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Distribution of Nickel, Copper and Cobalt in the Grain Fractions of Bottom Sediments of the Sokołda River and its Tributaries (Poland)

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ABSTRACT

In recent years, the interest in the occurrence of heavy metals in the natural environment has been observed. The heavy metal contamination can lead to serious environmental problems. The aim of the study was to estimate the total content of heavy metals: Ni, Cu and Co, in the surface layer of the bottom sediments of the Sokołda river and its tributaries, and to determine the relationship between the grain size and scope of their metal content. Determination of metals in the bottom sediment samples was performed by means of atomic absorption spectrometry (ASA). The research on the Sokołda river and its tributaries showed low levels of Ni, Cu and Co. It was proven that the majority of studied metals were contained in the smallest clay fraction <0.02 mm. On the other hand, the least studied metals were accumulated in 1.0–0.2 mm and 0.2–0.1 mm fractions. The 1.0–0.2 mm and 0.2–0.1 mm fractions contain around 80% of the tested metal forms, while the 0.02–0.063 mm and <0.02 mm fractions – only a few percent. This speaks for the determination of metals in the 1.0–0.1 mm fraction, that contains both coarser and clay fractions, and thus most reliably reflects the actual load of pollutants carried by the sediment. Studies have shown that the main sources of pollution in the Sokołda river catchment are primarily surface runoff, and to a lesser extent, wastewater (municipal and industrial).

Keywords: metals; heavy metals, bottom sediments, grain fractions, rivers;

INTRODUCTION

The heavy metal contamination can lead to serious environmental problems (Frankowski et al. 2009). Water ecosystems are one of the elements of the natural environment. River systems are considered the most important medium of transport and distribution of metals in the water and soil environment (Macklin 1992). River sediments are an important part of a riverbed, where many components, including heavy metals, retain and accumulate (Marcussen et al. 2008). The composition of riverbed sediments of the rivers flowing through non-industrialized areas mainly depends on the lithological structure of the catchment as well as the rate of weathering and erosion of the ground rocks (Bojakowska Sokołowska 1998). However, the widespread occurrence of heavy metal contamination, even at a considerable distance from industrial centers and intensively used areas, has become the cause of interest of many researchers in terms of the content, distribution, forms of occurrence, graining, as well as the methods of determining the safe content of these elements in sediments (Alomary, Belhadj 2007, Marcussen et al. 2008, E. Skorbiłowicz and M. Skorbiłowicz 2011). The geochemical composition of bottom sediments accumulated at the bottom of rivers is a very good indicator of the cleanliness of the surface water environment, especially in the case of the heavy metal content (Skorbiłowicz 2012). The metals bound in sediments, regardless of their form, do not form a stable system in the river system. There are a number of different physical and chemical factors that condition their mobility, transition into other forms or into solution (Ciszewski, Aleksander-Kwaterczak 2015). The activity of hydronium ions, oxidation-reduction potential, temperature, salinity, occurrence of organic matter as well as mineral composition, have a very significant impact on the form of metal occurrence in sediments (Tsai et al. 1998, Zhao et al. 1999, Frankowski et al. 2009, Florencka 2011). An important factor conditioning adsorption, and thus affecting the bioavailability of metals, is the particle size of sediments (Huang and Lin 2003). According to Aleksander-Kwaterczak et al. (2004), fine-grained particles, with a larger surface-to-weight ratio, show a greater adsorption capacity than larger particles with small specific surface area. Coarse sand deposits may also contain high concentrations of metals due to the presence of heavy minerals, for example galena or sphalerites (Forstner and Wittmann 1979). According to Liu et al. (2006), the study on particle size distribution in bottom sediments is an important issue needed to understand the environmental and hydraulic conditions and the process of heavy metal sedimentation. Zhao et al. (1999) claim that the metal content of river sediments strongly depends on the size distribution of the sediment particles.

The aim of the study was: (1) to estimate the total content of Ni, Cu and Co in the surface layer of the bottom sediments of the Sokołda river and its tributaries in the fractions: >2.0 mm, 1.0–2.0 mm, 0.2–1.0 mm, 0.1–0.2 mm, 0.063–0.100 mm, 0.02–0.063 mm, <0.020mm; (2) determining the impact of sediment particle size on the metal content range; (3) indication of potential, especially the anthropogenic sources of Ni, Cu and Co pollution.

METHODS

Study area

The object of research included the bottom sediments collected in the catchment area of the Sokołda river. Nine sediment collection points on the Sokołda river (points numbers 1–9) and seven on its tributaries were selected for research: Kłodziewo (10), Poganica (11), Sokółka Canal (12), Rów beyond the wastewater treatment plant in Sokółka (13), Jałówka (14), Kamionka (15), Łanga (16) (table 1). The number of test stands and their location depended on the presence of heavy metal pollution of the aquatic environment. Industry in the catchment area of Sokołda river is underdeveloped. It is associated with the dominant agricultural sector; therefore, the key position in it is occupied by the production and processing of food products, i.e. dairy, meat (poultry), as well as fruit and vegetable industries. There is a lack of developed industry in rural areas, only small service enterprises exist and the main occupation of the population is plant cultivation and cattle farming. Table 1 presents the main sources of pollution in the Sokołda river catchment. These are treated municipal wastewater (wastewater treatment plant in Sokółka – 2000 m^3/d), industrial (EKO-GRIL poultry producer, Dairy Cooperative “SOMLEK”), railway transport (Białystok – Kuźnica – Grodno railway line) and road (national road No. 19) and surface runoff from the agricultural and forest areas.

The catchment area of the Sokołda river is located in the north-eastern Poland. It is estimated that the river is about 54 km long and its catchment area is over 484 km^2. It is a typically lowland river, with a small drop and a calm current. It is a meandering river, along which there are numerous bends and meanders. The most important tributaries of this river include: Poganica, Kamionka and Jałówka. In addition, the Sokołda river is powered by, among others, waters of the Łanga and Woronicz watercourses as well as the Sokólski Canal and numerous drainage ditches. In the catchment area of the Sokołda river, especially in its upper and middle course, there are numerous hills. These are kem, moraine and ozowe hills formed during the last Baltic glaciation (Kondracki 1995). The soils occurring in the catchment area of the Sokołda river are quite diverse. These are mainly lessive and brown soils, as well as rusty and podzolic soils. In the river valleys, there are peat, peat-muck soils and alluvial soils. The forests that are part of the Knyszyńska Forest constitute a very important element of the terrain in this area. In the central and south-western part of the Sokołda river catchment, there are also Natura 2000 areas (Mioduszewski, 2002). The climate of the Sokołda river catchment is continental, characterized by low winter temperatures, hot summers and low rainfall. The average annual total precipitation is about 650 mm, 60% of which is rainfall during the growing season.

Analytical procedures

The bottom sediments were collected in the coastal zone where suspended material settles (Bojakowska, 2001). At each selected point in

Table 1. Measurement points located on Sokołda river and its tributaries, as well as sources of pollution

River	Measurement point	Pollution source
Sokołda (54 km) Catchment area 484 km^2	Bogusze (1)	Agricultural land
	Kuryły (2)	Pollution from the city of Sokółka
	Tartak (3)	Agricultural areas, transport (railway line Białystok – Kuźnica – Grodno)
	Mićkowa Hać (4)	Agricultural land
	Straż (5)	Transport (national road No. 19), tributaries: Jałówka and Kamionka
	Ostrówek (6)	Agricultural and forest areas
	Dworzysk (7)	Wet meadows of the Knyszyńska Forest, Korzenicha tributary
	Sokołda (8)	Agricultural and forest areas, tributaries: Migówka, Kowszówka, Łanga and Woronicza
	Surażkowo (9)	Estuary to Supraśl, agricultural and forest areas
Tributaries of the Sokołda river		
Kłodziewo 10 km	Żuki (10)	Meadows and pastures
Poganica 5 km	Wroczyńszczyna (11)	Agricultural and forest areas
Sokółka Canal	Canal estuary (12)	The canal flows through the southern and western outskirts of Sokółka (EKO-GRIL poultry producer, Dairy Cooperative “SOMLEK”), then flows into the Sokołda river. Near the mouth of this channel there is a ditch, which is treated wastewater from the sewage treatment plant in Sokółka.
Ditch after sewage treatment plant in Sokółka	Ditch estuary (13)	Treated sewage from the treatment plant in Sokółka
Jałówka (10 km)	Jałówka estuary (14)	Forest areas – Knyszyńska Forest
Kamionka (16 km)	Kamionka estuary (15)	Agricultural land
Łanga (8 km)	Woronicze (16)	Forest and agricultural areas

2016, several individual surface sediment samples were taken from a depth of 5 to 10 cm under water. After mixing the test material, a representative sample of approximately 1000 g was obtained. The samples were then air dried to the “air dry” state and stored until determination (Lis and Pasieczna 1995). Before proceeding with chemical analyses, the bottom sediment sample was dried at 40°C. The bottom sediments were mineralized with hydrochloric and nitric acid in a 3:1 volume ratio in a closed CEM microwave system. All determinations were performed in triplicate. The metal content of bottom sediments in the fractions: >2.0 mm, 1.0–2.0 mm, 0.2–1.0 mm, 0.1–0.2 mm, 0.063–0.100 mm, 0.02–0.063 mm, <0.020mm was determined with the AAS ICE 3500 Thermo Scientific atomic absorption spectrometer. The sediment analysis results were verified using NCS DC 73317a certified reference material. The calculated measurement error did not exceed 5% of the certified value.

In 16 bottom sediment samples, the dry sieve analysis was performed using sieves with the diameters of 2 mm, 1 mm, 0.2 mm, 0.1 mm, 0.063 mm and 0.02 mm. The mass fractions of individual fractions were calculated for each sample and expressed as a percentage. The potentiometric method and organic matter content were also indicated in sediments by determining the loss of combustion at 550 °C.

Assessment of bottom sediments pollution degree

The obtained results of the tested metals contents (Ni, Cu and Co) were given in relation to the air dry sediments. In order to assess the degree of heavy metal contamination of sediments, the proposed classification of water sediments in Poland was used (Bojakowska, Sokołowska 1998) and the contents of investigated metals were compared to the geochemical background proposed by Turekian and Wedepohl (1961). In order to assess the quality of bottom sediments of the Sokołda river and its tributaries, the degree of sediment pollution was also used, using the geochemical index (I_{geo}).

Geochemical index (I_{geo}) is defined using the following formula (Müller, 1979) [30]:

$$I_{geo} = \log_2(\frac{C_m}{1,5GM}) \tag{1}$$

where: C_m – content of analyzed metal (mg·kg^{-1}),
GM – geochemical background (mg·kg^{-1}).

The I_{geo} values are divided into seven classes, i.e. non-polluted sediment class 0 ($I_{geo} \leq 0$), slightly polluted sediment class 1 ($0 < I_{geo} < 1$), moderately contaminated sediment class 2 ($1 < I_{geo} < 2$), averagely contaminated sediment class 3 ($2 < I_{geo} < 3$), highly contaminated sediment class 4 ($3 < I_{geo} < 4$), very heavily polluted class 5 ($4 < I_{geo} < 5$), extremely contaminated sediment class 6 ($I_{geo} \geq 5$).

Statistical analysis

The statistical analyses began with the verification of the normal distribution of test results, for which the Shapiro-Wilk test was applied. This is one of the most powerful tests checking the normality of the obtained data. The results were significant with a probability of making an error of $p<0.05$. The arithmetic mean and standard deviation (SD) were also calculated. The Pearson's correlation analysis (parametric test) was used to examine the relationships between metals in the grain fractions of bottom sediments and identify their sources using the previously found normal distribution of test results. The correlation coefficient measures the strength of interrelationships between two heavy metals and allows their possible common source to be determined. The statistical analyses were performed using the licensed Statistica software – ver. 13.3 for Windows.

RESULTS AND DISCUSSION

The research on the heavy metal contamination has been conducted by many researchers (Abrahim 2007, Alomary and Belhadj 2007, Frankowski et al. 2009). The test results of bottom sediments of the Sokołda river and its tributaries (16 measurement points) in fractions [mm]: >2.0; 1.0–2.0; 0.2–1.0; 0.1–0.2; 0.063–0.100; 0.02–0.063; <0.020, are shown in Table 2 and Figures 1, 2, 3.

The tested bottom sediments were characterized by variable grain size and different content of Ni, Cu and Co. The analysis of results clearly showed that in the bottom sediments tested, the 0.2–1.0 mm fraction prevails (on average about 59.5%). In addition, the 0.1–0.2 mm fraction (representing an average of 16.5% of the mass of bottom sediments tested) has a significant share in the sediments from most of the measurement points. In contrast, , the fraction with a grain size lesser than 0.02 mm has the smallest share in the studied sediments, and thus the smallest impact on the overall quality of aquatic environment. On average, this fraction constitutes 0.5% of the bottom sediments tested. The share of other fractions was on average: 4.1% – fraction 0.063–0.10 mm, 3.5% – fraction 0.02–0.063 mm, and about 8% of the mass of sediments are fractions with a grain diameter >2 mm and 1.0–2.0 mm. According to Forstner and Muller (1974), in most riverbeds,

Table 2. Share of the analyzed fractions and the content of Ni, Cu and Co in bottom sediments of Sokołda river and its tributaries

Fraction	Arithmetic mean ± standard deviation, range, n-16			
	Share of fraction	Ni	Cu	Co
(mm)	(%)	mg/kg DM		
>2.0	8.0±7.20	12.3±3.70	10.3±3.66	8.2±1.82
	1.2–26.7	4.5–20.1	5.4–17.5	5.9–11.6
1.0–2.0	7.9±5,.05	8.5±2.76	7.2±3.39	5.8±2.17
	2.0–18.3	2.9–12.6	1.8–13.7	1.3–8.5
0.2–1.0	59.5±13.50	5.2±2.43	3.6±2.39	2.7±2.01
	32.7–83.2	2.7–11.2	1.4–10.8	0.6–8.1
0.1–0.2	16.5±7.46	6.1±2.66	4.8±2.50	2.9±1.56
	4.7–27.9	3.6–12.4	2.4–11.1	1.5–7.5
0.063–0.10	4.1±2.39	6.1±2.66	6.9±3.02	4.4±1.56
	1.2–8.9	3.6–12.3	3.6–13.9	1.4–7.4
0.020–0.063	3.5±3.25	10.3±2.81	8.9±3.20	6.3±1.68
	0.9–11.4	6.9–17.6	4.6–16.4	4.5–10.6
<0.020	0.5±0.19	29.3±14.16	23.6±7.85	10.4±3.23
	0.3–0.9	13.8–69.3	10.3–34.6	7.4–20.6
Organic substance (%)			7.3±7.32	1.64 – 27.5
Reaction pH_{H2O}			7.10 – 7.62	

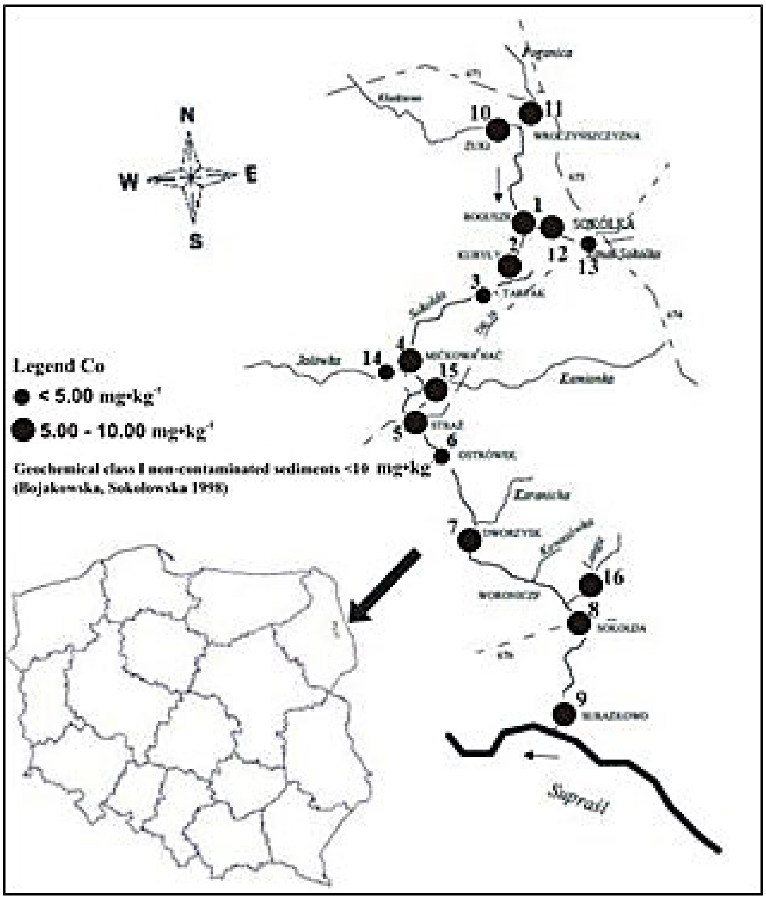

Figure 1. Average Co content in bottom sediments of the studied rivers

more than 90% of the sediment is a grain fraction above 0.063 mm, which was confirmed by the research in this work. Similar relationships in their research were also shown by Zhao et al. (1999), Aleksander-Kwaterczak et al. (2004), E. Skorbiłowicz and M. Skorbiłowicz (2011). This material most often comes from the erosion of rocks occurring in the catchment area, and only a small part is of anthropogenic origin. Bojakowska and Sokołowska (1998) claim that coarse-grained fractions are dominated by physical weathering of the rocks of the ground, whereas in the case of finer fractions, the components derived mainly from chemical weathering of the rocks are dominant.

The pH of the tested bottom sediments was in most cases neutral, and ranged from 7.10 to 7.62. The lowest value, pH 7.10, was recorded in the bottom sediment of the ditch behind the treatment plant, which indicates the impact of treated wastewater on the aquatic environment. The pH has a very significant impact on mobility, bioavailability of metals in sediments. It should be emphasized that the solubility of micronutrients increases as the pH value decreases.

The content of organic matter in the analyzed sediments ranged from 1.64% to 27.5% (average 7.3% ± 7.32%). The highest content of organic matter in the sediments from the Sokołda river was recorded at the Mićkowa Hać (4) measurement point – 19.8%, as well as at the Kuryła (2) and Straż (5) points – about 9%. However, at other measurement points, the content of organic substance was in the range of 1.6–6.2%. In the inflows of the Sokołda river, the highest content of organic matter was recorded in the sediments of Kamionka river (15) – 27.5% and Pogonica river (11) – 14.63%. The content of organic matter in the sediments from other rivers was below 5%. The presence of organic matter in bottom sediments plays a beneficial role in retaining impurities due to their sorption capacity. According to Hu et al. (2013), the amount of organic matter in sediments can be a good indicator of the bioavailability of metals and their mobility due to their affinity towards heavy metals.

According to Chen et al. 2007 and Lai et al. 2013, the sediment grain size distribution and organic carbon content are the two most important factors affecting metal enrichment. This was also

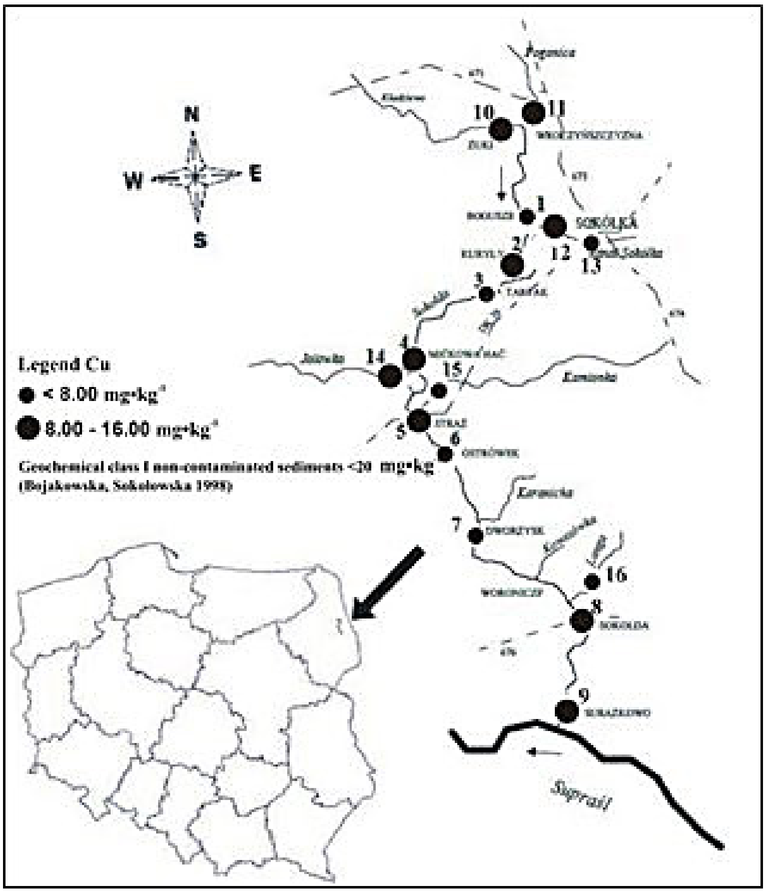

Figure 2. Average Cu content in bottom sediments of the studied rivers

confirmed by the studies of other authors: Zhao et al. 1999, Soto-Jimenez and Paez-Osuna 2001, Giusti 2001, Huang and Lin 2003. The tests of the Sokołda river bottom sediments and its tributaries showed that the Cu content ranged from 1.4 to 34.6 mg·kg^{-1}. The lowest content of this metal was found in the 0.2–1.0 mm fraction, and the largest in grains with a diameter <0.02 mm. The amount of Ni ranged from 2.7 to 69.3 mg·kg^{-1}. This metal was most accumulated in the fraction with particle diameter <0.02 mm. In contrast, the Co concentration was as follows from 0.6 to 20.6 mg·kg^{-1}. The smallest amounts of Co were determined in the 0.2–1.0 mm fraction, and the highest in grains <0.02 mm in diameter. The analyses of the Ni, Cu and Co content showed the largest accumulation in the finest fractions <0.02 mm and 0.02–0.063 mm (Table 1). The content of these metals in the sediment increased with decreasing grain size. Similar trends are presented in publications of various authors: Aleksander-Kwaterczak et al. (2004), Orescanin et al. (2004) or Florencka (2011). The research has also shown an increased metal content compared to slightly finer fractions in the thickest fractions (> 2.0 mm, 1.0–2.0 mm). The obtained results indicate that the <0.02 mm fraction contains about six times more Ni and Cu and almost four times more than the thicker fractions 0.2–1.0 mm. However, due to the fact that the 0.02–0.063 mm and <0.02 mm fractions constitute on average 4% of the mass of tested sediments, the thicker fractions, i.e. 0.2–1 mm and 0.1–0.2 mm, carry the largest metal load, because they constitute 76% of the mass of the tested deposits. This speaks for the determination of metals in the 1.0–0.1 mm fraction, which contains both coarser and clay fractions, and thus reflects their real load carried by the sediment most reliably.

The content of Ni, Cu and Co in the Sokołda river surface sediments did not show a large variation depending on the location of the sampling points (Figures 1, 2, 3). The largest amount of metals tested in the Sokołda river occurred in the bottom sediments collected at the Maćkowa Hać measurement point. The sediments collected at this point contained the most organic matter (19.8%). This confirms the findings of Tsai et al. (1998), Yu et al. (2000) and Buykx et al. (2000), Chen et al. 2007 and Lai et al. (2013): the content

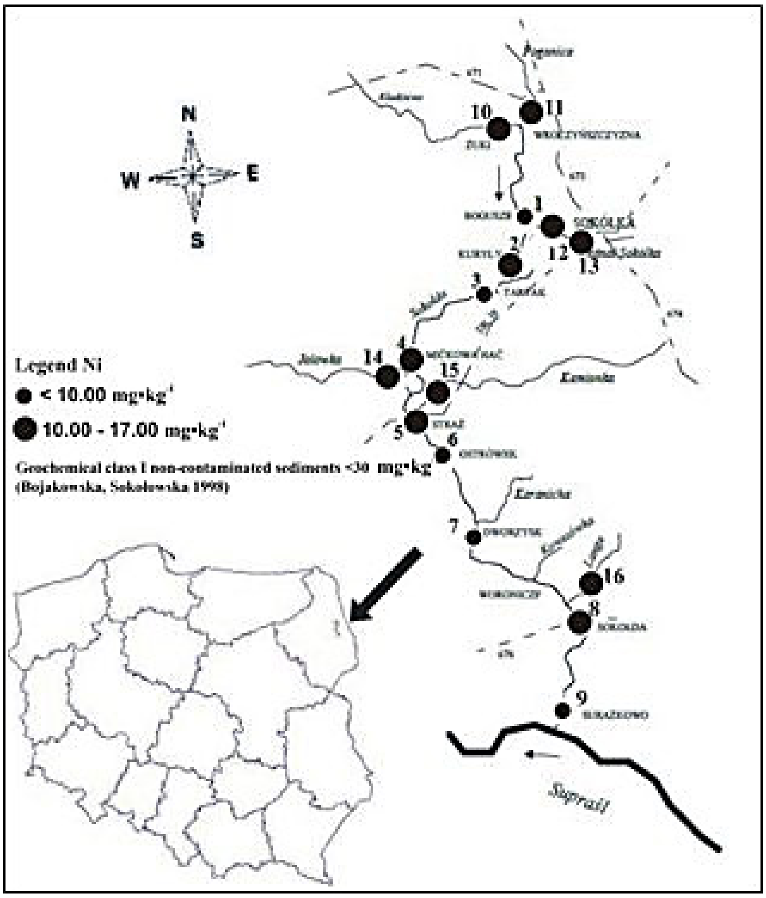

Figure 3. Average Ni content in bottom sediments of the studied rivers

of metals in bottom sediments is significantly influenced by, among others, the organic matter content. In the case of the analyzed sediments from the Sokołda river tributaries, the highest metal contents occurred in the sediments from the Sokółka Canal, to which treated wastewater from the wastewater treatment plant in Sokółka is discharged, and in the sediments from the Kamionka river (15), which contained 27.5% of organic matter. The tests carried out on surface bottom sediments of the Sokołda river and its tributaries have shown that the metal content is in the following order: Ni > Cu > Co.

It was shown that the content of studied metals (Ni, Cu and Co) in the bottom sediments of Sokołda river and its tributaries was small and the sediments were classified to the first geochemical class as unpolluted (Bojakowska, Sokołowska 1998). The catchment area of the Sokołda river includes the forest areas that are part of the Knyszyńska Forest, as well as the areas belonging to the Natura 2000 program. Another method for determining the quality of the aquatic environment is the geochemical index (Table 3).

The geochemical indices calculated for the examined metals are presented in Table 3. The indices calculated for Ni ranged from -2.88 to 0.58, and the average value was -1.9, which clearly indicates no enrichment of bottom sediments of the Sokołda river and its tributaries with this metal. The investigated sediments can also be considered unpolluted in the case of Cu and Co; the values of the geochemical indices are in the ranges from -2.71 to 0.96 for Cu, on average -1.6, and from -1.92 to 0.47 for Co, on average -1.5. The results obtained meet the condition of $I_{geo} \leq 0$ and are described as "practically uncontaminated sediment", i.e. class 0.

Nevertheless, even in such clean areas of Poland, the anthropogenic activity is visible, which

Table 3. Geochemical index values of metal in bottom sediments of Sokołda river and its tributaries

Metal	Geochemical index	
	Mean ± SD	Range
Co	-1.5 ± 0.37	-1.92 – 0.47
Cu	-1.6 ± 0.54	-2.71 – 0.96
Ni	-1.9 ± 0.62	-2.88 – 0.58

was confirmed by the results of the statistical analysis (Table 4). Studies have shown many significant correlations between the studied metals in individual sediment fractions (Table 4). The correlations found may indicate the coexistence of the studied metals in mineral fertilizers, manure, composts, plant protection products and sewage sludge, which are applied to fertilize the agricultural land located in the Sokołda river catchment. Migration and transport of metals in the river catchment are the basic factors causing their penetration into watercourses and accumulation in their bottom sediments.

CONCLUSIONS

The conducted research showed that the grain size distribution in the bottom sediments has a significant impact on the metal content in sediments. The amount of Ni, Cu and Co increased with a decrease in grain size. The largest amounts of the analyzed metals were found in the smallest clay fraction <0.02 mm, while the lowest in the 1–0.2 mm and 0.2–0.1 mm fractions. The 1–0.2 mm and 0.2–0.1 mm fractions carry around 80% of the metals tested, while the 0.02–0.063 mm and <0.02 mm fractions only carry a few percent. This speaks for the determination of metals in the 1–0.1 mm fraction, which contains both coarser and clay fractions, and thus reflects the actual load of pollutants carried by the sediment most reliably. The research on the Sokołda river and its tributaries has shown low levels of Ni, Cu and Co. The sediments were classified as unpolluted. The metals accumulated in the following order: Ni > Cu > Co. Presumably, the main sources of pollution in the catchment area of the Sokołda river are surface runoff as well as wastewater (municipal and industrial) and communication.

Table 4. Relationships between Ni, Cu and Co in the analyzed bottom sediments fractions of Sokołda river and its tributaries

Dependencies	Pearson coefficient	Significance level (p)
$Co_{2\text{–}1\ mm}$ – $Cu_{2\text{–}1\ mm}$	0.71	0.001
$Co_{2\text{–}1\ mm}$- $Cu_{1\text{–}0.2\ mm}$	0.82	0.002
$Co_{2\text{–}1\ mm}$- $Cu_{0.2\text{–}0.1\ mm}$	0.55	0.001
$Co_{2\text{–}1\ mm}$- $Cu_{0.1\text{–}0.063\ mm}$	0.57	0.001
$Co_{2\text{–}1\ mm}$- $Ni_{>2\ mm}$	0.59	0.001
$Co_{2\text{–}1\ mm}$- $Ni_{2\text{–}1\ mm}$	0.88	0.002
$Co_{2\text{–}1\ mm}$- $Ni_{1\text{–}0.2\ mm}$	0.71	0.001
$Co_{1\text{–}0.2\ mm}$ – $Cu_{2\text{–}1\ mm}$	0.71	0.001
$Co_{1\text{-}\ 0.2\ mm}$- $Cu_{1\text{–}0.2\ mm}$	0.79	0.001
$Co_{1\text{–}0.2\ mm}$- $Cu_{0.2\text{–}0.1\ mm}$	0.63	0.001
$Co_{1\text{–}0.2\ mm}$- $Ni_{2\text{–}1\ mm}$	0.88	0.002
$Co_{1\text{–}0.2\ mm}$- $Ni_{2\text{–}1\ mm}$	0.79	0.001
$Co_{1\text{–}0.2\ mm}$- $Ni_{1\text{–}0.2\ mm}$	0.85	0.004
$Ni_{2\text{–}1\ mm}$ – $Cu_{2\text{–}1\ mm}$	0.68	0.001
$Ni_{2\text{–}1\ mm}$- $Cu_{1\text{–}0,2\ mm}$	0.85	0.003
$Ni_{2\text{–}1\ mm}$- $Cu_{0.2\text{–}0.1\ mm}$	0.56	0.001
$Ni_{2\text{–}1\ mm}$- $Cu_{0.1\text{–}0.063\ mm}$	0.63	0.001
$Ni_{2\text{–}1\ mm}$- $Cu_{0.063\text{–}0.020\ mm}$	0.60	0.001
$Ni_{1\text{–}0.2\ mm}$- $Cu_{2\text{–}1\ mm}$	0.82	0.002
$Ni_{1\text{–}0.2\ mm}$- $Cu_{1\text{–}02\ mm}$	0.84	0.001
$Ni_{1\text{–}0.2\ mm}$- $Cu_{0.1\text{–}0.063\ mm}$	0.54	0.001

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