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Assessment of heavy metal contentin water bodies of Zhytomyr Oblast

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Abstract. Pollution of water bodies with heavy metals can lead to the death of fish and other aquatic organisms, a decrease in biodiversity and a threat to ecosystems, emphasising the importance of preserving the natural environment; pollution of water bodies can have serious economic consequences, in particular, a decrease in profits from fishing, tourism, and other activities related to water use, which requires the development of water management strategies. The purpose of the study was to determine the general trends in the content of heavy metals in the surface waters of the Teteriv River and fattening pond No. 1 of the LLC "SHF INTERRYBHOSP". Water samples were taken at the stream of the Teteriv River (Vidsichne Reservoir) and in the fattening pond No. 1 at a depth of 0.2-0.5 m from the surface for further laboratory analysis of the content of heavy metal ions (HM). The atomic absorption method of analysis was used to study water. Laboratory studies of surface waters in the Teteriv River and pond were performed according to the following indicators: hydrogen index (pH), lead, cadmium, manganese, zinc, and iron content. The results of the study of the content of heavy metals in the Teteriv River are presented, which showed that the content of such heavy metals as: Pb, Cd, Mn, Zn and Fe, in river water, with the exception of iron, exceed the limits of maximum admissible values of water quality indicators for fishery water bodies. Background HM indicators from fattening pond No. 1 did not show an excess of the MAC (maximum admissible concentration). High concentrations of lead, cadmium, manganese, and iron are explained by powerful anthropogenic pollution, the source of which is agricultural and industrial complexes of Zhytomyr Oblast. The results can be used to establish effective monitoring of water quality in reservoirs and develop strategies to reduce pollution in aquatic ecosystems

Keywords: water environment; aquatic organisms; background indicators; pollution; rivers

Introduction

Rivers perform various ecological functions, such as water transport, ecotourism, aquaculture, and influence the restoration of ecological balance (Ali *et al*., 2022). The studies by V. Aghadadashi *et al.* (2019), L.M. Cai *et al.* (2019) and M. Hossain *et al*. (2020) found that heavy metals (HM) such as lead, cadmium, mercury, chromium, nickel, etc., can accumulate in biological systems and be toxic even at low concentrations. Heavy metals pose a serious environmental threat to living organisms and aquatic ecosystems due to their inability to decompose, bioaccumulate, environmental stability, persistence, and biotoxicity. According to Y. He *et al.* (2019), HMs affect the physical and chemical properties of sediment and water, inhibiting microbial activity after release from the source. The study by M. Lian *et al*. (2019) indicates that HMs are harmful to the ecological environment through the food chain and have acute and chronic effects on the human body. Studies conducted by M.J. Kang *et al*. (2019) and H.E. Nour *et al*. (2019) confirm that HMs that do not decompose accumulate and remain in surface sediments for a long time, causing numerous diseases and complications in the human body.

Natural activities (e.g. geological weathering, precipitation, wave erosion, wind and bioturbation) and anthropogenic activities (e.g. rapid industrialisation, urbanisation, and agricultural runoff) play a key role in the spread of HMs in aquatic ecosystems such as rivers. In addition, human activity, which can cause industrial emissions, household waste generation, and extensive use of chemical fertilisers and pesticides, contributes to the accumulation and deposition of HMs in the surface sediments of aquatic ecosystems – this was confirmed by P.K. Lee *et al*. (2019), J. Rinklebe *et al*. (2019). Water quality is negatively affected

by HMs entering the water column, and surface sediments that change environmental parameters such as pH, temperature, salinity, etc.

The use of water resources is usually accompanied by a deterioration in their quality due to anthropogenic stress. This is manifested not only in changes in the physical and chemical composition of waters, but also in the quantitative and qualitative characteristics of aquatic organisms inhabiting reservoirs and watercourses. Rivers experience different anthropogenic loads depending on economic activity in the regions. This can include exhausting water abstraction for the needs of the population and households, discharge of wastewater from enterprises and housing and communal services, use of rivers as navigable arteries, construction of hydraulic engineering structures, etc. (Mosiienko, 2022a).

Considering the described events, the relevance of assessing the content of heavy metals in the surface waters of the Teteriv River is confirmed. The discharge of untreated wastewater containing heavy metals into the Teteriv River channel results in the saturation of water environment and aquatic life with toxic substances. The harmful effects of toxic HMs cover not only water, but also aquatic organisms and people who constantly use water and fish for food. Therefore, practical studies were conducted in the context of assessing the content of heavy metals in water and their impact on aquaculture.

Materials and Methods

The study was conducted in 2023, the water temperature of the Teteriv River at the time of sampling was +18°C, and the hydrogen index (pH) – 7.70 units. The water temperature from the pond was +16°C, the hydrogen index (pH) – 7.38 units. The object of the study was the surface waters of the Teteriv River and the surface waters of the fattening pond No. 1.

Water sampling was carried out according to the generally accepted method (Arsan *et al*., 2006). Samples were collected at the stream of the Teteriv River (Vidsichne Reservoir), 2.5 km downstream of Zhytomyr, and in the fattening pond No. 1. Random elements (the surface layer of water with random pollutants) were excluded during the selection process. Samples were taken below the surface layers (0.2-0.5 m) using a wide-mouth beaker with a rod. The volume of the water sample was 2 litres. The main sample was taken in plastic bottles. The main condition for taking water samples was clean dishes. The dishes were thoroughly washed in advance with a chromium mixture (0.3 n solution of potassium bichromate in concentrated sulphuric acid) and rinsed with tap water, after which they were washed at least three times with distilled water and dried in a drying cabinet. The same applied to plugs. Before taking the sample, the dishes were rinsed several times with water that was taken for analysis. Each water sample was labelled with the place, time, depth, sampling horizon, temperature, and the name of the person who took the sample.

The research was conducted in the Measurement Laboratory of the Educational and Scientific Centre for Ecology and Environmental Protection, located at the Polissia National University. Laboratory studies of surface waters in the Teteriv River were performed according to the following indicators: hydrogen index (pH), lead, cadmium, manganese, zinc, and iron content. A portable DLS-02 pH meter was used to determine the hydrogen index (ph). Before measuring, the electrode was first washed with distilled water, and then with test water, and only then immersed in the sample. Before immersion of the electrode, a sample of water was mixed so that its composition on the surface of the electrode corresponded to the general composition. In addition, a WSD-12 thermometer was immersed in the sample together with the electrodes to measure the temperature.

Samples were analysed for heavy metal content in accordance with the methods (Pupyshev, 2014) using atomic absorption

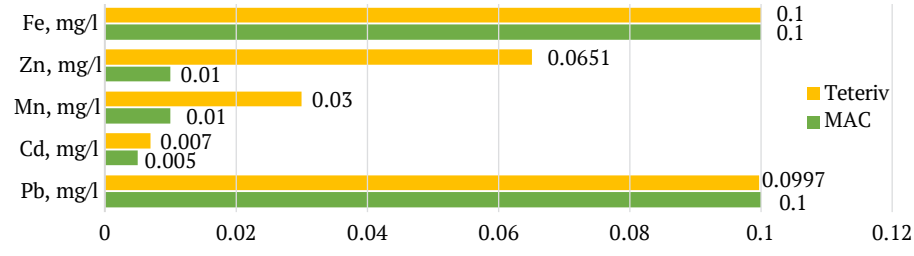
spectrophotometry (AAS) on the C-115M1 instrument. The atomic absorption method was used for water analysis, as this method has a high sensitivity of element determination, allows conducting an analysis with a high salt content, can be used in the emission mode, is highly reliable, has an automatic gas system, a light optical system, displays information on a digital indicator in units of optical density or concentration, and has electrothermal atomisation at a speed of 3-4 minutes. Statistical data analysis and chart generation were performed in the Statistica and Microsoft Excel software suites.

Results and Discussion

The Teteriv River, a right-bank tributary of the Dnipro, stretches for 365 km and has a water intake area of 15,100 km². Its water regime mainly depends on meltwater, which leads to high spring floods and low summer-autumn low water, which are often disturbed by short-term rain floods. Geographically, the Teteriv basin is located on the territory of the Ukrainian Shield and its slope, which extends into the Dnipro-Donetsk depression. This led to a higher hypsometric position of the river in comparison with other areas of the Ukrainian Polissia, and to the appearance of narrow and deeply embedded river valleys and a small number of swamps (only 4.5% of the total area of the river basin). The soil cover of the basin includes northern chernozems in the upper reaches and podzolic soils in the middle and lower reaches (Kuzminchuk & Shcherback, 2004).

Many studies have been conducted on anthropogenic contamination of river waters with both biogenic elements and surfactants (synthetic surfactants), pesticides, etc. Most of these studies were directly related to basins of big (for example, Dnipro, Dnister) (Strokal & Kovpak, 2021; Skyba *et al.*, 2023), small (Bosak *et al.*, 2020; Nahaieva *et al.*, 2020), and medium-sized rivers in various regions (Loboda & Kuza, 2023; Ukhan & Osadcha, 2023). However, the topic of analysing water pollution in the Zhytomyr Oblast remained rather neglected.

The analysis of the surface waters of the Teteriv River revealed that the background values of HMs were either at the MAC level or above the admissible values (Fig. 1). Lead and its compounds are essential components of surface waters and significantly affect their quality and functioning (Makarenko *et al.*, 2021). Many of these compounds are known for their mutagenic and carcinogenic properties. Lead enters rivers through wastewater from metallurgical and chemical enterprises, and as a result of coal burning, which was confirmed by M. Clarholm & U. Skyllberg, (2013), A.M. Iordache *et al.* (2022); K. Mashkova *et al.* (2022).



	Pb, mg/l	Cd, mg/l	Mn, mg/l	Zn, mg/l	Fe, mg/l
Teteriv	0.0997	0.007	0.03	0.0651	0.1
MAC	0.1	0.005	0.01	0.01	0.1

Figure 1. Comparison of HM concentrations in the water of the Teteriv River (Vidsichne Reservoir) with the MAC

Source: developed by the author

Based on the results of research, it can be noted that the background indicator of lead in the surface waters of the Teteriv River, which affects the activity of certain enzymes and intercellular communication in aquatic organisms, corresponded to the MAC and amounted to 0.0997 mg/l.

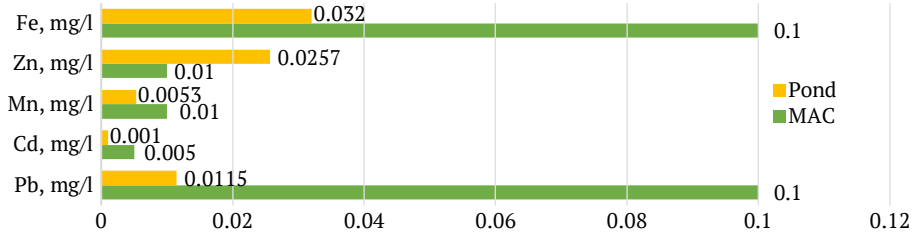
Cadmium in nature is mainly found in zinc and lead ores. It often enters water bodies as part of industrial wastewater from lead-zinc plants, chemical industry enterprises, ore processing facilities and metallurgical plants. The cadmium content did not significantly exceed the maximum admissible concentration of 0.007 mg/l, but this poses risks for structural and functional changes in the gills, intestines, liver and kidneys, stagnation and swelling of blood vessels in fish.

Manganese is one of the biologically active metals involved in the reactions of water photolysis and photosynthesis. The most common sources of manganese in a water body are iron and manganese ores, wastewater from metallurgical plants, water discharged from chemical plants, and mine water. In addition, one of the sources of manganese intake is organic residues that remain after the death of aquatic organisms and higher aquatic plants (Makarenko *et al.*, 2021; Mashkova *et al.*, 2022). Excess of manganese – 0.03 mg/l according to the results of laboratory tests, can affect the haematopoietic organs, which negatively affects the haemolytic parameters of fish blood.

Zinc, in terms of concentration in surface fresh waters, ranks second after manganese. The main source of zinc intake in water bodies are the processes of rock destruction. Since zinc is a biogenic metal, it is actively absorbed by aquatic plants and participates in photosynthesis. Zinc is a vital metal, but it can be toxic to fish, causing structural damage that affects growth, development, behaviour, and survival, as noted by O. Prokopchuk & V. Hrubinko (2016) and A. Makarenko *et al.* (2021). The content of zinc exceeded the maximum admissible concentration and amounted to 0.0651 mg/l, its intake in the Teteriv River could have occurred as a result of untreated wastewater from a pulp and paper mill and a cardboard factory. The accumulation of zinc, unlike other metals, is associated with its geochemical mobility.

Iron is one of the most common elements, but its concentration in natural waters is extremely low due to its limited migration capacity. It plays an important role in the vital activity of aquatic organisms and is largely absorbed by them. Iron deficiency can cause a number of diseases or even lead to death. Iron mainly comes from agricultural complexes located near the river, namely through drains (Rabcheniuk, 2016). The background iron index corresponded to the MAC of 0.1 mg/l, but was at the limit, which makes water of little use for the life of aquatic organisms. The results of the study confirm the assumption about the unsatisfactory state of water in the Teteriv River, and as a result, its harmful effect on aquatic organisms.

According to the results of laboratory studies, the background indicators of lead, cadmium, manganese, zinc, and iron in the water from fattening pond No. 1 did not exceed the maximum admissible concentration (MAC), in contrast to the background HM indicators in the Teteriv River. The maximum admissible concentration of heavy metals in fattening pond No. 1 indicates compliance with the technological requirements of ponds (Fig. 2).The analysis of the obtained concentrations of heavy metals in the reservoir shows that the content of some of them in the Teteriv River exceeded the MAC, which caused a violation of the ecological balance. After analysing the literature sources, it can be concluded that insufficient attention has been paid to studies of the content of heavy metals in the reservoirs of the Zhytomyr Oblast. There are fragmentary data from similar studies.



	Pb, mg/l	Cd, mg/l	Mn, mg/l	Zn, mg/l	Fe, mg/l
Pond	0.0115	0.001	0.0053	0.0257	0.032
MAC	0.1	0.005	0.01	0.01	0.1

Figure 2. Comparison of HM concentrations in water from the fattening pond No. 1 with MAC
Source: developed by the authors

The research was conducted during the period from 2006 to 2011 on the territory of the Polissia part of the Zhytomyr Oblast. The object of the study was the water of 13 small rivers. In the rivers of Zhytomyr Polissia, which mainly flow within the Ukrainian Shield, the water during the summer-autumn low-water period contained small concentrations of heavy metals, such as copper (Cu), cadmium (Cd), lead (Pb), zinc (Zn), Cobalt (Co), and nickel (Ni). However, there is an exception for manganese (Mn) and iron (Fe), whose concentrations exceed the maximum admissible values by 1.2-6.8 times and 1.5-12.3 times, respectively. This is conditioned by natural factors, such as the conversion of primary minerals to secondary ones, which leads to the release of iron and manganese compounds. In addition, iron and manganese can be washed out of iron-manganese nodules, which are often contained in the iluvial horizon of sod-podzolic soils in the study area, which was established by T.M. Myslyva & I.S. Kot (2011). The highest content of manganese, namely 0.63-0.68 mg/dm^3, was observed in the Zlobych and Irshytsya rivers. As for iron, the highest values, namely 2.12-3.71 mg/dm^3, were recorded in the Zheriv and Zlobych rivers.

In Korostyshiv District, the main water polluters of the Teteriv River are the Korostyshiv Municipal Utility Company "Vodokanal", which discharged 353.9 thousand m^3 of wastewater into water bodies in excess of the MAC, and the Korostyshiv Distillery. General and specific indicators were selected to assess the water quality of the Teteriv River. The research was conducted during 2010-2013. It was found that the manganese content significantly exceeded the norm. The highest value of this indicator was recorded in 2013, which was 0.068 mg/dm^3. The lowest rates were recorded in 2012, which amounted to 0.022 mg/dm^3. The study by N.S. Bordiug & L.M. Kostrytsia (2014) found that the iron content in the water of the Teteriv River in the Korostyshiv District exceeded the established MAC, which is a consequence of anthropogenic impact. In 2010, the highest concentration of it was detected, which was 0.47 mg/dm^3. It was found that in 2012, its content sharply decreased to the lowest value for the entire study period – 0.3 mg/dm^3.

When conducting studies of the Teteriv River within the Radomyshl District of Zhytomyr Oblast from 2006 to 2015, a sharp increase in the concentration of manganese was detected, in particular in 2014 and 2015, when its content in water was 7.3 and 8.8, compared to this, in 2008 the lowest value was observed, only 1.4 in MAC units. As for iron, the maximum content in general was recorded in 2008, when the indicator was 4.9 in MAC units. Instead, the lowest values were recorded in 2007 and 2015, when iron concentrations were 3.1 and 3.6 in MAC

units, respectively, as established by G.M. Marteniuk (2013). According to the data obtained, the concentration of manganese and iron in the rivers of Polissia exceeds the maximum admissible concentration by 2-12 times and 2-10 times, respectively.

In 2021, the Teteriv River, which is a source of water supply for Zhytomyr Oblast, experienced an eco-disaster due to extremely low precipitation, which led to a critical drop in the water level. Residents have about 1-1.5 months of water supply left. Over the past two years, the Teteriv River has been suffering from a large amount of untreated sewage entering it. Zhytomyr Oblast has a significant industrial and agricultural complex, which are often sources of pollution of water bodies, in particular the Teteriv River. According to the ecological certificate, there are 11 enterprises in the Zhytomyr Oblast that are the most polluting and have a negative impact on the region's water resources (Mosiienko, 2022). Zhytomyr Thermal Insulation Plant, Zhytomyr Cardboard Factory, PJSC Beer-Non-Alcoholic Plant "Radomyshl", PJSC "Bio Med Sklo", LLC "Cersanit Invest", PJSC "Ushitsky Construction Materials Plant", PJSC "Pershotravensk Electrotechnical Porcelain Plant" and other facilities are environmentally hazardous and can cause pollution of water basins in this region.

In 2021, the amount of conditionally clean non-treated return water discharged increased by 3.2% compared to 2020. The municipal enterprise of Zhytomyr in 2021 and in 2022 more than once discharged untreated wastewater from a sewage pumping station containing excess MAC of heavy metals in surface, return, and wastewater. As a result of the discharge in 2021, almost 120,000 m^3 of untreated wastewater entered the river basins of the Zhytomyr Oblast, which led to massive fish death, with more than 15,000 fish specimens dying. The water contained 4 times the normal amount of lead, 3 times the normal amount of phosphate, and 5 times the normal amount of nickel and nitrate, which led to a massive fish death. Among the aquatic inhabitants of the Teteriv River, which suffered the most destructive effects of heavy metals, were the silver carp *(Hypophthalmichthys molitrix)*, common carp *(Cyprinus carpio)*, northern pike *(Esox lucius)*, European perch *(Perca fluviatilis)*, etc. These fish species are most sensitive to increased toxicity in the aquatic environment. In August 2022, an oxygen deficiency was recorded in the Vidsichne Reservoir, and an excess of the concentration of manganese by 2.7 times and iron by 12.3 times, compared to the admissible values. Pollution of aquatic ecosystems poses a serious threat to the ichthyofauna, and can also lead to an excess of pollutants in fish products, which poses a risk to human health (Mosiienko, 2022b). Fish play a key role in aquatic ecosystems, occupying the upper trophic level. It is an important chain in maintaining the ecological balance of aquatic environments. However, through bioaccumulation and biomagnification processes, fish can accumulate pollutants, including heavy metals, from the water or from the living organisms it consumes. This creates a serious risk to the health of the person who consumes such fish. Therefore, it is important to control the level of pollution of water bodies and take measures to preserve their environmental integrity.

Conclusions

According to the results of the study, the background level of lead in the surface waters of the Teteriv River met the MAC and was 0.0997 mg/l. The cadmium content did not significantly exceed the MAC of 0.007 mg/l. The results of laboratory tests revealed an excess of manganese of 0.03 mg/l. The zinc content exceeded the MAC and amounted to 0.0651 mg/l. The background iron level met the MAC of 0.1 mg/l, but was at the limit. Studies confirm the assumption of an unsatisfactory state of water in the Teteriv River. This can lead to a decrease in the number and diversity of aquatic life, including fish, invertebrates, and algae; disrupt the natural

balance of the ecosystem and cause a decrease in biodiversity.

The results of laboratory tests show that the background values of lead, cadmium, manganese, zinc, and iron in the test water from the fattening pond No. 1 did not exceed the maximum admissible concentration (MAC). Low levels of heavy metals in the water indicate that water from fattening pond No. 1 is safe for human consumption and use. It can be assumed that as a result of the armed aggression against Ukraine, agriculture has suffered heavy losses and reduced its capacity, but still remains one of the key economic sectors of Ukraine. The anthropogenic impact on the Teteriv River channel was established. The activities of enterprises and agriculture lead to an increase in the accumulation of heavy metals in water, so it is recommended to establish measures to reduce the anthropogenic load on the ecosystem of the Teteriv River.

The study highlights the need for measures to prevent further pollution of the region's river systems. In particular, these measures include: establishing systematic control over the use of water by enterprises and organisations, and monitoring the discharges of industrial and agricultural waste; increasing attention to issues related to the prevention of pollution and salinisation of surface and underground waters; conducting experimental studies of the content of heavy metals. These measures focus on preserving and protecting the region's water resources and ensuring an environmentally friendly environment for aquatic life.

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Conflict of Interest

None.

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Оцінка вмісту важких металів у водоймах Житомирської області

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Анотація. Забруднення водойм важкими металами може призвести до загибелі риби та інших водних організмів, зменшення біорізноманіття та загрози екосистемам, що підкреслює важливість збереження природного середовища; забруднення водних об'єктів може мати серйозні економічні наслідки, зокрема зниження прибутку від рибальства, туризму та інших діяльностей, пов'язаних з використанням води, що вимагає розробки стратегій управління водними ресурсами. Мета роботи полягала у визначенні загальних тенденцій вмісту важких металів у поверхневих водах р. Тетерів та нагульному ставу №1 ТОВ «СГФ «Інтеррибгосп». Відбір проб води проводився на струмені потоку р. Тетерів (водосховище Відсічне) та в нагульному ставу №1 на глибині 0,2–0,5 м від поверхні для подальшого лабораторного аналізу щодо вмісту іонів важких металів (ВМ). Для дослідження води застосовано атомно-абсорбційний метод аналізу. Лабораторні дослідження поверхневих вод р. Тетерів та ставу проводили за такими показниками: водневий показник (pH), вміст свинцю, кадмію, марганцю, цинку та заліза. Представлені результати дослідження вмісту важких металів у р. Тетерів, які показали, що вміст таких важких металів як: Pb, Cd, Mn, Zn та Fe, у річковій воді, за винятком заліза, перевищують межі гранично допустимих значень показників якості

води для рибогосподарських водойм. Фонові показники ВМ з нагульного ставу №1 області не показали перевищення ГДК (гранично допустима концентрація). Високі концентрації свинцю, кадмію, марганцю та заліза пояснюються потужним антропогенними забрудненнями, джерелом яких є аграрні та промислові комплекси Житомирщини. Результати можуть бути використані для встановлення ефективного моніторингу якості води у водоймах та розробки стратегій зменшення забруднення водних екосистем

Ключові слова: водне середовище; гідробіонти; фонові показники; забруднення; річки