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Variability and Heavy Metal Pollution Levels in Water and Bottom Sediments of the Liwiec and Muchawka Rivers (Poland)

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Abstract: In recent years, human impact on the Earth's ecological environment has become increasingly visible, with serious negative consequences. One of the most important pollutants are heavy metals which can easily bind to sediments. Due to their toxic behavior, persistence, lack of biodegradability and bioaccumulation, they are considered key river pollutants that need to be controlled. This study examined two rivers: the Liwiec and Muchawka rivers located in south-eastern Poland. The mouth of the Liwiec River is the Bug River, which is partly the border between Poland and Belarus. In turn, the mouth of the Muchawka River is the Liwiec River. The objectives of the study were the following: (1) To complete a qualitative analysis of heavy metals (Cd, Pb, Cu, Ni, Zn) in the waters and bottom sediments of the Liwiec and Muchawka rivers; (2) To assess the degree of heavy metal contamination; (3) To identify the sources of contamination. The analysis included samples of surface water and bottom sediments collected (16 water and 16 bottom sediment samples were taken from the Muchawka River and 32 water and 32 bottom sediment samples were taken from the Liwiec River) in June and September 2022. The variability of characteristics, such as temperature, precipitation and humidity, contributes to seasonal changes in the distribution characteristics and sources of heavy metals. The study showed that only a small part of the heavy metals entering rivers are present in the water depth in the dissolved state, and most of them enrich the sediment, resulting in much higher concentrations of heavy metals in the sediment than in the water column. The differences in the distribution of some elements in water and sediment are due to the fact that surface sediments retain long-term records. Therefore, sediment can be considered a potential source of heavy metals in the aquatic environment. In general, the content of heavy metals determined in bottom sediments was not high but indicative of anthropogenic human activity. There is a possibility of re-release of heavy metals from the sediment into the water when hydrodynamic conditions or environmental factors (pH, redox potential, etc.) change, which could lead to secondary water pollution. The data obtained will be of great importance to both researchers studying river systems and the population living in the area.

Keywords: heavy metals; river pollution; sediment; surface water

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1. Introduction

Heavy metals are among the most important environmental pollutants due to, among other things, their persistence, toxicity and ability to integrate into food chains [1–5]. They enter the environment from natural and anthropogenic sources. The most important natural sources are mineral weathering from volcanic eruptions, activity and erosion [6]. Anthropogenic sources, on the other hand, include mining, metallurgy, the use of pesticides and (phosphate) fertilizers in agriculture, sewage sludge disposal, electroplating, industrial discharges and the atmosphere [7–9].

Heavy metals are not biodegradable, so they can accumulate in all elements of the environment and living organisms. Therefore, the accumulation of heavy metals in soil and water poses a serious threat to the environment and human health [10–14]. In wetlands, heavy metals are found in rivers, lakes, bottom sediments, plants and other living organisms, among others. Consequently, the distribution of heavy metals can vary over a fairly wide range. Due to the fact that wetlands contain a variety of aquatic organisms that are important sources of food and water for humans, the levels of heavy metal concentrations in these products can threaten human health. This threat can occur as a result of daily food use or through the long-term effects of bioaccumulation in the food chain. Therefore, ongoing research on the distribution of heavy metals, their migration and transformation in various environmental elements and living organisms is very important [15,16]. Concentrations of metals in sediments are a good and popular indicator of the health and contamination status of water bodies. Moreover, sediments can act as a sink and source of metals in water reservoirs. Thus, settled metals can be resuspended and released into the water column. For this reason, there are ecological and health problems in aquatic ecosystems, i.e., lakes and water reservoirs. In addition to the analysis of metals in sediments, these pollutants in the water column should also be analyzed. Such analyses provide important information for the effective management of water quality in aquatic environments [17–19].

The uptake and accumulation of heavy metals by plants (including aquatic plants) takes place mainly through two pathways, i.e., through the root system and the leaf surface [20,21]. Different plant species show different abilities to remove or accumulate heavy metals. Some plant species can accumulate selected heavy metals. An example is *Spirodela polyrhiza*, which accumulates zinc [22].

Bioaccumulation of heavy metals depends on many factors, both biotic and abiotic, which include pH, temperature and dissolved ions in water. Pesticides, fertilizers and wastewater used in agriculture negatively affect the environment, including various bodies of water, vegetation and other organisms living in them [23–27].

For several decades, heavy metals have been recognized as major pollutants in many systems. Many studies have clearly indicated that about 90% of heavy metals present in the aquatic environment can be associated with fine-grained sediments (0.2–20 μm in diameter) [28–31]. Dispersal pathways of heavy metals in rivers are very similar to those in suspended sediments and are largely controlled by physical processes and geomorphic features of river catchments. The main factors controlling the loss of sediment-bound heavy metals in river systems include their concentration, the size of the suspended sediment particles and floodplain topography [32–37].

In this article, the rivers analyzed are tributaries of the Bug River, which is one of the longest rivers in Poland. It flows through Ukraine, Belarus and Poland. A large part of the area where the authors conducted their research is included in the "Natura 2000" area. In the lower reaches of the Bug River, at the mouth of the Liwiec River, is the Bug Landscape Park. The flora of the park has about 1300 species, including 38 species of trees and 59 species of shrubs. There are 60 protected species and 170 counted as rare at a national or regional scale. Until recently, the area of the Liwiec River valley was used for tourism purposes. At present, due to the pollution of the bottom (siltation reaching 70%) and the lack of necessary infrastructure, the reservoir is not used for tourism and recreation. The condition of the waters of these rivers is moderate, which indicates the need for research on improving their quality. Considering the literature data, it is also easy to see that the number of studies conducted in the area is negligible.

The main objectives of this study were the following: (1) To complete qualitative and quantitative analyses of heavy metals in the surface water and bottom sediments of the Liwiec and Muchawka rivers; (2) To assess the degree of contamination with these metals; (3) To identify the sources of pollution. The migration of metals between water and bottom sediments and vice versa is a complex process, and its understanding is essential to determine the transformations taking place in aquatic ecosystems. The research undertaken was conducted to demonstrate whether the bottom sediments of surface waters can pose a threat to the environment due to the possible release of toxic heavy metals. The results obtained will allow the bioavailability of individual metals to be assessed and can be used for better management to reduce pollution.

2. Materials and Methods

2.1. Study Area

To conduct the study, 90 samples of surface water and bottom sediment were collected from two rivers: the Liwiec River and the Muchawka River. The latter is 32.1 km long and is a left tributary of the Liwiec River. Its sources come from the vicinity of the village of Pluty and flows mainly through agricultural land of several other villages and the city of Siedlce, marking its western border. Both rivers are located in south-eastern Poland (Figure 1).

Figure 1. Location of surface water and bottom sediment sampling. The purple line—the Muchawka River, the blue line—the Liwiec River.

A reservoir has been built on the Muchawka River, which is used for recreational purposes. The water level of the Muchawka River is moderate. The Liwiec River is the longest left-bank tributary of the Bug River. The length of the Liwiec River is over 126 km, while the catchment area is 2780 km^2. It is assumed that the Liwiec River forms the southern limit of the Podlasie region and runs mainly through farmland. The chemical status of the surface water of the Liwiec River is described as moderate. An analysis of other constituents has revealed that the annual average and maximum concentrations of polycyclic aromatic hydrocarbons were exceeded [38].

2.2. Sampling and Sample Preparation

Both the Muchawka and Liwiec are typically lowland rivers. There are mainly farmland, meadows and pastures along these rivers. Samples of surface water and bottom sediment from the Muchawka River were taken at two locations: Wisniew-Kolonia (S1) and Siedlce (S2). On the other hand, bottom sediment and surface water samples from the Liwiec River were taken in four localities: Mordy (S3), Mokobody (S4), Paplin (S5) and Kamieńczyk (S6). Samples of surface water and bottom sediments were collected along the aforementioned rivers, on average every 15 km, in June and September 2022. They were collected in the riparian zone, where the processes of suspended sedimentation and concentration of heavy metals take place. Bottom sediment samples were collected from a depth of 5–10 cm below the water surface. The bottom sediment samples collected from each river on a given date were mixed to obtain one representative test sample of about 1 kg [39,40]. A quantity of 16 water and bottom sediment samples each were taken from the Muchawka River, while 32 water and 32 bottom sediment samples were taken from the Liwiec River.

2.3. Analytical Procedures

The collected bottom sediment samples were dried at 40 °C, sieved through a 0.2 mm diameter nylon sieve and further analyzed. Then, bottom sediment samples of 0.5 g were mineralized with 8 mL of a mixture containing concentrated HNO_3 and 2 mL of 30% H_2O_2 in a closed microwave system. All heavy metal determinations in both surface water and bottom sediment were performed in parallel in three series. After filtration, sediment samples were quantitatively transferred to 50 mL volumetric flasks [41]. Subsequently, the content of the analyzed heavy metals in the sediments and surface water was determined using the flame atomic absorption spectrometry method on an AA–20 Varian spectrometer (Australia). The obtained analytical results were verified using NCSDC 73,377 certified reference material (Table S1, Supplementary Materials). The precision and accuracy of the method were evaluated by analyzing the recovery of analytes from five standard solutions with different concentrations of all analyzed metals.

Calculation of the measurement error showed that it did not exceed 5% of the certified value. The acidity of the surface water and bottom sediment in aqueous suspension was measured following the procedure of [42] for determining water and wastewater using a pH electrode according to ISO 10523:2008 [43]. The conditions and parameters under which the quantitative analysis of heavy metals in surface water and bottom sediments was carried out are shown in Table S2 (Supplementary Materials).

The content of heavy metals in bottom sediments was analyzed for fractions with particle diameters < 200 µm. Taking the geochemical criteria into account, the classification of the analyzed bottom sediments was carried out in accordance with the literature data (Table 1).

Table 1. Cleanliness classes of bottom sediments based on geochemical criteria [44].

Metal	Zn	Pb	Cd	Ni	Cu
Class I (unpolluted)	200	30	1	16	40
Class II (poorly polluted)	500	100	3.5	40	100
Class III (polluted)	1000	200	6	50	200
Class IV (heavily polluted)	>1000	>200	>6	>50	>200
Geochemical background (mg/kg DM)					
	73	15	<0.5	5	7

One of the most frequently analyzed pollutants in the environment are heavy metals. Their content in various elements of the environment is most often discussed in relation to the geochemical background or applicable standards and directives. In the present study, the results obtained during the analysis of surface water were compared to the 2019 directive in effect in Poland (Table 2) [45] and the results obtained by other authors.

Table 2. Permissible content of selected heavy metals in surface waters [45].

Metal	According to the 2019 Standard (mg/L)		
	I Class	II Class	III Class
Cd	0.005	0.005	0.005
Pb	0.05	0.05	0.05
Cu	0.05	0.05	0.5
Ni	0.05	0.05	0.2
Zn	3	5	5

3. Results and Discussion

3.1. Heavy Metal Concentrations in Surface Waters

The results obtained are presented in Tables 3 and 4 and Figures 2 and 3. The following parameters were calculated for all analyzed heavy metals, both for surface water and bottom sediment samples: minimum, maximum, arithmetic mean, median and standard deviation.

Table 3. Basic statistical data of the content of studied indicators in surface waters in the Muchawka River and the Liwiec River.

River	Element (mg/L)	Min–Max	Mean	Median	Standard Deviation
Muchawka (n = 16)	June (pH = 6.94–7.26)				
	Cd	0.02–0.08	0.05	0.04	0.17
	Pb	8.5–10.6	9.3	9.6	1.2
	Cu	0.2–1.8	0.7	0.8	0.7
	Ni	0.3–1.1	0.8	0.7	1.1
	Zn	15.3–20.1	17.6	17.2	2.4
	September (pH = 6.85–7.39)				
	Cd	0.03–0.08	0.04	0.05	0.19
	Pb	8.7–11.4	10.2	10.4	1.3
	Cu	0.2–1.7	0.8	0.7	0.8
	Ni	0.2–1.4	0.9	0.6	0.7
	Zn	15.6–19.4	16.9	16.4	2.1
Liwiec (n = 32)	June (pH = 6.87–7.37)				
	Cd	0.03–0.06	0.04	0.04	0.12
	Pb	9.7–12.3	11.1	10.8	1.1
	Cu	0.3–1.6	0.9	0.7	0.8
	Ni	0.3–1.5	0.9	0.7	0.6
	Zn	16.4–19.6	17.9	17.5	2.2
	September (pH = 6.90–7.31)				
	Cd	0.02–0.11	0.04	0.07	0.14
	Pb	9.5–13.1	11.3	11.6	1.6
	Cu	0.3–1.2	0.7	0.6	0.4
	Ni	0.1–0.5	0.3	0.3	0.8
	Zn	16.7–19.5	18.1	17.6	1.5

The main sources of pollution in the two studied rivers are due to the operation and development of cities and villages within the catchments. The environmental quality of these catchments is affected by crop protection and fertilization, small-scale food, meat, and timber industries, vehicle traffic, as well as sewage treatment plants and the lack or incomplete efficiency of the sewage system.

The geochemical background, i.e., the concentrations of individual substances naturally occurring in the environment, was used to assess the degree of pollution of surface water and bottom sediments. The determination of the geochemical background through environmental studies made it possible to estimate whether the study area is subject to anthropogenic impact and whether the effects of pollution are already perceptible [46,47]. The average content of a given element in the Earth's crust proposed by Turekian and Wedephol [48] has been factored into background assessment for several decades. The concentrations obtained at that time were compared with the background value determined globally and locally for Polish sediments by Bojakowska and Sokolowska [49].

Nowadays, with the increasing scarcity of water in many countries around the world, including Poland, the results of environmental studies are also increasingly compared with relevant standards, bearing in mind the potential use of water by humans. In the case of surface waters, which carry loads of various pollutants that are subsequently deposited in bottom sediments, the assessment is most often performed with reference to relevant

Polish, European or world standards and the results of studies by other authors. Such a comparison is also made in this paper, with reference to the latest regulation of the Minister of Maritime Affairs and Inland Navigation, on the requirements to be met by surface waters used for supplying the public with water intended for human consumption, dated 13 September 2019 [45]. The regulation establishes three categories of water quality. A particularly important parameter relating to surface water quality requirements is the content of heavy metals.

Table 4. Basic statistical data of the content of studied indicators in bottom sediments in the Muchawka River and the Liwiec River.

Bottom Sediments in River	Element (mg/kg DM)	Min–Max	Mean	Median	Standard Deviation
Muchawka (n = 12)	June (pH = 6.92–7.23)				
	Cd	0.1–0.8	0.6	0.5	0.2
	Pb	10.3–13.2	11.7	11.6	1.4
	Cu	0.7–4.3	2.6	2.2	1.8
	Ni	2.3–7.9	4.8	3.9	1.2
	Zn	16.2–21.3	19.1	18.3	2.2
	September (pH = 6.81–7.42)				
	Cd	0.1–0.6	0.4	0.3	0.5
	Pb	9.8–13.4	11.5	10.9	1.3
	Cu	0.9–5.2	2.7	1.4	2.8
	Ni	3.3–8.4	6.2	5.7	2.6
	Zn	14.4–20.8	17.3	18.1	2.4
Liwiec (n = 32)	June (pH = 6.88–7.36)				
	Cd	0.2–0.7	0.5	0.4	0.5
	Pb	10.4–13.1	11.6	11.8	1.1
	Cu	0.9–7.4	3.6	2.4	3.1
	Ni	3.3–9.4	6.7	5.9	3.2
	Zn	16.4–22.9	19.3	17.1	2.3
	September (pH = 6.91–7.34)				
	Cd	0.2–0.5	0.4	0.3	0.6
	Pb	10.6–13.9	12.2	11.8	1.2
	Cu	0.7–9.4	5.7	4.4	3.3
	Ni	3.9–9.9	8.1	5.9	3.9
	Zn	19.1–25.3	22.1	21.2	2.1

The total content of cadmium in the analyzed surface waters of the Muchawka River in June ranged from 0.02 mg/L to 0.08 mg/L, with an arithmetic mean of 0.05 mg/L and a median of 0.04, while the standard deviation was 0.17. Very similar results were also obtained in August. A comparison of the cadmium content in the Muchawka water samples (Table 5) with the permissible content resulting from the Ministerial Order (Table 4) [45] showed that the waters of this river should be specified as unclassified. In terms of cadmium content, the waters of the Liwiec River should also be described as unclassified waters. The results obtained were in the range of 0.03–0.06 mg/L. The mean cadmium content was 0.04 mg/L, the standard deviation was 0.12 and the median was 0.04 (Table 3). Slightly lower mean cadmium content in both rivers was found in September, i.e., 0.04 mg/L each, in the two rivers studied.

Very similar to cadmium, the results of lead analysis were obtained in surface water samples collected from the Liwiec River. The concentrations of this element in the months studied were very similar and ranged from 0.02 to 0.05 mg/L. The average lead content in June was 11.1, while in September it was 11.3 mg/L (Table 3). Slightly lower lead content was determined in the Muchawka River in both June and September, 9.3 and 10.2 mg/L, respectively.

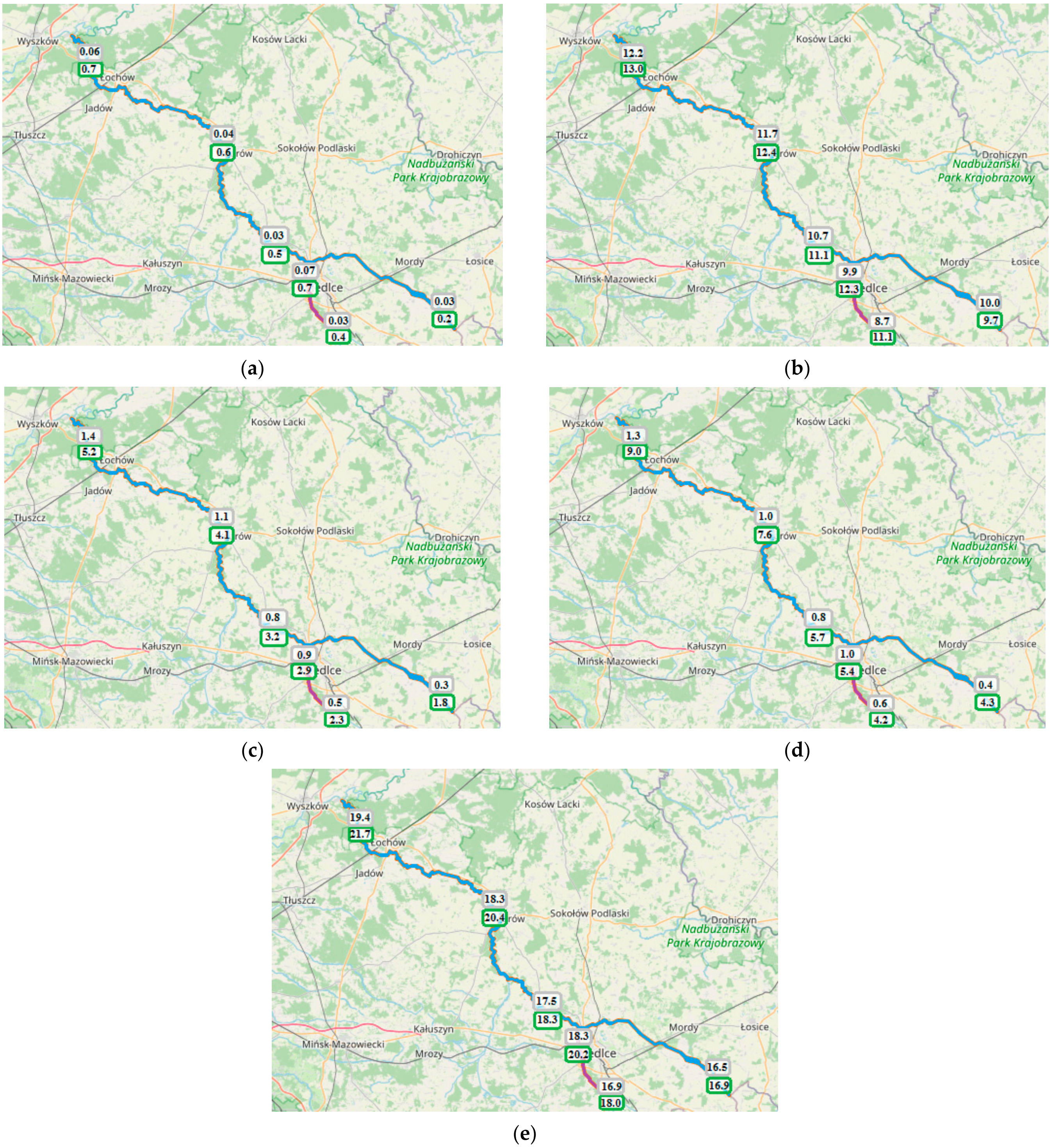

Figure 2. Distribution of analyzed heavy metals at sampling sites in June: (**a**) cadmium, (**b**) lead, (**c**) copper, (**d**) nickel, (**e**) zinc. Gray shape—concentration of metals in surface water (mg/L), green shape—concentration of metals in bottom sediment (mg/kg).

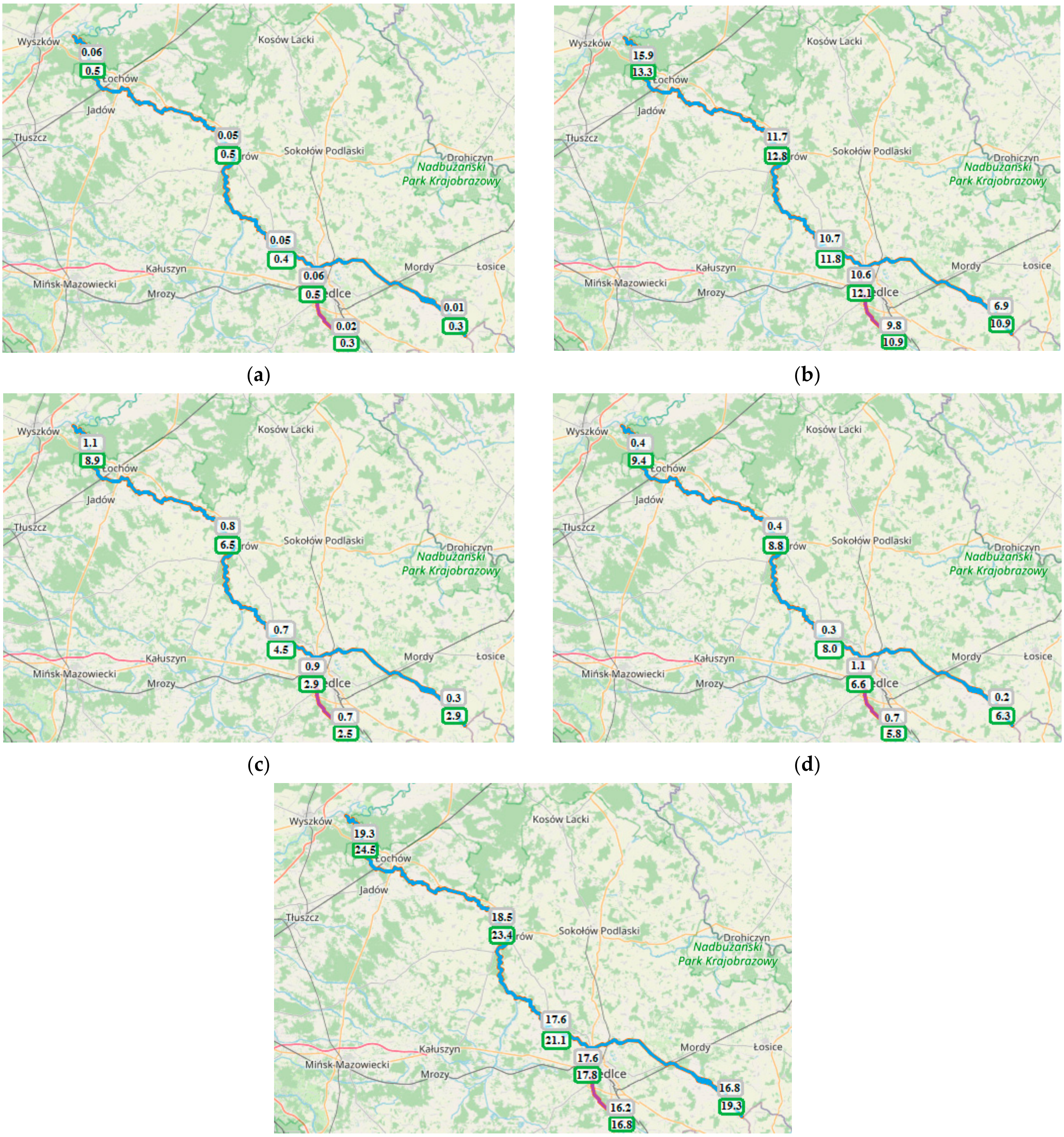

Figure 3. Distribution of analyzed heavy metals at sampling sites in September: (**a**) cadmium, (**b**) lead, (**c**) copper, (**d**) nickel, (**e**) zinc. Gray shape—concentration of metals in surface water (mg/L), green shape—concentration of metals in bottom sediment (mg/kg).

Another element whose content in surface waters and bottom sediments was analyzed was zinc. It is one of the most abundant metals and an essential trace element for organisms, but its excessive amount in the aquatic ecosystem impairs the normal biological metabolism of aquatic organisms. In addition, it becomes frothy and imparts a metallic taste to the water. Its content in the waters of the Muchawka River in June ranged from 15.3 to

20.1 mg/L, with an average of 17.6 mg/L. In September, on the other hand, the zinc content ranged from 15.6 to 19.4 mg/L, while the arithmetic mean was 16.9 mg/L. The median values were, respectively, 17.2 and 16.4, with standard deviations of 2.4 in June and 2.1 in September.

The analysis of the zinc content of the Liwiec River's waters in the months studied shows that it was higher and ranged from 16.4 to 19.6 mg/L in June (mean 17.9, median 17.5) and from 16.7 to 19.5 mg/L in September (mean 18.1 mg/L, median 17.6). Relating the results obtained for the Muchawka and Liwiec rivers to the permissible concentration of zinc indicated in the Ministerial Order of 2019 indicated that these waters should be described as unclassified.

The collected water samples were also analyzed for the content of nickel and copper. In the case of the Muchawka River, the nickel content in June ranged from 0.3 to 1.1 mg/L, with a mean of 0.8 and a median of 0.7 mg/L, while in September from 0.2 to 1.4 mg/L, with a mean of 0.9 and a median of 0.6 mg/L (Table 3). Very similar results for the nickel content in the Liwiec River were obtained in June, while in September they were slightly lower and ranged from 0.3 to 1.5, with a mean of 0.9 mg/L. In contrast, the copper content in the Muchawka River ranged from 0.2 to 1.8 mg/L in both months, with a mean of 0.7 and a median of 0.8 mg/L. In the Liwiec River, on the other hand, the average copper content was 0.9 mg/L in June, and in September it was in the range of 0.3–1.2 mg/L (Table 3).

The comparison of the obtained values of the analyzed heavy metals in the surface waters of the two rivers, the Muchawka and the Liwiec, with the data contained in the Ministerial Order of 2019, indicates that the studied waters belong to unclassified waters. Cadmium found in mineral fertilizers containing phosphates can potentially pose a threat to human and animal health and the environment, as it accumulates in the environment and enters the food chain. The high cadmium content found in the analyzed water is likely to be the result of the runoff of mineral fertilizers used by farmers, since the land around the studied rivers is agricultural.

Due to increasingly frequent droughts and poor water management strategies, rivers and lakes are drying up. Desiccation, especially of salt lakes and rivers, can have serious consequences for the surrounding environment, as heavy metal-contaminated sediments can spread through the atmosphere in the form of fine dust [16].

3.2. Heavy Metal Concentrations in Bottom Sediments

Water classification was used to assess the degree of contamination of bottom sediments with heavy metals. The results obtained for the bottom sediments of the Muchawka River and the Liwiec River are shown in Table 4.

Zinc contamination of sediments is mainly due to anthropogenic activities. In the study region, agricultural sources, such as liquid fertilizers, urban sewage and storm water runoff, are the main contaminants. A large amount of zinc in water is absorbed by suspended particles and deposited in sediments, which are the main source of nutrients for benthic organisms. In the aquatic environment, sediments are the pathway through which zinc enters the biosystem. The zinc content in the analyzed sediment samples from the Muchawka River ranged from 16.2 to 21.3 mg/kg and was comparable in both months, i.e., June and September (Table 4). The average zinc content in June was 19.1 mg/kg, while in September it was 17.3 mg/kg of dry sediment. Similar values were obtained for the Liwiec River: 19.3 mg/kg of air-dried sediment in June and 22.1 mg/kg in September (Table 4).

Given the geochemical background of zinc at 55 mg/kg (Table 4) [44], it can be concluded that the analyzed bottom sediments of both rivers are still little contaminated with this metal. The medians for zinc content in the studied sediments were about four times lower than the median for Poland (73 mg/kg) [50].

The average cadmium content in the bottom sediments of the Muchawka River was 0.6 mg/kg in June and 0.4 mg/kg in September. Almost identical values were obtained for the Liwiec River. Analyzing the results obtained by other authors (Table 5), it can be concluded that similar values were obtained in studies of sediments from the Supraśl, Slupia and Odra rivers.

Table 5. Contents of heavy metals (mg/kg) in the bottom sediments of the Muchawka River and the Liwiec River, considering the results of other authors.

Related River (Country)	Analytical Method	Min–Max					Ref.
		Zn	Pb	Cd	Ni	Cu	
Muchawka (Poland)	AAS	14.4–21.3	9.8–13.4	0.1–0.8	2.3–8.4	0.7–5.2	in study
Liwiec (Poland)	AAS	16.4–25.3	10.4–13.9	0.2–0.7	3.3–9.9	0.7–9.4	
Morawa (Czech Republic)	ICP-MS	66–321	14–55	0.1–4.8	n/a	22–63	[51]
Odra (Poland)	ICP-MS/AAS	333–2591	19–343	3–21.7	37–108	31–298	[52]
Słupia (Poland)	AAS	14–96	6–244	0.1–0.7	3–14	2–45	[53]
Moji-Guacu (Brazil)	PIXE	17–92	3–31	n/a	8–38	9–48	[54]
Tisza (Hungary)	ICP-MS	130–570	18–304	0.2–3.7	64–88	40–137	[55]
Vistula (Poland)	ICP-MS	180–860	28–122	1–8	n/a	n/a	[56]
Elba (Germany)	ICP-OES	1356	40–172	3–6	30–90	62–174	[57]
Navasota (USA)	AAS	n/a	18–30	0.2–0.4	n/a	16–22	[58]
Supraśl (Poland)	AAS	10–67	3.5–35	0.4–1.1	5.4–18	0.8–16	[59]
Yellow River (China)	AAS	58–93	29–37	217–393	n/a	20–55	[60]
Odra (Poland)	AAS	3–35	1–2	0.6–0.99	7–23	2–28	[61]

Notes: AAS—atomic absorption spectrometry, PIXE—proton-induced X-ray emission, ICP-MS—inductively coupled plasma mass spectrometry, ICP-OES—inductively coupled plasma optical emission spectroscopy; n/a—not analyzed. A minima and maxima are not given, and the ranges.

A concentration not exceeding 1 mg/kg dry weight was proposed for sediments of quality class 1 [44]. None of the samples analyzed exceeded the cadmium content for quality class 1. For other authors (Table 5), only at two points on the Supraśl River (Fasty) and the Biala River (Bialystok) were cadmium concentrations higher than 1 mg/kg d.m. The content of cadmium in the sediments of the studied rivers was also significantly lower than in the Vistula River [62] and comparable or slightly higher than in the Dunajec River [63].

The nickel content in the studied bottom sediments ranged from 2.3–8.4 in the Muchawka River to 3.3–9.9 in the Liwiec River. The medians for nickel ranged from 3.9 to 5.9 mg Ni/kg, respectively (Table 4), and were lower than the median for Europe (16 mg Ni/kg). Our study found significantly lower nickel content compared to the results of other authors (Table 5). Nickel binds to fairly stable chelate and cationic and ionic complexes.

Figures 2 and 3 show the distribution of the analyzed heavy metals in the surface water and bottom sediment of the samples studied. The comparison of the average content of heavy metals in the studied bottom sediments clearly indicates that slightly higher values were obtained in the samples collected from the Liwiec River. Similar relationships can be indicated for the analyzed surface water samples.

Of the heavy metals analyzed, zinc was present at the highest values, while cadmium at the lowest. Slightly higher content in relation to cadmium was found for lead, both in the surface water samples and in the bottom sediments of both rivers (Figures 2 and 3). The differences in the results obtained and the pH values along the studied rivers are largely due to the runoff of fertilizers used by farmers and the existing tributaries to the studied rivers. In the vicinity of the second sampling point, in the village of Borki-Paduchy, the Muchawka River is tributary to the Zbuczynka River. The water in this river is slightly brown. In turn, seven more smaller rivers flow into the Liwiec River. Some of them receive water from nearby sewage treatment plants.

The concentrations of metals detected in surface waters and bottom sediments at the analyzed points are also shown in Figure 4. The variability of metal concentrations (at all sampling points) in both surface waters and bottom sediments was as follows: Zn > Pb > Cu > Ni > Cd.

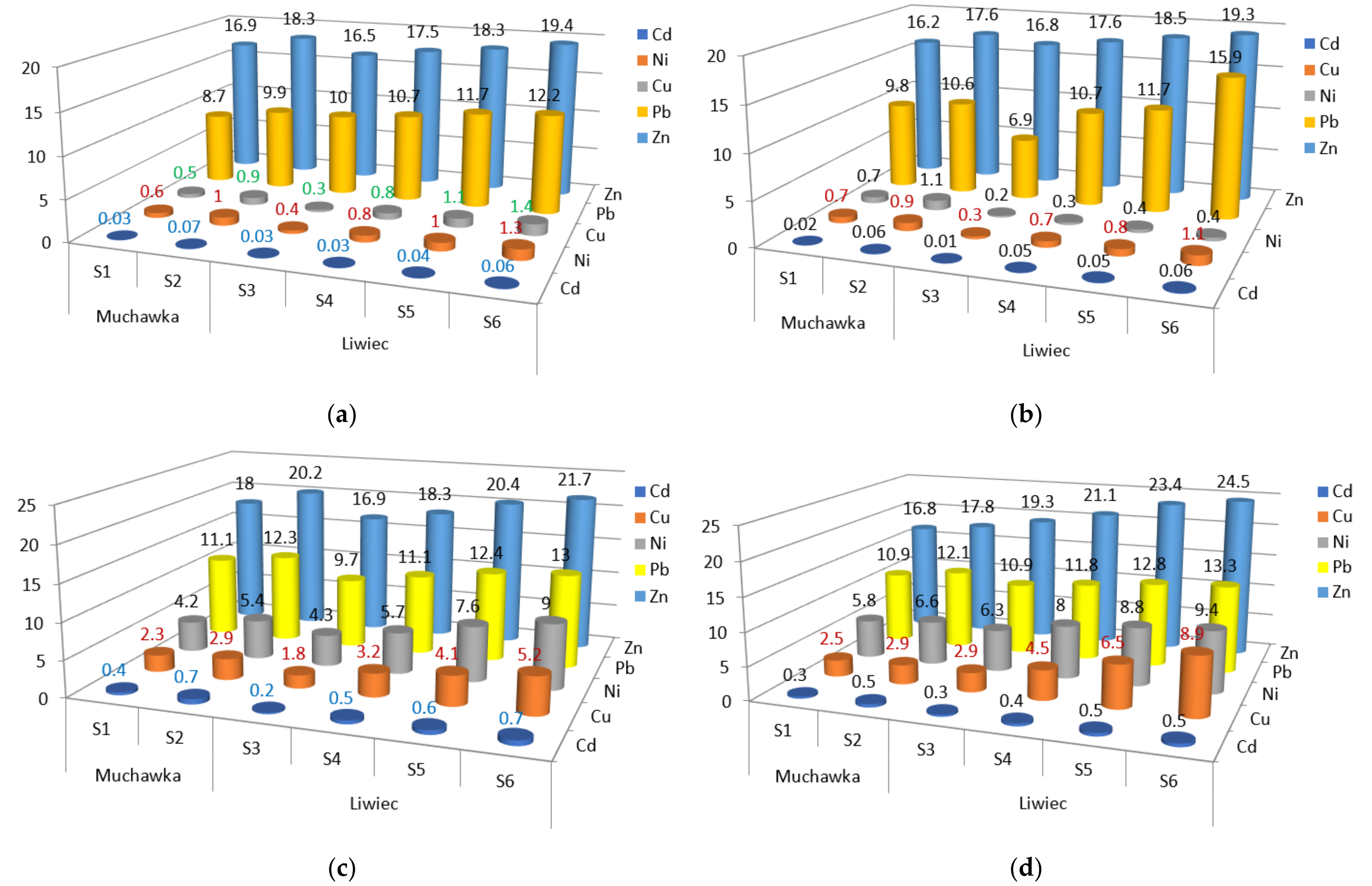

Figure 4. Metal concentrations detected at sampling sites: (**a**) surface waters in June, (**b**) surface waters in September, (**c**) bottom sediments in June, (**d**) bottom sediments in September.

It was found that the concentration of most metals was higher in bottom sediments than in surface waters The study showed that only a small part of the heavy metals entering rivers are present in the water depth in the dissolved state, and most of them enrich the sediment, resulting in much higher concentrations of heavy metals in the sediment than in the water column. Similar results have also been proven in many other studies [8,15,64]. Metal concentrations were higher at S6 than at other sampling sites for bottom sediments or surface waters. High concentrations of metals may be related to the pollution of the seven rivers flowing into the Liwiec, which are additionally supplied with water from nearby sewage treatment plants.

Concentrations of metals in the bottom sediments were compared in relation to the geochemical background and literature data of other authors for Poland and Europe [46,47]. The analysis of bottom sediment contamination presented in the literature shows that the content of heavy metals is determined within very wide limits (Table 5) [51–61].

The comparison of the obtained results with the values of the geochemical background (Table 3) shows that the content of the analyzed metals is low, and the studied sediments can be classified in quality class 1. Despite obtaining low values for the content of heavy metals in the studied bottom sediments, the pollution index and the degree of sediment contamination were also calculated using the method proposed by Hakanson (Table 6) [65].

Table 6. Degrees of sediment contamination according to Hakanson [65].

Pollution Index, C_f	Degree of Contamination, C_d	Pollution
<1	<8	poor
1–3	8–16	moderate
3–6	16–32	significant
≥6	≥32	very strong

The contamination index for a given metal was calculated from the equation $C_f = C_i/C_0$, where C_i is the metal content of the sediment, and C_0 is the geochemical background value. The degree of C_d contamination, on the other hand, is the sum of the contamination indices determined for each metal.

The data in Table 7 indicate that the degree of contamination of the bottom sediments of the studied rivers is low. Both in June and September, the values of sediment contamination indices (except for cadmium) were below one. Only in June, the cadmium contamination indices for both rivers were equal to one or slightly exceeded this value.

Table 7. Indicators and degrees of contamination of the studied bottom sediments.

Average for the River	C_f					C_d	Pollution
	Zn	Pb	Cd	Ni	Cu		
Muchawka (June)	0.26	0.78	1.2	0.96	0.37	3.57	poor
Muchawka (September)	0.24	0.75	0.8	1.24	0.39	3.42	poor
Liwiec (June)	0.26	0.77	1	1.34	0.51	3.88	poor
Liwiec (September)	0.30	0.81	0.8	1.62	0.81	4.34	poor

4. Conclusions

The results of the bottom sediment quality assessment presented in this paper allow us to conclude that the contamination of the studied sediments with heavy metals is low. The content of almost all analyzed metals practically does not exceed the geochemical background value. Appropriate selection of background values is a key factor in the assessment.

Variability in parameters, such as temperature, precipitation and humidity, contributes to seasonal changes in the characteristics of the distribution and sources of heavy metals. Only a small fraction of heavy metals entering the rivers are present in the water column in a dissolved state, while the remaining part enriches the sediments; as a result, the concentrations of these metals in the sediments were slightly higher than in the water column. The differences in the distribution of some elements in the water and the sediment are due to the fact that surface sediments may contain contaminants accumulated over many years. Therefore, bottom sediments can be considered a potential source of heavy metals in the aquatic environment.

The determined content of heavy metals in bottom sediments was not high but sufficient to demonstrate the impact of human activity. Changes in environmental factors (pH, redox potential, etc.) or hydrodynamic conditions can lead to the release of heavy metals from sediments and secondary pollution of water.

The analytical results obtained will be of great importance both to the population living in the area and to scientists studying river systems. The research conducted showed that bottom sediments contain low concentrations of heavy metals. The analyzed sediments were classified as slightly contaminated.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w15152833/s1, Table S1. Results for reference material NCSDC 73377 achieved by means of AAS technique, ($n = 5$, $p = 95\%$). Table S2. Conditions and parameters of AAS analysis Cd, Pb, Cu, Ni, Zn.

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