Mon23-066

Dynamics of heavy metal compounds allocation in urbohydrotops of Kyiv region in post-military conditions

***I. Tsyhanenko-Dziubenko** *(Zhytomyr Polytechnic State University)*, **H. Kireitseva** *(Zhytomyr Polytechnic State University)*, **L. Demchuk** *(Zhytomyr Polytechnic State University)*

SUMMARY

The Russian-Ukrainian war, which began in 2014 and is still ongoing, has had numerous consequences not only in terms of humanitarian, political and economic impacts, but also in terms of its impact on various ecosystems, including aquatic ones. The main aspects of this impact include: pollution, physical damage, loss of biodiversity, species migration, and changes in water quality. The hostilities have led to the destruction of infrastructure, resulting in the release of oil products, chemicals and other pollutants into water bodies. Military ammunition, especially older models, can contain heavy metals such as lead, copper and zinc. The use of ammunition in or near water bodies can lead to the release of chemical contaminants into the environment. The explosion and subsequent fall of military munitions can lead to the deposition of residues containing trace heavy metal compounds. Wastes generated by the military, including spent ammunition, scrapped or damaged equipment and other debris, can enter water bodies, especially if not properly managed or disposed of. Mitigating the impact of heavy metals in water bodies requires joint efforts from both military and environmental agencies. Regular monitoring, safer disposal methods, remediation efforts, and public awareness, are important components of the solution. The aim is to analyze the dynamics of the heavy metal compounds allocation in urbohydrotops of Kyiv region in post-military conditions and develop practical approaches to restore the war-tainted aquatic ecosystems of the Kyiv region. Given the geopolitical situation, Ukraine has found itself in, since 2014, it's evident that military operations could have had significant impacts on its hydro ecosystems. A thorough assessment (within the dynamic aspect) will be beneficial not only for Ukraine but for the global community, as it offers a chance to understand and learn from the ecological impacts of military operations.

Introduction

Military operations affect the environment as a complicated multifactor complex of factors (*Kireitseva, 2023*). At the same time, the ecosystems that are under their pressure are complex dynamic systems that respond to external influences as a single entity. Therefore, to assess the impact of military operations, we should not focus only on a limited number of individual factors, but should consider all key changes as a system. At the same time, we need to modelize the impact of these changes in the future (*Demchuk, 2022*). During military operations, the environment is susceptible to the destructive pressure, affects by numerous different factors – physical, chemical and biotic (*Atiyeh, Gunn, Hayek, 2007*).

The aim is to analyze the dynamics of the heavy metal compounds allocation in urbohydrotops of Kyiv region in post-military conditions and develop practical approaches to restore the war-tainted aquatic ecosystems of the Kyiv region.

To achieve the aim of the research, we set the following tasks:

- to analyze the data of hydrochemical analysis and chemical analysis of bottom sediments of post-militant water bodies in the Bucha district for 2022;
- conduct chemical analysis of field samples of post-militarised water bodies in 2023;
- to analyze the dynamics of the content of heavy metal compounds in the aquatic environment and bottom sediments of the studied post-militant urbohydrotops in the Kyiv region using the methods of variation statistics.

Method and Theory

Quality sampling of river waters and bottom sediments was carried out in July 2022 and July 2023 from the fishing and recreational lakes in Moshchun, Bucha district, Kyiv region (fig. 1, 2) according to the current methodological recommendations. Chemical analysis was carried out according to the established standard analytical-chemical methods. Quantitative and qualitative determination of the heavy metal compounds content was conducted with the help of the Atomic emission spectroscopy (AES). AES is a robust and powerful technique for the determination of heavy metals in surface waters and sediments, offering high sensitivity and the ability to analyse multiple elements simultaneously. Proper sample preparation, calibration, and understanding of potential interferences are essential for accurate and reliable results. Advantages for Heavy Metals Determination are high sensitivity and low detection limits. Simultaneous multi-element analysis is possible, especially with ICP-AES. AES operates on the principle that atoms in excited states emit radiation of characteristic wavelengths when they return to a lower energy state. Here are the technological characteristics and considerations for using AES to determine heavy metal content in surface waters and sediments:

- The most common sources are flames (like air-acetylene or nitrous oxide-acetylene flames) and plasma sources (such as Inductively Coupled Plasma or ICP).
- Optical System consists of monochromators and detectors. The monochromator separates the Emitted radiation into its component wavelengths and the detector measures the intensity of each wavelength.
- Sample Introduction. For surface waters, a nebulizer and spray chamber are commonly used.

- For sediment's samples are typically converted to liquid form through extraction or digestion procedures before being introduced into the instrument.

- AES, especially when coupled with ICP (ICP-AES), has excellent detection limits, often in the parts-per-billion (ppb) range for many heavy metals.

Figure 1 *Fishing lake near the village Moshchun.*

Figure 2 *Recreational lake near the village Moshchun.*

Results

Heavy metals are classified according to their toxicity. Scientists identify three main groups, namely, essential (those that are included to meet the physiological and biochemical needs of living organisms), non-essential (those that have lost their toxicity) and trace (highly toxic) (*Gandziura, 2021*). In 2022 and 2023, the presence of 4 heavy metals, namely Fe^{2+}, Mn^{2+}, Cu^{2+}, Al^{3+} (*Maksymenko, 2022*), was detected in the water environment of both lakes of the study area (fig. 3).

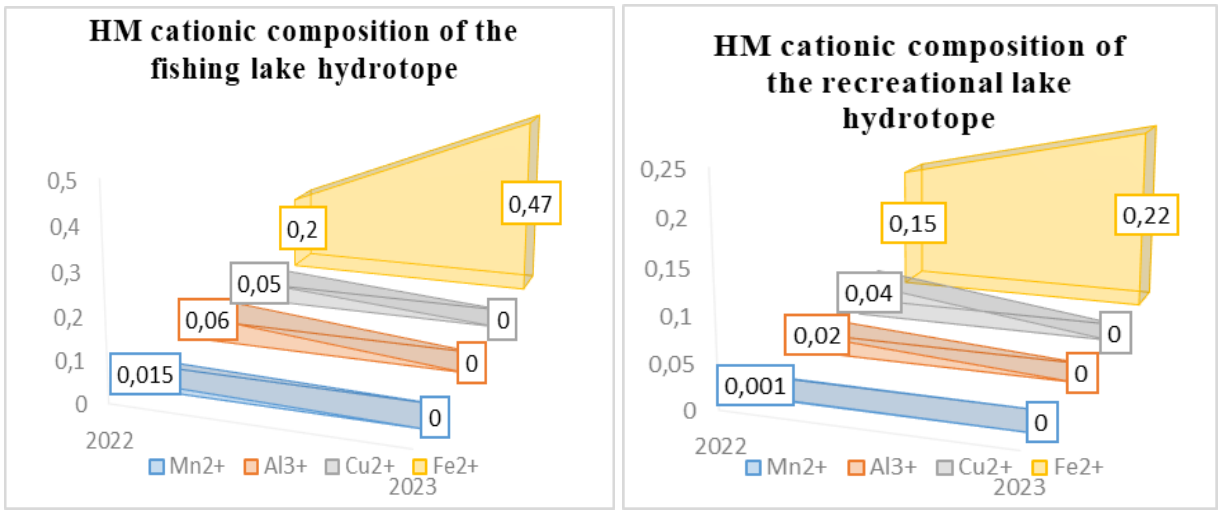

Figure 3 *Dynamics of the heavy metal compounds of water surfaces of the village Moshchun*

It is worth noting that in both reservoirs, an annual increase in the content of Fe^{2+} compounds were recorded (in the fishing lake, an increase of 135%, and in the recreational lake, an increase of 46.67%). There are several main reasons for this phenomenon, which are related to the consequences of military operations in the study area in 2022, namely the long-term effects of destruction, slow decomposition of waste after military operations, large areas of destroyed cover may be left behind, causing erosion. This can lead to a constant flow of iron from soils to water bodies, especially during rain events. Remnants of military equipment, ammunition and other waste can corrode or decompose,

releasing iron over time. Changes in the water regime due to military operations can cause water to be stirred up in a water body, releasing previously settled iron from the sediments. As for other cations, the content of which in the aquatic environment was recorded in 2022 (Mn^{2+}, Cu^{2+}, Al^{3+}), in 2023 their absence was detected. This phenomenon can be explained both by the deposition of heavy metal cations in the form of insoluble complexes to bottom sediments and by the processes of self-purification of water bodies by the biological component of water bodies.

In this regard, quantitative and qualitative studies of the content of heavy metal compounds in the bottom sediments of the studied lakes were carried out. In addition to Fe^{2+}, Mn^{2+}, Cu^{2+}, Al^{3+}, the presence of other groups of heavy metals was also revealed (tab.1).

By comparing the 2022 with the 2023 data, the essential HM content in fishery lake indicates a significant increase, namely the Fe^{2+} content increased almost 5 times (+377.7%), the Mn^{2+} content also increased almost 5 times (+378.0%). A somewhat lighter growth trend is observed for Cu^{2+} (+132.6%) and Al^{3+} (+191.6%).

Table 1 *Composition of HM in the sediments in hydrotopes studied in Moshchun's reservoirs*

Reservoir	Sampling date	Essential HM			Non-essential HM
		Fe^{2+}	Mn^{2+}	Cu^{2+}	Al^{3+}
		Average HM content, mg/kg			
Fishery lake	*2022*	360,50±4,326	10,46±0,059	0,86±0,001	237,00±1,896
	2023	1722,0±20,664	50,0±0,280	2,0±0,028	691,0±5,528
Recreational lake	*2022*	466,50±5,600	15,99±0,090	3,10±0,040	298,00±2,380
	2023	356,0±4,272	15,0±0,084	1,0±0,014	293,0±2,344

A fishing pond has many fish, which can lead to a greater accumulation of heavy metals in both water and bottom sediments. And the excretion processes of toxic compounds that take place in the organisms of ichthyologist biosystems constantly contribute to an increase in the background parameters of the hydrotope. The downward trend in the content of HM compounds can be traced in all the studied indicators of the recreational lake. This is reflected in the highest order in the dynamics of Cu^{2+} content (-67.7%). All other indicators also tend to decrease (Fe^{2+} -23.7%, Mn^{2+} -6.2%, Al^{3+} -1.7%). A recreational lake may be subject to regular monitoring and cleaning because it is used for human recreation. On the opposite side, fishing ponds may not receive such regular attention.

Conclusions

1. During hostilities, water bodies are subjected to destructive pressure and many different factors. In order to study the distribution of heavy metal compounds in urban hydrotopes of the Kyiv region in post-war conditions, samples of river water and bottom sediments were taken. In accordance with the current methodological recommendations, qualitative analysis of water samples was carried out in July 2022 and a year later in July 2023 from fisheries and recreational water bodies affected by the hostilities in the village of Moshchun, Bucha district, Kyiv region.

2. In 2022 and 2023, the presence of 4 heavy metals was detected in the water environment of both lakes in the study area. It is worth noting that an annual increase in the content of Fe^{2+} compounds was recorded in the water of both reservoirs. By comparing the 2022 with the 2023 data, the

essential the HM content of the sediments in fishery lake indicates a significant increase. The downward trend in the content of HM compounds can be traced in all the studied indicators of the recreational lake.

3. Comparison of the data on the presence of heavy metals in the bottom sediments shows a significant increase in the content of essential HMs in the bottom sediments of the fishery lake. A recreational lake may be subject to regular monitoring and cleaning because it is used for human recreation. On the opposite side, fishing ponds, may not receive such regular attention.

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