM) and the examined samples were analyzed in duplicate to eliminate any batch-specific error. A number of 90 analyses was used to calculate these statistic parameters for each of the six water reservoirs (Table 3). The concentration of nickel in the investigated reservoirs falls within the range of 4.7-38.2 $\mu g\ g^{-1}$ (Table 2), whereas the mean concentration of nickel ranges from 8.94 to 24.90 $\mu g\ g^{-1}$ (Table 3). The largest nickel concentrations were observed in the Niedźwiadek reservoir and in the Narożniki reservoir, while the smallest – in the Maziarnia reservoir.

According to the geoaccumulation index (I_{geo}), the sediments of reservoirs: Maziarnia (I_{geo} = 0.53) and Cierpisz (I_{geo} = 0.37), were unpolluted (class I). Also according to the geoaccumulation index (I_{geo}), sediments of the remaining reservoirs were assessed as moderately polluted with Ni (class II), since I_{geo} = 1.63 for the Niedźwiadek reservoir and I_{geo} = 1.61 for the Narożniki reservoir.

It was not possible to determine the variations in nickel content throughout the reservoir due to the fact that the debris samples were collected only at three sites. In order to determine the differentiation of river debris in the sediments accumulated in the reservoir, it is necessary to collect more samples.

Table 2. Physicochemical parameters of sediments of the investigated reservoirs

Parameters	Unit	Reservoirs			
		Maziarnia	Cierpisz	Niedźwiadek	Narożniki
ρ_0	$t\ m^{-3}$	1.59-1.71	1.03-1.65	0.79-1.39	0.94-1.19
ρ_s	$t\ m^{-3}$	2.60-2.67	2.57-2.63	2.53-2.61	2.49-2.59
O_M	%	1.65-5.53	2.89-4.19	3.37-9.14	5.53-7.88
Grain size (mm)					
1-0.05	%	51-76	52-64	22-49	7-40
0.05-0.002	%	22-37	31-41	42 - 63	49-71
< 0.002	%	2-12	3-7	9-15	11-23
Concentration of nickel in dry weight of sediments in 0-50 cm layer					
Ni	$\mu g\ g^{-1}$	4.7-17.7	5.7-15.9	13.6-38.2	14.5-37.6

Table 3. Concentration of nickel ($\mu g\ g^{-1}$ dry weight) in sediments

Parameters		Reservoirs			
		Maziarnia	Cierpisz	Niedźwiadek	Narożniki
Samples collected from the surface layer (layer: 0-1cm)					
number of analyses		n = 90	n = 90	n = 90	n = 90
mean		8.94	9.77	22.30	24.90
SD (-)		2.9	2.6	5.7	7.1
CV (%)		33	26	26	29
Samples collected from the sediment profile (layer: 0-50 cm)					
sampling site No I	mean	9.02	8.83	21.93	24.78
	SD	2.5	2.2	4.9	6.9
	CV (%)	31	23	24	27
sampling site No II	mean	8.86	9.94	24.06	25.19
	SD	2.9	2.5	5.8	7.3
	CV (%)	30	27	26	31
sampling site No III	mean	8.91	10.31	24.11	24.89
	SD	3.0	2.7	5.6	7.2
	CV (%)	33	25	27	30

The sediment samples for testing were collected during the siltation measurements of the examined reservoirs. These measurements were conducted once per year in cross sections in the period of five years, in 2005-2007 and 2012-2013. Based on the results of silting measurements, it was possible to identify the zones in a given reservoir where the most intense sediment deposition occurred. On the basis of the collected sediment sample examinations, it was possible to demonstrate the potential range of mean nickel concentrations in different parts of the reservoirs, i.e. at the inlet, in the center and by the dam. Mean nickel concentrations, determined based on the analyses conducted on the surface sediment samples (0-1 cm), separated from the entire sediment sample collected from the depth of 0-50 cm, were used for this purpose. The recorded concentrations of nickel were the highest in the parts of the reservoir, where the largest amount of sediment is accumulated. Distribution of sediments in the analyzed small reservoirs is diverse. In the reservoirs Cierpisz (Fig. 2.b) and Niedźwiadek (Fig. 2.c), which have a rectangular plan view, the largest volume of sediment is accumulated at the inlet to each of these reservoirs. This is due to a rapid increase of width at the inlet part of these reservoirs. Mean concentrations of nickel at inlets to these reservoirs are significantly higher than the mean nickel concentrations in other parts, i.e. by 3.6 and 14.4% in the Cierpisz reservoir and by 0.2 and 9.0% in the Niedźwiadek reservoir (Table 3). On the other hand, in the reservoirs with elongated shape, i.e. in Maziarnia (Fig. 2.a) and Narożniki (Fig. 2.d), the largest volume of sediment is deposited in the center and by the inlet to these reservoirs. This is due to their elongated and narrow inlet part, causing the sediment transport to the central part of these reservoirs. In these reservoirs, the variation in nickel content is not as evident as in the case of the aforementioned reservoirs. In these reservoirs the difference between the highest and the lowest concentration is 1.8 and 1.6% for the Maziarnia and Narożniki reservoirs, respectively.

3.3. Nickel content in water flowing into the investigated reservoirs

Maximum, minimum and mean concentrations of nickel, identified in the samples of water flowing into the investigated reservoirs are presented in Table 3. The highest maximum nickel concentration was found in water supplying the Narożniki reservoir, while the lowest maximum concentration – in water supplying the reservoir in Cierpisz. The coefficient of variation (CV), calculated for nickel concentrations in water flowing into each of the studied reservoirs is greater than 60%, which indicates very large variation of nickel concentrations in water.

The content of nickel in water flowing into the analyzed reservoirs, assessed according to the EQS (Directive, 2013), indicates that there is no risk of environmental contamination. The threshold annual mean concentration of nickel and its compounds for inland surface waters according to EQS is 20 mg l^{-1}. The obtained maximum values in the analyzed water samples are from 40% to more than 33 times lower than the EQS level (Table 4). The concentration of nickel in water flowing into the examined reservoirs also does not exceed the WHO standards (Guidelines, 2011), whereby Drinking Water Equivalent Level for nickel in water is 0.7 mg l^{-1}. This value is 3.5-times greater than the threshold nickel concentration for water, given by the EQS.

3.4. Seasonal differences in the nickel concentrations in sediments and water

The concentrations of nickel in sediments and water flowing into the studied four small reservoirs, were segregated based on different meteorological seasons. The coefficient of variation (CV), calculated for the concentrations of nickel in sediments of each reservoir indicates small or average variation in the concentration of this metal. The smallest differences in the concentrations of nickel in sediments were recorded in winter, with the exceptions for the results obtained of sediments of the reservoirs in Maziarnia and Cierpisz (Fig. 3).

Table 4. Concentration of nickel (mg l^{-1}) in water

Parameters	Reservoirs			
	Maziarnia	Cierpisz	Niedźwiadek	Narożniki
max	0.0266	0.0062	0.0298	0.0499
min	0.0003	0.0001	0.0019	0.0011
mean	0.0069	0.0016	0.0108	0.0184
SD (-)	0.0071	0.0013	0.0069	0.0127
CV (%)	102.97	82.13	63.70	68.90

On the other hand, the variation in nickel concentrations in the samples of water collected at inflows to these reservoirs is large during summer and autumn and very large in spring and winter (Fig. 4). This corresponds to the values of coefficient of variation in the ranges of 40-60% and 60-80%, respectively.

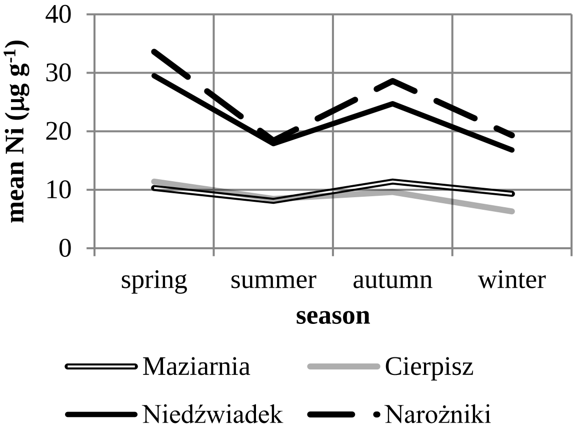

Figure 3. Seasonal variations in nickel concentration in sediments of the investigated reservoir

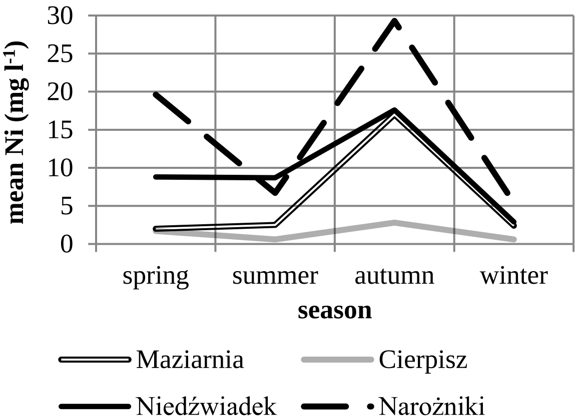

Figure 4. Seasonal variations in nickel concentration in water flowing into the investigated reservoir

The determined nickel concentrations in sediments and water supplying the analyzed reservoirs in each season allowed to determine the relationship between the concentration of nickel in the sediment as a function of its concentration in inflowing water. Data, presented in Figure 4, were subjected to the correlation analysis, describing the relationship between the dependent variable (C_S – concentration of nickel in the sediment) and independent variable (C_W – concentration of nickel in water). The coefficient of determination R^2, being the measure of the regression model fit to the data series, reached 0.7305 for the correlation between the variables C_S and C_W in spring (Fig. 4), which is the highest R^2 value. The lowest R^2 value was obtained for autumn, i.e. 0.507. The R^2 values for winter and summer are 0.6687 and 0.6241, respectively. Separation of seasons allowed to obtain the correlation values with relatively high coefficients of determination. Without separation of seasons, the single correlative relationship for all measured data is characterized by a coefficient of determination of only 0.5607.

4. DISCUSSION

The investigated small dam reservoirs accumulate substantial amount of pollutants in their sediments, including heavy metals. Heavy metal concentrations determined in the sediments of the investigated reservoirs were referred to as “total”. Total concentration of heavy metals might serve as a useful indicator for appropriate assessment of sediment contamination. The nickel content in the water, and ultimately in the deposited sediment, is influenced by rock formations of the area, crossed by the tributaries. High nickel content in river alluvia in non-industrialized areas is observed in the regions of occurrence of metamorphic and ultra-alkaline rocks (Muller et al., 1994). Such rocks do not occur in the catchment areas of the studied reservoirs.

The total concentration of nickel in sediments of the studied four small reservoirs in the upper Vistula basin ranges from 4.7 to 38.2 μg g^{-1} in dry weight. These values are comparable with nickel concentrations observed in sediments of two other large Polish reservoirs, i.e. Dobczyce and Czorsztyn, where the nickel content ranged within the values of 17–83.1 and 15.6–68.3 μg g^{-1}, respectively (Szarek-Gwiazda et al., 2011). According to Szarek-Gwiazda et al., (2011), the nickel concentrations in Polish, Russian, Chinese, Lithuanian and Spanish reservoirs fall within the range of several to several dozen μg g^{-1}.

The relatively low concentrations of nickel in the studied sediments of small reservoirs in southern Poland is undoubtedly due to low concentrations of nickel in water. This is somewhat related to low Ni content in soils and geological deposits of the catchment, as well as due to small area of these catchments, ranging from 18 to 233 km^2. Catchments of the studied reservoirs are mainly used for agricultural purposes, but some of them are highly forested – e.g. 43% of the catchment of the Cierpisz reservoir and 50% of the catchment of the Niedźwiadek reservoir are covered with forests. Also, the small areas of catchments and short sections of rivers supplying water to these reservoirs, ranging from 1.8 to 44.5 km, affect the amount of pollutants flowing into the reservoirs.

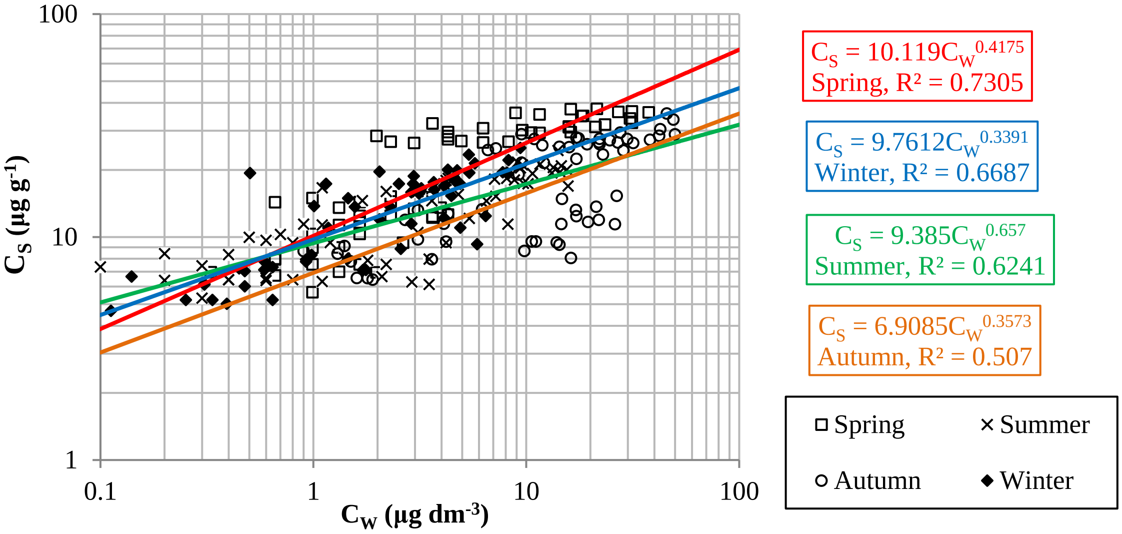

Figure 4. Seasonal relationship between the concentration of nickel in sediment (C_S) and in water (C_W) flowing into the studied small reservoirs

Location of the reservoirs in lower sections of rivers and closing the catchment of larger area with the reservoir's dam, can lead to an increase in the concentrations of pollutants accumulated in the reservoir sediments, including nickel. The land use of catchment is the factor that has a significant impact on the sediment contamination. The analyzed reservoirs are located in agriculturally used catchments and the concentration of nickel in their sediments ranges from 4.7 to 38.2 µg g^{-1} (Table 2). These are low values as compared to the concentrations observed in sediments of the reservoirs located in urbanized catchments, where these values amount to 170 µg g^{-1} (Kwapuliński et al., 1991; Loska et al., 2003) or even up to 700 µg g^{-1} (Kulahci & Doğru, 2006) These values are also low as compared to big reservoirs. For example, the mean concentrations of nickel in Halali reservoir varied between 4.55 - 9.91 µg g^{-1} (Malik et al., 2015). Nickel co-occurs frequently in reservoir sediments with other heavy metals. According to the study of Zhang et al., (2012), there are high correlation coefficients for the relationship between the nickel and chromium content as well as for the nickel and copper content, while Davutluoglu et al., (2011) found correlations between high concentrations of nickel and chromium as well as nickel and aluminum.

The concentration of nickel in sediments of the studied four small reservoirs is more than 2,500 times higher than the concentration of this element in water flowing into these reservoirs. Smaller differences between the nickel concentrations in sediments and water were recorded by Gałka & Wiatkowski (2010). According to these authors the concentrations of nickel in water flowing into the small reservoir located in Psurów were more than 1,170 times smaller than the concentrations of this metal in the reservoir sediments. It should be emphasized that the mean concentration of nickel in sediments of the Psurów reservoir was very low and its value amounted to 7.02 µg g^{-1} in dry weight. Also, according to Sojka et al., (2018), the concentrations of nickel in water samples were from 2.1 to 5.7 times lower than the concentrations of this metal in bottom sediments of the Stare Miasto Reservoir.

The nickel concentration values in sediments of reservoirs in the upper Vistula basin are also comparable to those obtained by Colas et al., (2013) based on the analyses conducted in four small reservoirs in France. The concentration of nickel in sediments of these reservoirs ranged from 6.50 to 16.90 µg g^{-1} in dry weight. As shown by the data presented in the study by Colas et al., (2013), these concentrations were on average 2.5 times higher than the concentrations of nickel in sediments collected from the riverbed downstream of the reservoirs. Foster & Charlesworth (1996) showed that the total nickel concentrations in the post-1850 sediments of selected lowland lakes and reservoirs in England unaffected by mining activity range from 9.0 to 165.3 µg g^{-1}.

The volume concentration of nickel in the studied sediments significantly exceeds the permissible values of this element according to the EQS, indicating very high contamination with nickel. However, according to the geoaccumulation index (I_{geo}), the sediments of two reservoirs are unpolluted (class I – reservoirs in Maziarnia and Cierpisz). In the remaining four reservoirs the sediments are moderately polluted as compared to the geoaccumulation index (I_{geo}). Moreover, the contamination of sediments with nickel was assessed according to the sediment quality guidelines (SQGs). The criterion set by MacDonald et al. (2000) was used in many studies which were performed to develop the sediment quality guidelines (SQGs). Mean nickel concentrations in sediments of two reservoirs at Narożniki and Niedźwiadek are higher than the TEL value, i.e. 18 μg g^{-1}. Also, mean nickel concentrations in the surface layers of sediments of these reservoirs exceed the PEL value (i.e. 36 μg g^{-1}). Moreover, the mean concentrations of nickel in sediments of these three reservoirs exceed the threshold effect concentration (TEC = 22.7 μg g^{-1}). Mean concentrations of nickel in sediments do not exceed the probable effect concentration (PEC = 48.6 μg g^{-1}).

On the other hand, entirely different assessment results were obtained for the nickel content in water flowing into the investigated reservoirs. No risk of environmental contamination was found, as the observed maximum nickel concentrations in water were from 40% to more than 33 times lower than the threshold value of the EQS (Directive, 2013). The concentration of nickel in water also does not exceed the WHO (Guidelines, 2011) limit value (Drinking Water Equivalent Level for nickel is 0.7 mg l^{-1}).

According to Tueros et al., (2009) the European Union Water Framework Directive (WFD) requires the identification of all possible sources of priority substances affecting water quality. However, the Environmental Quality Standards for WFD do not give sufficient consideration to the effect of sediments and assessment of their contamination on the quality of water bodies (Tueros et al., 2009). Although previous studies indicated the need to consider the impact of pollutants in sediments on the water quality, the necessity to take into account the impact of resuspension of pollutants on the quality of water is now increasingly emphasized (2012). Another important issue is that the same levels of contamination for water, sediment and/or biota, are established in the EQS (Directive, 2013). This means that, as in the case of the investigated reservoirs, water flowing into these reservoirs is not contaminated with nickel, whereas the sediment accumulated in the reservoirs poses threat to the aquatic environment. Moreover, the concentrations of nickel in water and sediments differ between seasons. The highest mean Ni concentration in sediments of each reservoir was recorded for the samples collected in spring. On the other hand, the smallest mean Ni concentrations were observed in winter (Fig. 4). The mean concentration of Ni calculated for all samples collected in the studied reservoirs in spring is 23.60 μg g^{-1}, while in winter samples it equals to 14.15 μg g^{-1}. Much smaller differences in the mean nickel concentration in sediments collected in winter as compared to the mean concentration of this element in spring, summer and autumn were found for the analyzed small reservoirs of the upper Vistula basin. Mean Ni concentration in winter compared to the mean Ni concentration in spring, summer and autumn is lower by more than 1.1 to 2-times, from 1.2 to more than 1.5-times and from 0.9 to 1.2-times, respectively for each of these seasons. The obtained data show that the nickel concentration in the surface layers of sediments increases in the period from winter to spring, in spring reaching its highest mean values throughout the year. There is a slight decrease of mean nickel concentrations from spring to summer and a further increase occurs in autumn. A similar trend in the changes of nickel concentrations in sediments was observed by Kwapuliński et al., (1991), who found high Ni content in the Goczałkowice reservoir sediments during the spring season, after the snow melting period, and again during the autumn circulation. Algül & Beyhan (2020) found that there was no consistent trend in the seasonal variation of heavy metals in the sediments of the Lake Bafa, however all concentrations increased in autumn. In contrast, Kocharyan et al., (2003) observed that the concentrations of nickel in sediments of the Russian reservoir Kuibyshev increased from spring to summer and decreased from autumn to spring. This means that contrary to the obtained results of analyses conducted in the small reservoirs, the concentration of nickel in summer was the highest throughout a year. However, in winter the Ni concentration in sediments of the Kuibyshev reservoir was the lowest, similarly as in the small reservoirs analyzed in this study. According to Yuan et al., (2020) the highest concentrations of nickel and four metals (Cr, Cu, Mn and Zn) in Qingcaosha reservoir were also found in spring and summer. Senze et al. (2010) and Dong et al. (2015) found the opposite seasonal changes in the Ni content in water and sediments. According to Dong et al., (2015), concentrations of nickel, but also Mn, Zn, Cu, Pb and Cd in the overlying water and surface sediments of the Tiaozi River were the highest in winter and the lowest in summer. Senze et. al., (2010), based on the results of studies conducted over a year, i.e. from May 2008 to June 2009, showed that the concentration of nickel in the sediments of the Owiesno reservoir was the highest in the winter season. It was on average from 50 to 100 times higher than in spring, from 60 to more than 170 times higher than in summer and from 4 to more than 13 times higher than in autumn. This means that the lowest Ni concentrations were found in summer and they increased from summer until winter. After winter these concentrations decreased. According to the authors of the cited study, the recorded increased concentrations are most probably the result of occasional local sewage discharge. These studies were carried out in a relatively short period of time and therefore the observed changes may concern specific conditions. The studied small reservoirs are located in the climatic zone with distinctive four seasons. Davutluoglu et al., (2011) found that based on the average seasonal (wet and dry) metal contents of the sediments, there is no significant difference between metal concentrations for the samples collected in dry and wet seasons. This was concluded based on the results of studies on the concentrations of heavy metals in sediments of the river Seyhan conducted in October 2009 and June 2010. It should be, however, noted that as reported by Davutluoglu et al., (2011), the metal concentrations observed during wet season were slightly higher than those of dry season, possibly due to temperature change and biodegradation of the organic matter in the sediments. Also Aduwo & Adeniyi (2018) report that in the sediment samples of Owalla reservoir As, Cd, Cu, Ni, Pb and Zn had higher mean values in the rainy season than in the dry season. On the other hand, Geffard et al., (2005) demonstrated monthly variation in the concentrations of heavy metals (Cd, Cu and Zn) in sediments. The studies were carried out over a period of one year (from April to October). Furthermore, the team of Geffard et al., (2005) observed that the mobility of Cd, Cu and Zn increases in the summer season. Also Kamau et al., (2007) showed the seasonal and spatial variations of copper, iron, manganese, lead and zinc in the sediment of the Lake Naivasha. The samples of sediment were collected in March and May 2003, during the dry and wet seasons, respectively. According to Rabee et al., (2009), the concentrations of metals (Ni, Cu, Pb, Mn and Cd) in the sediments of the Tigris and the Euphrates rivers showed clear seasonal variations in the case of all metals (although the seasonal variation of these metals were not regular) due to different discharge rate of water in rivers. The results of metal concentration analyses in the period of less than one year may be the basis to determine temporal, but not seasonal changes.

Temporal variations in the nickel concentrations in reservoir sediments were recorded by Szarek-Gwiazda et al., (2011). The results of their studies showed that the Ni concentrations in sediments increased from November to May. As was indicated, this is probably associated with the seasonal changes of Ni content but also with the flood event which occurred in the Raba river in September 2007. This assumption is confirmed by the studies of different authors (Rabee et al., 2009; Zhang et al., 2012; Hilschervá et al., 2010) who found the effect of hydrological conditions on the content of heavy metals or other pollutants in water, as well as transported debris. According to Szarek-Gwiazda et al., (2011), the phenomenon of decreasing trace metal content in the sediments of the river Po (Italy) during flood conditions was found by Vignati et al., (2003). This observation is also confirmed by the results presented in the paper by Foster & Charlesworth (1996). Szarek-Gwiazda et al., (2011) suggested that floods may rinse a part of the contaminated sediments in two large reservoirs in Poland. The lowest mean concentrations in the sediments of the investigated reservoirs were observed in the summer season, when heavy rains cause fast floods, conducive to rinsing of the surface part of the sediment accumulated in the reservoirs.

The smallest mean concentrations of nickel in water flowing into the reservoirs in winter (Fig. 4) indicate slight leaching of this metal from the catchment in winter. On the other hand, the highest mean concentrations were observed in spring and autumn (Fig. 4). According to Bahnasawy et al. (2011), metals in water and fish in Lake Manzala in Egypt exhibited a significant seasonal and regional variation, in which all metals attained their maximum value during summer, while the lowest levels were found during winter. Variation in the mean concentrations of nickel in water flowing into the studied reservoirs during winter as compared to spring and summer proved to be relatively small. Mean concentrations of nickel in water in the winter season are less than two to more than three times higher than the mean highest concentrations of nickel in the seasons of spring and autumn. The increase in nickel concentration in water and in sediments during the autumn period may be caused by the temperature change after summer and greater biodegradation of organic matter.

On the other hand, higher concentrations of this metal in the spring period may result from increased runoff of meltwater and intense spring rains causing leaching of the soil and its compounds in the period without vegetation covering the ground. The high load of suspended matter rinsed by the intensive rain from the catchment surface to the reservoirs increased the Ni content in sediments.

However, in summer, as reported by Vignati et al. (2003), floods may rinse a part of the contaminated sediments, deposited in reservoirs earlier, i.e. in spring. Sukhodolska (2017) states that there is a tendency to decrease the concentration of most metals in the abiotic substances of the water reservoir during the growing season and an increase after that season. Much smaller seasonal variation of nickel content in waters of the Indian rivers in the Angul-Talcher region was demonstrated by Reza & Singh (2010). In summer the mean nickel concentration was 15.73 mg l^{-1}, while in winter – 16.35 mg l^{-1}. Also slight variation in the content of nickel in water was reported by Davutluoglu et al., (2011), with mean concentration of 152.11 mg kg^{-1} in the wet season and mean concentration of 147.83 mg kg^{-1} in the dry season. On the other hand, Nwadinigwe et al., (2014) and Doamekpor et al. (2018) reported that Ni concentrations in water were higher in the dry season compared to the wet season.

5. CONCLUSIONS

The concentration of nickel in sediments of the studied four small reservoirs in the upper Vistula basin, ranging from 4.7 to 38.2 μg g^{-1} in dry weight, significantly exceeds the permissible limits of this element according to the EQS, indicating very high contamination of sediments with this element. However, according to the geoaccumulation index (I_{geo}), the sediments were classified as low polluted to moderately polluted. Because of the significantly lower values of nickel concentration in water, it was concluded that there is no risk of environmental contamination, since the specified maximum concentrations of nickel in water proved to be from 40% to even more than 33 times lower than the threshold value of the EQS (Directive, 2013). The concentration of nickel in water also does not exceed the limit value specified by the WHO (Guidelines, 2011). The total concentration of nickel, detected in sediments of the studied reservoirs, cannot provide sufficient information to assess the environmental impact of contaminated sediments. The studies of seasonal and temporal variations of nickel concentration in sediments should also define the chemical form of this metal. The different chemical forms of metals in sediments determine their mobility, potential toxicity and bioavailability. Future research should also cover these aspects.

This study demonstrated that there was a seasonal variation in the concentration of nickel in water and sediments of the analyzed reservoirs. The highest mean nickel concentrations in sediments were observed for the samples collected in spring, while the lowest mean concentrations of this element were observed in winter. This variability, as well as the different strength of the statistical relationship between C_S and C_w may result from the nature of the measured data that include the total nickel concentration. These data do not take into account the influence of, among others, factors such as: the chemical composition of the material that builds the inflow channels to the reservoirs, the nickel content in organisms living in the water, or the nickel content in various particle size fractions of the sediment accumulated in the reservoir. Thus, the continuation of such research will need to take into consideration the various forms of the examined heavy metal, its mobility and source of origin.

The developed seasonal relationship between the concentration of nickel in the sediment and in water flowing into the investigated reservoirs may be used for the preliminary assessment of the potential contamination of sediments based on the predetermined concentration of Ni in water. This dependence shows that with the increase in Ni concentration in water flowing to the reservoirs, an increase in Ni concentration in the deposited sediment is expected.

Confirmation of the seasonal variation is extremely difficult because it requires conducting long-term studies, involving at least a few seasons. At the same time, it is essential to define the contamination of living organisms and surface water, flowing into the reservoirs.

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