SOCIAL SCIENCES

LEVELS OF HEAVY METALS IN SEVERAL RIVERS OF THE WESTERN BUG AND DNIESTER BASINS IN THE LVIV REGION (WESTERN UKRAINE)

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Abstract. Lviv region, one of the most urbanized and industrialized regions of Western Ukraine, faces environmental problems, including pollution of surface waters. The study was aimed to investigate the levels of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the waters of three tributaries of the Western Bug River (Poltva, Rata and Kamyanka), as well as in the Dniester River and its two tributaries (the Zubra and Vivnya rivers) within the Lviv region. The results show that the degree of contamination of the Western Bug tributaries with heavy metals is considerably higher at the mouths of the rivers compared to river sources. In particular, metal concentrations at the mouth of the Rata River were 1.23–3.98 times higher than at its source, while water samples at the mouth of the Kamianka River were characterized by higher levels of Fe, Mn, Zn and Cd (2, 12–6.55 times) compared with the source of the river. Concentrations of several heavy metals, especially Fe, exceeded the maximum allowable levels in the waters of the analyzed rivers. Results of the study suggest a significant anthropogenic load in the catchment areas of the analyzed rivers within the Lviv region.

Keywords: heavy metals, surface waters, Lviv region, Western Bug, Dniester.

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Introduction

Surface water resources can be adversely affected by virtually all types of human activity. Water quality of rivers, lakes and other reservoirs is influenced by pollution from industrial facilities, discharges from sewage treatment plants or seepage from landfills, as well as diffuse pollution from agricultural activities and deposition from the atmosphere due to both precipitation and dry fallout. The main polluters of surface waters are industrial, mining and refinery enterprises, animal husbandry and irrigated agriculture (*Glińska-Lewczuk et al., 2016; Bojarczuk et al., 2018*).

Anthropogenic load leads to a significant decline in freshwater quality, which has been documented for many countries, including Ukraine (*Burgess et al., 2009; Lenart-Boroń et al., 2017; Vystavna et al., 2018*). The environmental consequences of deteriorating water quality such as eutrophication and the degradation of sensitive aquatic ecosystems are particularly relevant for small rivers, which are important components of regional landscapes. Of all the pollutants released into the aquatic environment from anthropogenic sources, heavy metals are amongst the most hazardous because of their persistence in the environment, and also due to the high toxicity, mutagenicity and carcinogenicity of many of them (*Al-Saleh et al., 2017; Pratush et al., 2018; Bharatraj and Yathapu, 2018*). Because of the potential of some heavy metals for long-range transport and subsequent deposition on land and surface waters, metal contamination can be found in water bodies remote from the emission sources.

Lviv region, being one of the most urbanized and industrially developed regions of Western Ukraine, simultaneously faces environmental problems, including surface water pollution arising from oil production and refining, emissions from enterprises of various industries and inefficient waste management (*Mnykh, Sokil, 2014; Lozynskyi et al., 2017; Vystavna et al., 2018*). In addition, agricultural runoff from cultivated lands and livestock farms also contributes to the pollution of surface waters in the region. Water contamination with debris, nutrients, persistent organic pollutants, oil and heavy metals due to anthropogenic causes leads to physical alterations and destruction of habitats, loss of biodiversity of aquatic ecosystems and a significant reduction in the use of water bodies for recreational purposes (*Vignati et al., 2013; Antonyak et al., 2015; Hoivanovych et al., 2018*).

Reserves of natural surface water in the Lviv region contain more than 8,950 watercourses, including rivers, streams and springs with a total length of 16,343 km. The Western Bug River and the Dniester River with a network of branched tributaries belong to the main rivers of the region.

The purpose of this study was to investigate the levels of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the waters of the left tributaries of the Western Bug River (the Poltva, Rata and Kamianka rivers), as well as in the Dniester River and its two tributaries: the Zubra River (left tributary) and the Vivnya River (right tributary). The catchment areas of these rivers are located in different parts of Lviv region.

Materials and methods

Six rivers flowing through different areas of the Lviv region were selected to study the concentration of heavy metals. One of them, the Dniester River, belongs to very large rivers, the other two (the Poltva River and the Rata River) can be classified as the large rivers *(Khilchevskyi et al., 2018)*, and the other three (the Kamianka River, the Zubra River and the Vivnya River) belong to the small rivers. Brief characteristics of the rivers and localization of sampling sites are given in Table 1.

The analysis of water samples were conducted in summer-autumn period in accordance with standard water quality testing methods (*Rice et al., 2012*). The samples were taken from the surface horizon of water from a depth of 0.5–0.7 m using plastic samplers of 1 dm^3. Water was filtered through a membrane filter and the concentrations of cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc

(Zn) were determined by atomic absorption spectrophotometry. The measurements were carried out using a C-115PK Selmi (Ukraine) spectrophotometer at wavelengths corresponding to the absorption maximum of each of the metals according to standard methods (*Novikov et al., 1990*). The metal content in the water was presented as the mean, minimum and maximum concentrations for each sampling point.

Table 1

Characteristics of the rivers and localization of sampling sites selected for the study

River characteristics		Sampling site No	Localization of sampling sites
Poltva River	Length 60.0 km, catchment area 1,440 km^2; flows within the Pustomyty and Busk districts of the Lviv region	1	sampling was carried out in the vicinity of the city of Lviv
		2	river mouth, the city of Busk
Rata River	Length 76.0 km, catchment area 1,820 km^2; flows within the Zhovkva and Sokal districts of the Lviv region	3	river source, sampling was carried out downstream of the city of Rava-Ruska
		4	river mouth, the village of Mezhyrichcha
Kamianka River	Length 38.0 km, catchment area 142 km^2; flows in the Zhovkva and Kamianka-Buzka districts of the Lviv region	5	river source, sampling was carried out downstream of the village of Kulykiv
		6	river mouth, sampling was carried out downstream of the city of Kamianka-Buzka
Dniester River	Length 1360 km, catchment 72,100 km^2; in its upper course, the river flows through the Lviv region	7	sampling was carried out at a section of riverbed near the village of Veryn (Mykolaiv district) located 40 km south of Lviv
Zubra River	Length 46.0 km, catchment area 242 km^2; originates and flows in the southern part of the city of Lviv; flows through the Pustomyty and Mykolaiv districts of the Lviv region	8	water samples were taken in the vicinity of the village of Zubra in Pustomyty district at a distance of 12 km from the centre of Lviv
Vivnya River	Length 33.0 km, catchment area 80 km^2; flows in the Mykolaiv districts of the Lviv region	9	water samples were taken at a section of riverbed near the village of Vivnya in Stryi district located about 60 km south of Lviv

Concentrations of heavy metals in river water were compared with the maximum allowable levels (MAL) of these substances in surface waters intended for human use and fisheries activities. In accordance with the quality standard of surface waters adopted in Ukraine, the MAL values for the studied metals are as follows (μg/L): Fe: 300; Mn: 100; Zn: 1000; Cu: 1000; Cr(VI): 50; Ni: 100; Co: 100; Cd: 5 (in water for fish farming); Pb: 30 (*Kofanov and Ognyanik, 2008; Klymenko et al., 2012*).

Results and discussion

According to the results obtained in the study, the concentrations of heavy metals in analyzed river waters of the Lviv region differ depending on the metal being studied, the localization of the sampling site and human activity in the catchment areas. Among the metals analyzed, the iron concentration reached the highest levels in the waters of all the water bodies studied. The mean Fe concentration in the rivers ranged from 302 µg/L (in water of the Vivnya River) to 1440 µg/L (in the mouth of Kamianka River) (Tables 2, 3). The second highest mean concentration of Fe after the Kamianka River was recorded in the water of the Poltva River, namely of 790 µg/L (Table 3). In both of these studied sites, the iron content of water was significantly higher than the maximum allowable level in surface waters intended for human use, namely, 4.8 and 2.63 times, respectively. Iron content of water in other rivers (except for the Vivnya River, in which the Fe level was almost equal to MAL) also exceeded the MAL value, but to a lesser extent.

With regard to the waters of the Western Bug tributaries, our data show that the quality of water in Poltva, Rata and Kamianka rivers largely depends on the site of sampling. The concentration of a number of heavy metals was found to be significantly higher at the mouths of all three rivers as compared to their sources (Table 2).

Table 2

Concentration of heavy metals in the tributaries of the Western Bug River within the Lviv region, µg/L

Analyzed metal		Poltva River		Rata River		Kamianka River	
		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Fe	Mean	490	790	455	580	400.5	1440
	Value range	480–500	480–1100	330–580	500–660	130–671	1430–1450
Mn	Mean	80,7	101.0	54.1	214.7	46.4	133.6
	Value range	77.2–84.2	84.2–117.7	52.3–55.9	223.4–206	42.3–50.5	121.3–145.8
Zn	Mean	44,6	46,1	10.2	18.7	10.2	66.8
	Value range	44.5–44.7	44.7–47.5	2.30–18.1	6.3–31.1	9.0–11.3	55.4–78.2
Cu	Mean	12,4	14,7	5.3	4.25	19.9	7.05
	Value range	6.5–18.3	11.1–18.3	4.4–6.2	1.8–6.7	8.5–31.3	6.2–7.9
Cr	Mean	20.7	20.8	4.85	12.75	18.5	10.5
	Value range	3.9–37.4	4.1–37.4	4.3–5.4	5.6–19.9	17.6–19.4	2.6–18.4
Ni	Mean	26.15	27.75	13.75	17.65	21.95	22.8
	Value range	23.4–28.9	23.4–32.1	13.2–14.3	16.5–18.8	18.8–25.1	21.1–24.5
Co	Mean	12.1	13.75	10.5	12.9	13.8	15.3
	Value range	11.8–12.4	12.4–15.1	6.8–14.2	10.5–15.3	12.1–15.5	14.1–16.5
Cd	Mean	6.5	6.85	3.2	4.5	6.15	13.15
	Value range	6.5–6.6	6.5–7.2	3.1–3.3	4.3–4.8	6.1–6.2	6.6–19.7
Pb	Mean	29.5	30.1	25.5	35.6	34.5	27.7
	Value range	26.6–32.4	27.7–32.4	17.8–33.2	16.0–54.2	26.7–42.3	19.0–36.4

This applies primarily to the water of the Rata River at site 4 (mouth of the river), which is characterized by a higher level of nearly all analyzed metals (except Cu) compared to site 3 (river source). Namely, the concentrations of Fe, Mn, Zn, Cr, Ni, Co, Cd and Pb were, respectively, 1.27, 3.98, 1.83, 2.63, 1.28, 1.23, 1.41, and 1.38 times higher at site 4 than at site 3. Similarly, in the water of the Kamianka River, the concentrations of Fe, Mn, Zn, and Cd were, respectively, 3.60, 2.88, 6.55, and 2.12 times higher at site 6 (river mouth) compared to site 5 (river source). In the water of the Poltva River, the concentrations of Fe, Mn, Cu and Co were higher by 1.61, 1.25, 1.19 and 1.14 times at site 2 as compared to site 1.

At the same time, the mean Mn concentration in the mouths of the Rata and Kamianka rivers exceeded the MAL value for this metal by 2.15 and 1.34 times, respectively (Table 2). The mean Pb concentration in the Western Bug tributaries was close to the MAL value; however, the threshold level was exceeded by 1.19 and 1.15 times in the waters of the Rata River's mouth (site 4) and at the source of the Kamianka River (site 5), respectively. In the waters of the Poltva and Kamianka rivers, the mean Cd concentrations were higher than the maximum permissible levels at all the analyzed sites.

Results regarding high levels of heavy metals in the mouths of tributaries of the Western Bug River may indicate a high level of pollution in the catchment areas of the studied rivers. Within the Lviv region, the analyzed rivers flow through areas with a high level of industrial activity. Namely, these are Busk and Sokal districts of Lviv region. In particular, 14 large enterprises operate in Busk district (mainly in the city of Busk), which represent the food, woodworking and furniture industries, as well as the production of machinery and equipment. Within the Sokal district, the coal industry is mostly developed (there are 9 mines and Central concentrating factory). In addition, the Kamianka River flows for several kilometres within the city of Kamianka-Buzka, and the mouth of the Poltva River is located in the territory of Busk. These facts can explain the high level of analyzed heavy metals in the water of the rivers sampled at sites 2, 4 and 6. The high level of contamination of the Western Bug tributaries with heavy metals has also been reported by other authors (*Khilchevskyi et al., 2018*).

Among the watercourses analyzed in this study, the Vivnya River belonging to the Dniester basin was almost the least contaminated with heavy metals. In particular, the levels of Fe, Cu, Zn, Co, Cd and Pb in the water of Vivnya River, were significantly lower compared to the water of other small rivers (the Zubra and Kamianka), as well as compared to the large rivers that were analyzed. However, the level of Fe in its water was close to the maximum allowable level (Table 3). At the same time, with the exception of this metal, none of the other metals analyzed at site 9 exceeded the MAL values. It can be considered that the relatively low concentration of most metals in the water of the Vivnya River is due to its geographical position, since the river flows mainly in the agricultural area and its riverbed is remote from the industrial cities of the Lviv region.

In contrast, the Zubra River, the left tributary of the Dniester River, which originates and flows in the southern part of the city of Lviv, is characterized by a significantly higher level of contamination with heavy metals compared to the Vivnya River. According to the obtained results, the concentration of all analyzed metals in Zubra's water is 1.4–4.3 times higher than in the water of the Vivnya River (Table 3). At the same time, the mean concentrations of Fe exceeded the MAL by 2.5 times, while the Cd concentration was close to the maximum allowable level.

Table 3

Concentration of heavy metals in the waters of the Dniester River and its two tributaries (the Zubra and Vivnya rivers) within the Lviv region, µg/L

Analyzed metal		Dniester River	Zubra River	Vivnya River
		Site 7	Site 8	Site 9
Fe	Mean	576	750	302
	Value range	532–620	678–822	274–330
Mn	Mean	45.5	42.6	26.6
	Value range	38.7–52.3	35.4–49.8	12.26–28.7
Zn	Mean	57.8	23.4	11.0
	Value range	42.6–73.0	19.25–27.6	6.18–15.8
Cu	Mean	15.8	22.0	5.16
	Value range	9.1–22.4	16.2–27.8	3.4–6.92
Cr	Mean	23.5	28.4	20.6
	Value range	12.4–34.50	24.6–32.14	14.1–27.0
Ni	Mean	17.8	21.3	15.8
	Value range	12.0–23.5	19.6–23.0	9.8–21.7
Co	Mean	14.8	14.2	6.32
	Value range	13.6–16.0	10.4–18.0	5.4–7.24
Cd	Mean	3.67	4.52	2.44
	Value range	3.2–4.14	3.32–5.71	2.19–2.68
Pb	Mean	14.10	18.7	9.15
	Value range	8.32–.19.8	16.0–21.4	5.7–12.6

As regards to the Dniester River, its water at the sampling point (site 7) was characterized by a higher degree of contamination with some metals such as Mn, Zn and Co as compared with tributaries, the Zubra River and the Vivnya River. However, the levels of most metals that were analyzed did not exceed the maximum allowable levels. The exception was the concentration of Fe, which exceeded the MAL value by 1.92 times (Table 3). In general, the level of contamination of the Dniester River with most heavy metals analyzed at the sampling point (the village of Veryn in the Mykolaiv district) was found to be comparable to the level of pollution of the Western Bug tributaries. At the same time, the obtained results indicate a significant anthropogenic load in the catchment areas of the analyzed rivers within the Lviv region.

Conclusions and suggestions

1. The level of heavy metal contamination of the waters of the Western Bug tributaries (the Poltva, Rata and Kamianka rivers) was found to be considerably higher at the mouths of the rivers in comparison to the river sources. In the water of the Rata River's mouth, the concentrations of Fe, Mn, Zn, Cr, Ni, Co, Cd and Pb were respectively higher by 1.27, 3.98, 1.83, 2.63, 1.28, 1.23, 1.41, and 1.38 times than at the river source. At the mouth of the Kamyanka River, the concentrations of Fe, Mn, Zn and Cd were respectively higher by 3.60, 2.88, 6.55 and 2.12 times than in water samples at the source of the river (downstream of the village of Kulykiv), while in the water of Poltva River sampled at the river mouth (the city of Busk), the concentrations of Fe, Mn, Cu and Co were from 1.14 to 1.61 times higher than in water sampled in the vicinity of the city of Lviv.

2. In the waters of the analyzed rivers of the Lviv region, concentrations of several heavy metals exceeded the maximum allowable levels. Namely, the Fe concentration in the Rata, Poltva and Kamianka rivers exceeded MAL level by 1.33–4.8 times, and in the Dniester and Zubra rivers – by 1.92 and 2.5 times, respectively. The mean Mn concentration in the mouths of the Rata and Kamianka rivers exceeded the MAL value by 2.15 and 1.34 times, respectively, while the Cd concentration in the Poltva and Kamianka rivers were higher than the maximum allowable levels by 1.23–2.63 times.

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