

## Environmental monitoring of heavy metal content in the hydrographic network of a large city river

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### ABSTRACT

Samples of edaphotopes were taken from a depth of 0–15 cm for analyses in this study. It was found that the water in the areas of the Hnidavske swamp and Teremniv ponds was the most polluted. The level of Zn ( $0.01 \text{ mg/dm}^3$ ) exceeded the maximum permissible concentration (MPC) at site 5 (Lypnyany village, outside the city of Lutsk, the content was  $0.015 \text{ mg/dm}^3$ ) and Hnidavske marsh ( $0.019 \text{ mg/dm}^3$ ). At all study sites, Cr ( $0.001 \text{ mg/dm}^3$ ) ranging from  $0.002$  to  $0.005 \text{ mg/dm}^3$ , Co ( $0.005 \text{ mg/dm}^3$ ) from  $0.008$  to  $0.01 \text{ mg/dm}^3$ , and Ni ( $0.01 \text{ mg/dm}^3$ ) from  $0.02$  to  $0.036 \text{ mg/dm}^3$  were also found to exceed the MPC. However, Cd levels ( $0.005 \text{ mg/dm}^3$ ) did not exceed the MPC and was within the normal range at all study sites ( $0.0016$ – $0.003 \text{ mg/dm}^3$ ).

**Key words:** city, environmental safety, pollution, radiation background, river, water

### HIGHLIGHTS

- Modern data on the content of heavy metals in the river water of a large city were analyzed in this study.
- The problem of fresh water pollution in conditions of its shortage is discussed.
- Discharging sewage into the river and its problems are discussed.
- The importance of modernization of treatment facilities is necessitated.
- Water quality monitoring should be at an adequate level.

GRAPHICAL ABSTRACT



1. INTRODUCTION

River basin pollution with heavy metals is an important environmental problem at present. Studying the heavy metal content and its migration is especially relevant for regions and countries facing a shortage of drinking (fresh) water (Sysa *et al.* 2019; Kochmar *et al.* 2024). Surface and groundwater bodies are polluted in countries where military operations take place, including Ukraine. Expended ammunition, especially rocket fuel, is extremely toxic. Once released into the environment, toxic substances from expended ammunition cause irreversible ecological processes in the biota. Globally, including Ukraine, significant research is being conducted on the heavy metal content in natural and underground water bodies. Among such studies, it is worth noting scientific works devoted to both large national rivers and their tributaries. In particular, Fesiuk *et al.* (2023) reported that, due to excessive concentrations of pollutants in wastewater discharged into the Styr River, pollution levels exceed the maximum permissible concentration (MPC) (fishery) in river water. In 2022, this exceedance was 37.8 times for ammonium nitrogen, 9.9 times for nitrite, 44 times for phosphate, 5.69 times for total iron, 2.5 times for manganese, 6 times for chromium (VI), 10.8 times for biological oxygen demand (BOD), and 67% for suspended solids.

Heavy metals cause serious health consequences to the human body, especially the risk of cardiovascular and oncological diseases (Nersesyan *et al.* 2021; Serhiyenko & Serhiyenko 2021). Excess heavy metals in the human body can provoke the emergence of dangerous diseases and the exacerbation of existing chronic diseases affecting people of all ages. These phenomena are accompanied by post-traumatic stress disorders and diabetes mellitus (Serhiyenko *et al.* 2022; Serhiyenko & Serhiyenko 2022). In the Danube River basin, samples (Damian *et al.* 2022) of coastal (floodplain) sediments, river sediments, and suspended sediments were collected at different locations to determine the concentration of heavy metals (copper, lead, zinc, cadmium, mercury, nickel, chromium, and arsenic) and organic components (anthracene, fluoranthene, benzo(e) pyrene) and their distribution as hazardous substances. In accordance with Directive 2013/39/EU and the standards of the EU Water Framework Directive, sediment quality was assessed. Most of the concentrations assessed in river sediments and coastal (floodplain) sediments are within the limits of the Environmental Quality Standards (EQS). For As, Cu, Pb, and Zn, there is a tendency toward exceeding the EQS at some sites. The highest exceedances were reported for lead, which was found to be up to 987 mg/kg. It was found that self-purification processes are quite active in the Kolodnytsia River (a tributary of the Dniester River), which is due to the hydrological features of the river and the presence of hydrodynamically active areas

in the foothill part of the basin. At present, there is no steady excess of pollutants over the MPC (Hnativ *et al.* 2023). Sukhodolska (2017) presented results showing that the water quality in small rivers of the Rivne region (Ukraine) in terms of heavy metals (Zn, Cu, Mn, Fe, Ni, Co) does not meet the permissible levels, except for Pb and Cd, whose concentrations do not exceed the MPCs for fisheries.

The average background copper content in bottom sediments of rivers in Ukraine is 28 mg/kg and that in surface waters is 0.106 mg/dm<sup>3</sup> as reported by Lyuta (2021). For copper, the minimum background level was found to be 10 mg/kg in the Danube catchment (Tisza and Prut subbasins) and the maximum 50 mg/kg. The difference between the maximum background value and the minimum value is a factor of 5. Important studies of heavy metal content in river water are being conducted in countries such as the United States, Japan, and Germany, as well as in countries experiencing a shortage of drinking water such as India, Bangladesh, and Indonesia. The results of studies of the Netravati River basin (India) show that sediment contamination with lead can pose a significant threat to aquatic biota, and constant exposure to pollutants, even at low concentrations, causes changes in the metabolic activity and community structure of river biota (Gayathri *et al.* 2021). Heavy metals can accumulate in different organisms and respond to changes in various molecular and cellular biomarkers in different organisms, such as plankton, benthos, fish, crustaceans, and shrimp, as well as in the food chain, which can affect human health. The absorption mechanism can occur through dietary accumulation, bioaccumulation, or bioconcentration, which can impair the health of wildlife, such as fish and invertebrates. In the long term, this leads to environmental and human health degradation (Stepova *et al.* 2020; Kadim & Risjani 2022). An investigation of sediment samples taken from two of the largest rivers in Poland, Oder and Vistula rivers, revealed that the point and local pollution caused high heavy metal concentrations from the lower to the upper reaches of the Oder river. In the Vistula River, the content of heavy metals (Ni, Cd, Cr, Pb, and Zn) decreases from the lower to the upper reaches, which may be caused by sedimentation in reservoirs along the river, modern wastewater treatment plants in large cities, and self-purification processes (Jaskuła & Sojka 2022). Jaskuła *et al.* (2021) evaluated the risk of harmful effects of excess heavy metal content in the sediments of the Warta River. The assessment of the potentially toxic impact of heavy metals deposited in sediments based on threshold effect concentration (TEC), midpoint effect concentration (MEC), probable effect concentration (PEC), toxic risk index (TRI) revealed that the environmental risk posed by heavy metals in river sediments was considerably lower in 2017 than in 2016. The cluster analysis identified two groups of sampling stations where the sediments showed similar chemical characteristics. Research by Calmuc *et al.* (2021) aimed to determine the content of heavy metals in surface sediments of the Danube River up to the location where it flows into the Danube Delta Biosphere Reserve. Cd, Ni, Zn, Pb, and Cu contents were measured during two different seasons, fall and spring, using the inductively coupled plasma mass spectrometry (ICP-MS) method. The results showed low Ni and Cd content and low potential environmental risk to the aquatic environment.

To evaluate the potential risk to human health, an analysis was conducted on the heavy metal contamination present in the surface waters of the upper Ganges River in India. The spatial and temporal distributions of Fe, Mn, Zn, Cr, and Pb were examined at eight locations during the pre- and post-monsoon seasons of 2017. The mean concentration of heavy metals was found to be elevated, frequently exceeding the limits set for surface water by the Bureau of Indian Standards and the World Health Organization. As indicated by the Heavy Metal Pollution Index, 87% of the rivers were classified as moderately or severely polluted (Prasad *et al.* 2020). Khan *et al.* (2021) aimed to assess the state of heavy metal pollution and health risks associated with the water from the Gomti River used by millions of people (India). It was found that the contamination level for Cd was '11.93', which means a 'high' risk level due to heavy metal contamination of the Gomti River over an approximately 61 km long stretch, including areas upstream, midstream, and downstream of the city of Lucknow. The results of the carcinogenic risk assessment indicate that children are more susceptible to health risks and immediate action is needed to control elevated levels of heavy metals at all sampling sites.

The extent of anthropogenic contamination of sedimentary deposits within the Matanza-Riachuelo Basin in Argentina, with regard to the presence of cadmium, chromium, copper, nickel, lead, and zinc, was evaluated through the application of a range of analytical indices. The findings indicate that the maximum and average values of the total carcinogenic risk of Cr and Ni suggest a potential risk to children's health. The analysis of the data collected confirms that the lack of land use planning and poor environmental legislation provided an inadequate basis for sustainable development. The potential environmental risk associated with microplastics has prompted a heightened level of scrutiny. Nevertheless, data on microplastics in estuaries in the Southeast Asian region are limited. All collected samples were characterized by a predominance of small microplastics of 0.05–0.3 mm. The most prevalent particles in surface water and sediments were polypropylene and polyethylene, respectively. Toxic metals (chromium, copper, nickel, lead, cadmium, and zinc) were detected in microplastics

from surface water samples. Given the Chao Phraya River estuary's status as a significant aquaculture region in Thailand, the contamination of the area by microplastics could potentially have a detrimental impact on both aquaculture and human health (Ta & Babel 2020).

Thus, after analyzing the research of scientists on the pollution of rivers with heavy metals, we can conclude that this problem is relevant for many countries, especially those where military operations are underway and those that are affected by a lack of drinking water. It is worth noting that almost all the research results indicate increased amounts of heavy metals in river water. The reasons for this are the discharge of surface water into rivers from industrial and mining enterprises and the ingress of liquid household waste and wastewater into the water. The relevance of further research on heavy metals in surface waters is undeniable. It should be a key component of comprehensive monitoring of fresh (drinking) water quality. The investigation of fresh water for hazardous substances is a topical issue, especially in regions with water scarcity (Karmakar *et al.* 2021; Agbasi & Egbueri 2022; Egbueri *et al.* 2022; Agbasi *et al.* 2024). The presented research highlights the content of heavy metals in the urban Styr River, which flows through the regional center of Ukraine (Lutsk). The research presented is new and unique, as it reflects the content of heavy metals in both water and coastal edaphotopes. Moreover, the radiation background at the sampling sites was measured.

## 2. MATERIALS AND METHODS

### 2.1. Study area

The Styr River directly forms the hydrographic network of Lutsk. The quality of its water is influenced by its tributaries – the Sapalayivka, Omelyanyk, Zhydivka, and Chornohuzka rivers. On the eastern side of the city of Lutsk, on the Sapalayivka River, the Teremniv Ponds were built (near Teremnivska Street). Their area is 5.91 ha. The ponds play a significant role in regulating the hydrological regime of the Sapalayivka River. The Teremniv Ponds were granted the status of a local natural monument in 1993. Also hydrologically connected to the Styr River by canals is the Hnidavske marshland, which requires detailed hydrological studies in the future due to its specific ecosystem. In our previous studies (Kopylov *et al.* 2023), we presented the characterization of the water content of the Styr River and pollution dynamics based on the 'Clean Water' map. We also identified the main factors of anthropogenic impacts on water quality. The content of heavy metals in water and coastal edaphic habitats was partially discussed in a scientific paper (Kopylov & Popovych 2024), but the complex content was not considered and the results were presented only for three chemical elements.

For the analysis of the heavy metal content in the Styr River and the edaphotopes of the coastline, we sampled eight sites, six of which were directly in the Styr River, the seventh site was the Hnidavske marsh, and the eighth site was the Teremniv lake. Figure 1 shows Lutsk hydrographic network with sampling sites for heavy metals in water and coastal edaphotopes.

### 2.2. Sampling method

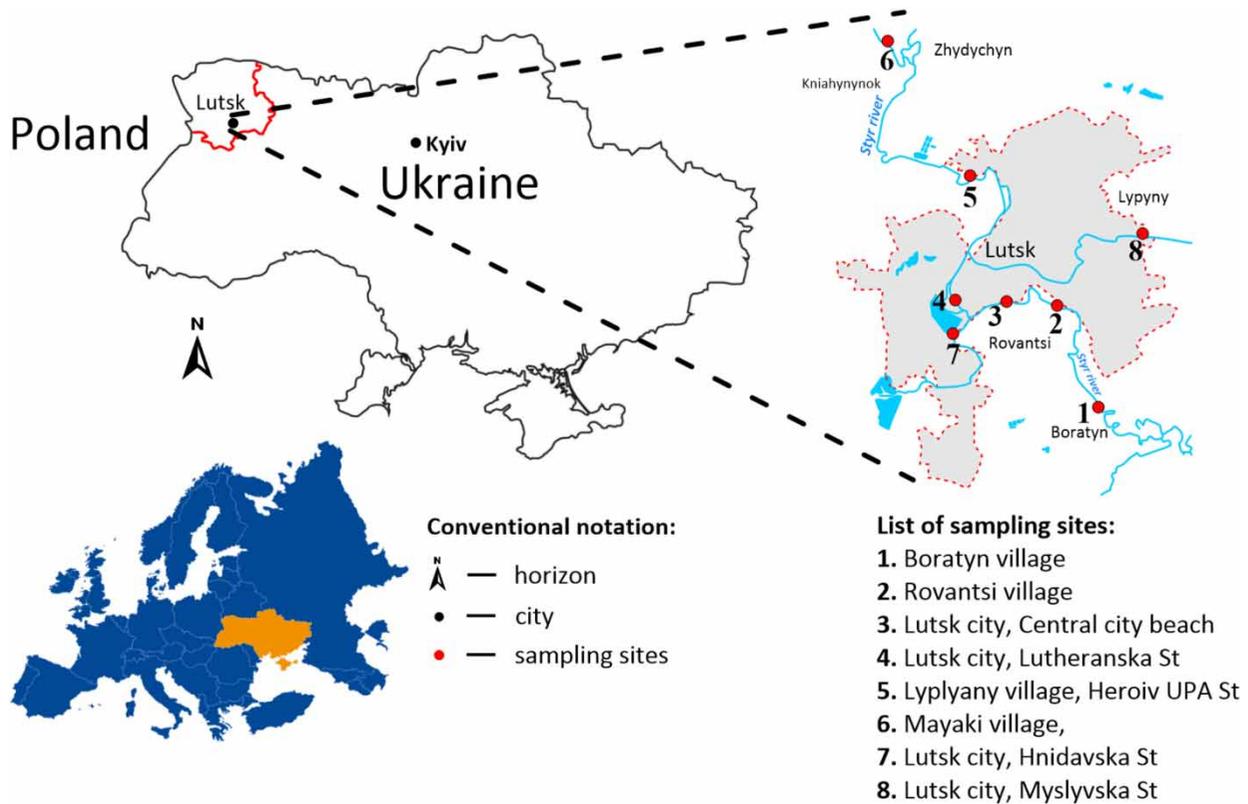
Samples 1–6 were collected on 25 June 2023, and samples 7 and 8 were collected on 26 June 2023. Edaphotopes and a water sample from the center of the riverbed were collected from a depth of 0–15 cm. The edaphic samples were taken following the standard (DSTU ISO 10381-1:2004). Water samples were collected in glass boxes, and edaphotope samples were collected in metal boxes, following common standards. The MPCs of heavy metals in rocks were compared with the data reported in publications (Kofanov & Ognianik 2008; Order of the Ministry of Health of Ukraine 2020). The environmental characteristics of the study sites are presented in Table 1.

The data on air temperature and lighting during the sampling in Lutsk revealed that there was a clear heat island within the city with a temperature of +29.5 °C in the center and a decrease in temperature near water bodies and sampling sites. The highest values of illumination also occurred in the central part of the city (61,000 lx) with a decrease outside the city and in the sampling areas (Figure 2).

The purpose of our research was to conduct ecological monitoring of heavy metals in the water and coastal edaphotopes of the Styr River within the city of Lutsk (Ukraine) and to identify possible factors associated with their entry into the water.

### 2.3. Research devices

The background radiation at the experimental sites was measured using the Soeks environmental detector by the provisions of the Radiation Safety Standards of Ukraine. The intensity of lighting was determined using a digital luxmeter with a remote sensor (model LX1010BS, measuring range 1–100,000 lx), with a measurement accuracy of  $\pm 4\%$  and an ambient temperature of  $-10$  to  $+50$  °C. Humidity and air temperature were determined using a UNI-T UT333 digital thermo-hygrometer



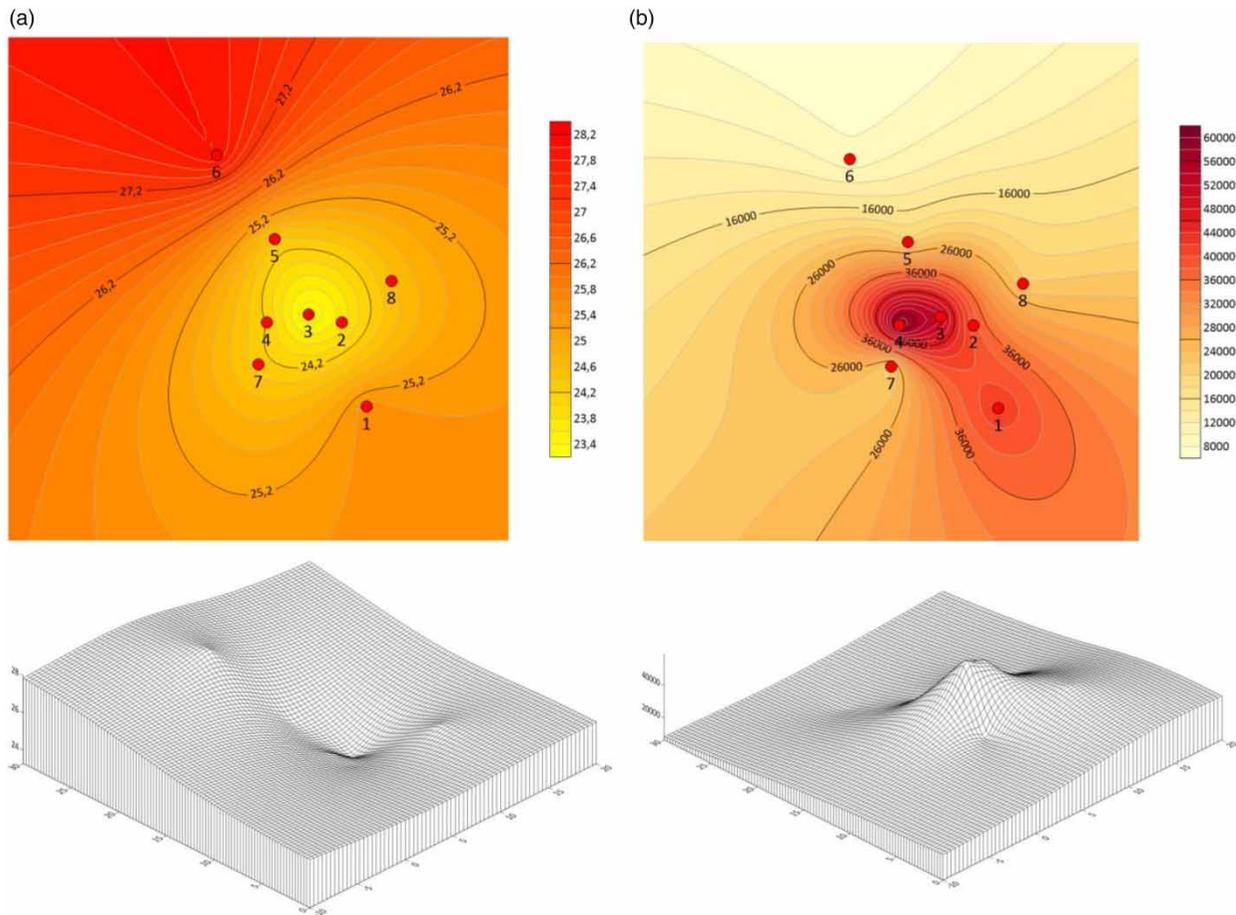
**Figure 1** | Hydrographic network of Lutsk with sampling marks.

**Table 1** | Environmental characteristics of the studied sections of the Styr River (June 2023)

Sample site	Sampling time	Lighting level (lx)	T air (°C)	W air (%)	T water surface (°C)	Radiation level (μSv/h)	Wind speed (m/s)
1. Boratyn (50.7089822 25.3747323)	12:30	42,000	25.5	52.8	23.8	0.08	3.9
2. Rovantsi (50.7366998 25.3581113)	12:55	38,500	23.7	56.5	21.1	0.22	3.6
3. Lutsk, Central city beach (50.7380890 25.3336791)	13:15	52,500	23.2	55.6	19.5	0.1	3.4
4. Lutsk, Lutheranska str. (50.737289, 25.313842)	13:40	60,800	24.2	52.8	22.7	0.11	2.1
5. Lypanyany, Heroiv UPA str. (50.7719745 25.3189323)	14:10	20,400	24.4	53.6	23	0.15	2.5
6. Mayaky (50.8069892 25.2842275)	14:35	8,700	28	44	26.2	0.11	2.8
7. Lutsk, Hnidavska str. (50.729680, 25.310865)	13:00	21,000	24.3	54.8	25.5	0.12	2.6
8. Lutsk, Myslyvska str. (50.756437, 25.392037)	13:45	22,100	24.6	55.1	26.4	0.13	2.5

(humidity 0–100%; temperature: –10 to +60 °C), with an error of  $\pm 1$  °C/  $\pm 5$ %. The wind speed was measured using a mini-anemometer HT-383, with a measurement accuracy of  $\pm 1.5$  m/s and a measurement range of 0–30 m/s.

The objectives of the study were to determine the quantitative content of heavy metals in the water of the Styr River in the hydrographic network of Lutsk, determine the quantitative content of heavy metals in the coastal edaphotopes of the river's hydrographic network, determine the level of heavy metal pollution of water and coastal edaphotographs, and propose measures for reducing the content of heavy metals in the water and coastal edaphotographs of the river.



**Figure 2** | Air temperature and lighting conditions in Lutsk city: (a) air temperature (°C) and (b) lightening (lx).

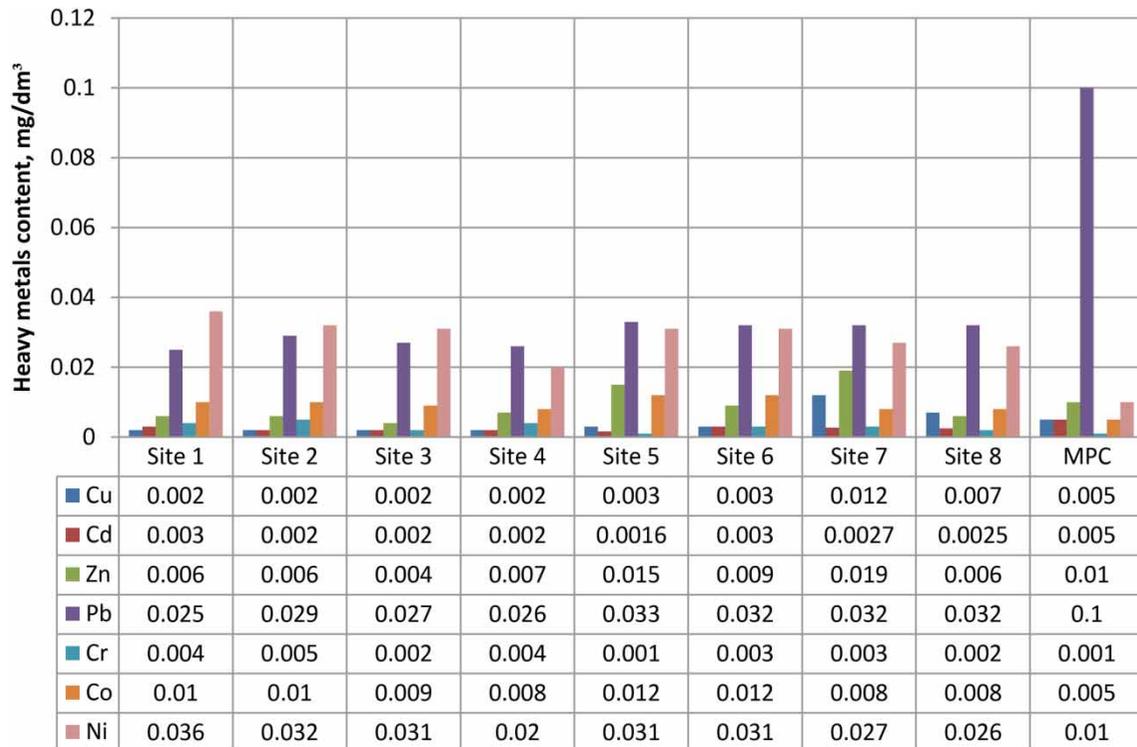
### 3. RESULTS AND DISCUSSION

#### 3.1. The content of heavy metals in water

The analysis of heavy metals in the water of the Styr River showed that the most polluted areas were those within the Hnidavske marsh and Teremniv ponds. These sites are characterized by stagnant water and have a slight leakage directly into the river. The Cu content exceeds the MPC ( $0.005 \text{ mg/dm}^3$ ) among the study sites –  $0.012 \text{ mg/dm}^3$  for Hnidavske marsh and  $0.005 \text{ mg/dm}^3$  for Teremniv ponds. The Zn level ( $0.01 \text{ mg/dm}^3$ ) exceeded the maximum permissible concentration (MPC) at site 5 (Lypnyany village, outside the city of Lutsk, the content was  $0.015 \text{ mg/dm}^3$ ) and Hnidavske marsh ( $0.019 \text{ mg/dm}^3$ ). At all study sites, Cr ( $0.001 \text{ mg/dm}^3$ ) ranging from 0.002 to  $0.005 \text{ mg/dm}^3$ , Co ( $0.005 \text{ mg/dm}^3$ ) from 0.008 to  $0.01 \text{ mg/dm}^3$ , and Ni ( $0.01 \text{ mg/dm}^3$ ) from 0.02 to  $0.036 \text{ mg/dm}^3$  were also found to exceed the MPC.

Exceedance of the MPC for Cd ( $0.005 \text{ mg/dm}^3$ ) was not observed and was within the normal range for all study sites ( $0.0016\text{--}0.003 \text{ mg/dm}^3$ ). The Pb content in water did not exceed the standard ( $0.1 \text{ mg/dm}^3$ ) and was in the range of  $0.025\text{--}0.033 \text{ mg/dm}^3$  at all study sites. Detailed data on the content of heavy metals in water at the study sites are shown in Figure 3.

Surface runoff from the cities changes surface water quality indicators (Aralu *et al.* 2024). A comparison of surface runoff and drainage shows that runoff per day into the Styr River from the city increases by 6–11 times with the average maximum amount of precipitation. Surface runoff carries pollutants into the rivers of Lutsk, which partially contributes to the pollution of their water. The level of water pollution in the Styr River also depends on the distance to the probable source of pollution.



**Figure 3** | Heavy metal content in the Styr River water (mg/dm<sup>3</sup>).

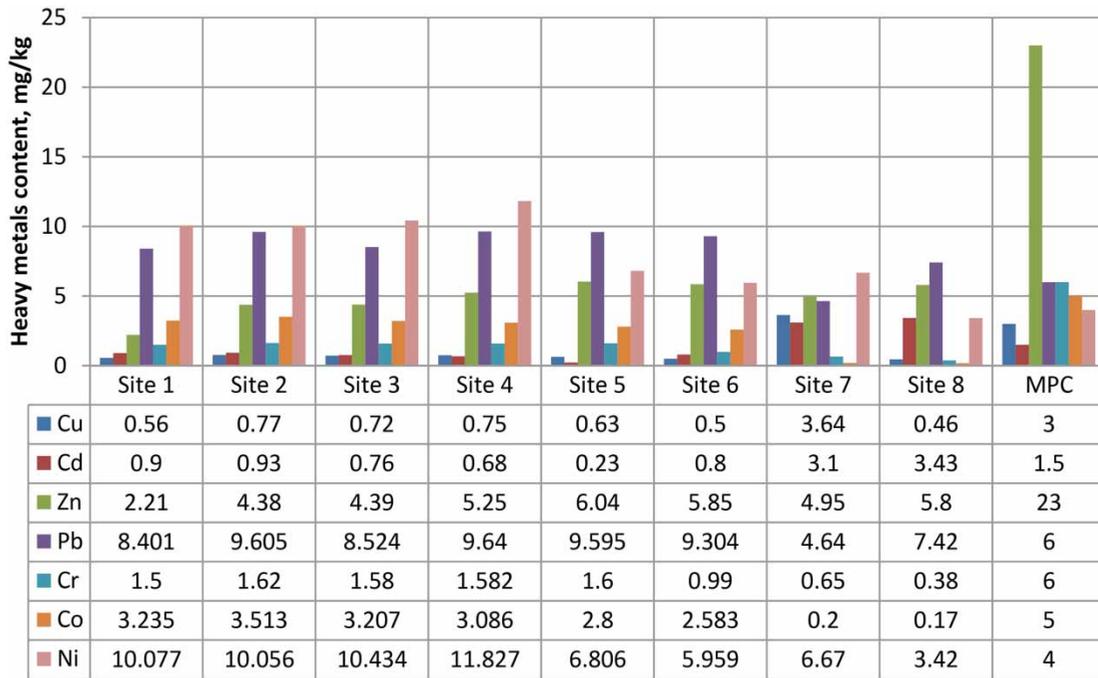
### 3.2. The content of heavy metals in edaphotopes

The results of the study of heavy metals in the coastal edaphotopes of the Styr River showed that the most polluted areas are those within the Hnidavske marsh and Teremniv ponds. The Cu content exceeded the MPC (3 mg/kg) only for the Hnidavske marsh site (3.64 mg/kg), and for the rest, it was in the range of 0.46–0.77 mg/kg. In particular, the Cd content exceeded the MPC (1.5 mg/kg) in the studied areas of edaphotopes – 3.1 mg/kg for Hnidavske and 3.43 mg/kg for Teremniv ponds. The Pb content did not exceed the MPC (6 mg/kg) only for the Hnidavske marsh site (4.64 mg/kg), and for the rest, it was in the range of 7.42–9.64 mg/kg. Exceedance of the MPC for Ni (4 mg/kg) was observed at all study sites, except for the Teremniv pond edaphotopes, which ranged from 6.67 to 11.827 mg/kg.

Exceedance of the MPC for Zn (23 mg/kg) was not observed and was within the normal range for all study sites of edaphotopes (2.21–6.04 mg/kg). The MPC for Cr (6 mg/kg) did not exceed at all study sites and was in the range of 0.38–1.62 mg/kg. The Co content did not exceed the MPC (5 mg/kg) and ranged from 0.17 to 3.513 mg/kg. Detailed data on the content of heavy metals in coastal edaphotopes in the studied areas are shown in Figure 4.

Cadmium compounds are extremely toxic even in small concentrations and, therefore, are classified as hazard class I. Exceedance of the MPC of cadmium in the soils of the coastal zone was detected at sites 7 (Hnidavske marsh) and 8 (Teremniv ponds). Zinc is a heavy metal of hazard class I. High migration of zinc in the soil is characterized by high humidity. Lead is also considered to be one of the most toxic chemical elements even in small quantities, and belongs to hazard class I. Zinc and lead contamination of the soils in the coastal zone of the Styr River and its tributaries is characterized by levels below the MPC.

Copper is a chemical element that belongs to heavy metals of hazard class II. It has low phytotoxicity but is very toxic to humans. In case of excessive intake in humans and animals, it is carcinogenic and has a toxic effect on the heart, blood, and other organs. The copper content in the soil exceeds the MPC at site 7 (Hnidavske marsh). Nickel is a hazard class II element that can cause acute and chronic poisoning if it contacts the skin and enters the respiratory system. In almost all areas, except for Teremniv Ponds, its content exceeds the MPC. The content of chromium, cobalt, and manganese in the soils of the coastal zone of the Styr River and its tributaries is characterized by low values.



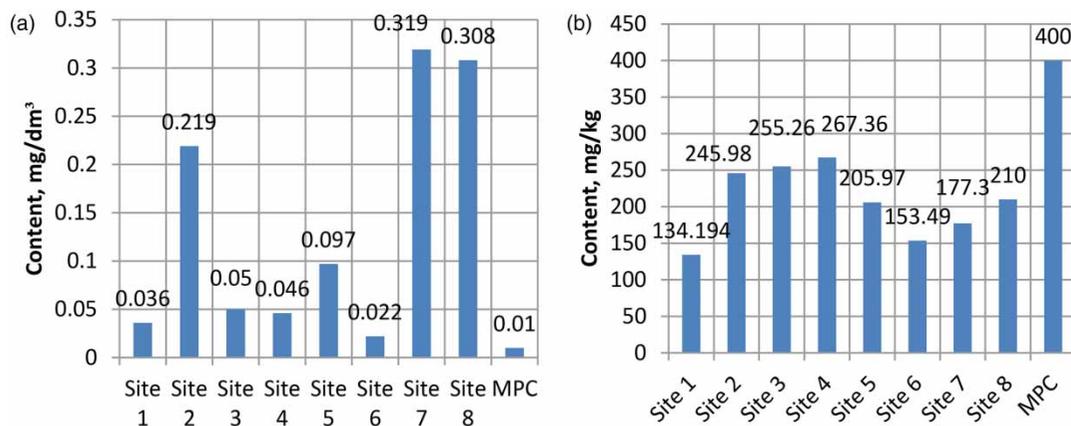
**Figure 4** | Content of heavy metals in the coastal edaphotopes of the Styr River (mg/kg).

Exceedance of the MPC for Mn ( $0.01 \text{ mg/dm}^3$ ) in water was observed in all studied areas and was in the range of  $0.022\text{--}0.097 \text{ mg/dm}^3$ . In the coastal edaphotopes, the Mn content was within the normal limit ( $400 \text{ mg/kg}$ ) and ranged from  $134.194$  to  $267.36 \text{ mg/kg}$  (Figure 5).

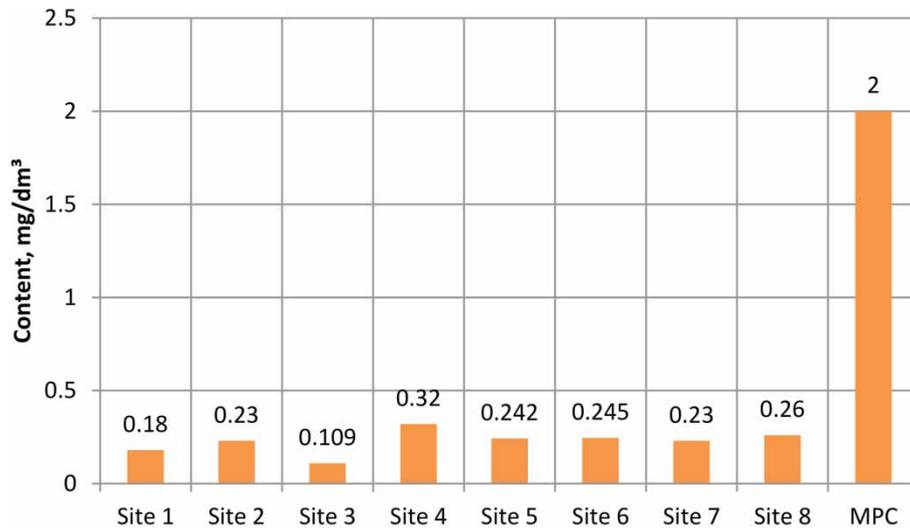
The distribution of heavy metals in the water and soils of the coastal zone of the Styr River and its tributaries is characterized by significant heterogeneity. The mosaic-like distribution of chemical elements depends on the distance to the source of pollution, the type of landscape (agricultural or urban), and the intensity of contaminated surface runoff from the surrounding area. Even within the same polluted area, water and soil can differ greatly in the nature and level (rank) of chemical contamination (Aswal *et al.* 2023).

### 3.3. Sr content in water

The Sr content in water does not exceed the limit ( $2 \text{ mg/dm}^3$ ) and varies from  $0.109$  to  $0.26 \text{ mg/dm}^3$  (Figure 6).



**Figure 5** | Mn content in water (a) and coastal edaphotopes (b) of the Styr River (within the area of Lutsk).



**Figure 6** | Sr content in the water of the Styr River (within the city of Lutsk).

Exceeding the MPC of heavy metals in water causes negative irreversible biochemical processes in the organisms of aquatic phytocoenoses, fish, animals, and humans. Scientific research (Shahjahan *et al.* 2022) has analyzed the effects of heavy metals on fish physiology, paying special attention to hematobiochemical properties, immunological parameters, and basic molecular mechanisms. Researchers concluded that all these indicators are significantly affected by heavy metals and are key biomonitoring tools for assessing their toxicity. The main organs of fish, such as the gills, liver, and kidneys, including the intestines and muscles, showed different organ-specific pathologies under the influence of acute and chronic exposure to different heavy metals.

Our research results showed that the water in the Styr River and the reservoirs of its hydrographic network is contaminated with Cu, Zn, Cr, Co, Mn, and Ni. Exceeding the MPC of Cu in water causes abnormalities to the skeletal and vascular system (anemia, hemorrhages), reduced pigmentation, missing eyes, reduced viability of embryos and larvae, scoliosis, and tail curvature in fish. Zn causes low hatching rates, high mortality, abnormal pigmentation, hooked tail, and spinal deformities. Exceeding the MPC of Cr in water leads to reduced viability of embryos and larvae, and morphological changes (C-shaped body) (Taslina *et al.* 2022). It is clear that heavy metals affect aquatic and coastal aquatic phytocoenoses. In particular, an increase in the concentration of heavy metals in plants leads to the deformation of their organs, reduced fruiting and development, and ultimately to death.

The national security of every state is multifaceted and includes fresh water resources. In the context of sustainable development, preserving natural water resources is a pressing issue today. This is one of the top priorities of humanity, as described by the UN Development Program. Without water conservation, further development of humanity is impossible. The most important task is to preserve water resources in countries that suffer from a shortage of drinking water and in countries where military operations are underway. As a result of hostilities, natural resources are destroyed, and the environment, including surface and groundwater, is polluted by hazardous substances and chemical warfare agents. Therefore, the relevance of the presented research is undeniable.

#### 4. CONCLUSIONS

The study of heavy metal content in the Styr River and coastal edaphotographs of the hydrographic network revealed that the most polluted water was in the Hnidavske marsh and Teremniv ponds. This situation is primarily due to the fact that the water does not have sufficient self-purification due to the slow productivity of reservoirs and low runoff, which causes stagnation and accumulation of heavy metals in excessive amounts. Among those that exceed the permissible limits in water are Cu, Zn, Cr, Co, Mn, and Ni; in coastal edaphotopes, Cu, Cd, Pb, and Ni exceed the limits. To prevent pollutants from entering the water of the Styr River, it is necessary, first of all, to analyze the content of heavy metals in the wastewater discharged into the river from enterprises and housing and communal services of the city. It is also necessary to modernize the wastewater

treatment facilities and provide for a set of measures to treat wastewater entering rivers, including the construction of geo-mechanical barriers in certain areas of water discharges into rivers.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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