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Hydrochemical state of the post-military operations water ecosystems of the Moschun, Kyiv region

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SUMMARY

The scale of military operations in Ukraine has no analogues since the Second World War, therefore it is absolutely necessary to find out their impact on the environment both for further lawsuits against the aggressor country and for the development of measures to restore ecosystems damaged by military operations and ensure health of the population.

The aim is to assess the impact of various types of military operations on the state of hydroecosystems of Ukraine, to determine the damage caused to them and to develop a system of measures to restore them.

The results of the research will allow to quantify the consequences of the military operations impact on the ecosystems in a new way and develop a system of restoration measures for ecosystems that have been strongly affected by military operations to varying degrees, and ensure that the level of water quality is determined to preserve the health of the local population. Moreover, it will make a significant contribution to the development of the ecosystem functioning theory under martial law and military operations.

Introduction

The large-scale military operations in Ukraine have no analogues since the Second World War. Military operations define a set of anthropogenic factors which serve as the direct and indirect impacts on the environment. The destructive level of explosives and the active shelling that the Ukrainian environment experiences on a daily basis cannot be downplayed. Such actions have both pyrogenic and toxic effects. There is every reason to assert the need for a systematic analysis of the anthropogenically transformed consequences on the ecosystems as a result of military operations (*Gandziura, 2008*).

Due attention should be paid in the use of substances that are de facto elements of chemical weapons, which are very often used by the enemy army. These are toxic and radioactive components of weapons used or left on the battlefield. However, we cannot ignore the Directive 2000/60/EC of the European Parliament, a document signed by the Government of Ukraine aimed to bring domestic regulatory documents closer to Western European ones.

According to the Water Framework Directive (2000/60/EC), the ecological state of water bodies is a set of biotic, hydromorphological and chemical (generally physico-chemical) components. According to the directive, the ecological state is determined by a number of indicators: excellent, good, moderate, mediocre, bad. The corresponding assessment is carried out based on monitoring data, which should relate to the three components listed above (*Vyshnevskyi, 2021*).

The results of the research will allow to quantify the consequences of the military operations impact on the ecosystems in a new way and develop a system of restoration measures for ecosystems that have been strongly affected by military operations to varying degrees, and ensure that the level of water quality is determined to preserve the health of the local population. Moreover, it will make a significant contribution to the development of the ecosystem functioning theory under martial law and military operations.

The aim of the research is to assess the impact of different military operations types on the state of various hydraulic systems in Moshchun.

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

1. to conduct hydrochemical analysis of the water reservoirs;
2. to manage a chemical analysis of bottom sediments;
3. to establish an integral measure of anthropogenic transformation by structural and functional indicators of aquatic and coastal-water communities of macrophytes and coastal-aquatic vegetation by hemerobia parameters;
4. to establish the water quality environment and show the prospects of the water resources exploitation in Moshchun, which was under occupation and massive shelling.

Method and Theory

Quality sampling of river waters and bottom sediments was carried out in July 2022 from the reservoirs of fishing and recreational lakes in Moshchun, Kyiv region according to the current methodological recommendations (fig. 1).

Chemical analysis was carried out according to the established standard hydrochemical and analytical-chemical methods. Quantitative and qualitative determination of the heavy metal compounds content was conducted with the help of the Atomic emission spectroscopy (AES). This is a multicomponent method that is acceptable for simultaneous determination of several elements, while atomic absorption spectrometry can only determine individual elements. This is an urgent scientific method for screening environmental studies. Advantages of this method include relatively small matrix effects, wide measurement range (1:10000), high performance (significantly higher than when using AAC). The disadvantages of the method include the possibility of spectral interference, overlapping emission lines of some elements (*Skalnyi, 2004*).

The results section of the research paper will make it possible to quantify the impact of military operations on ecosystems for the first time and develop a system of recovery measures for ecosystems that have been negatively affected by military operations to varying degrees, and ensure that the level of water quality is determined to preserve the health of the local population. It can be considered as a significant contribution to the development of the ecosystem functioning theory under martial law and military operations.

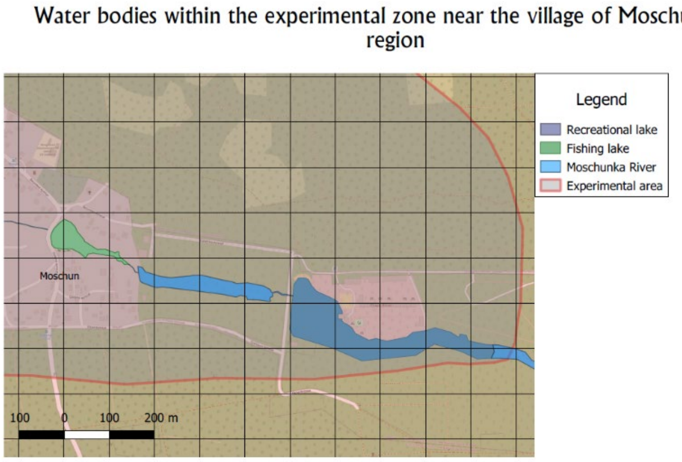

Figure 1 *Water bodies within the research area near Moshchun, Kyiv region*

According to the General Staff of the Ukrainian Armed Forces dated 18.07.2022, on March 23, 2022, Russian troops used prohibited phosphorous ammunition over the north-western outskirts of Kyiv. The approximate affected area is Hostomel-Irpin, Kyiv region (fig.2).

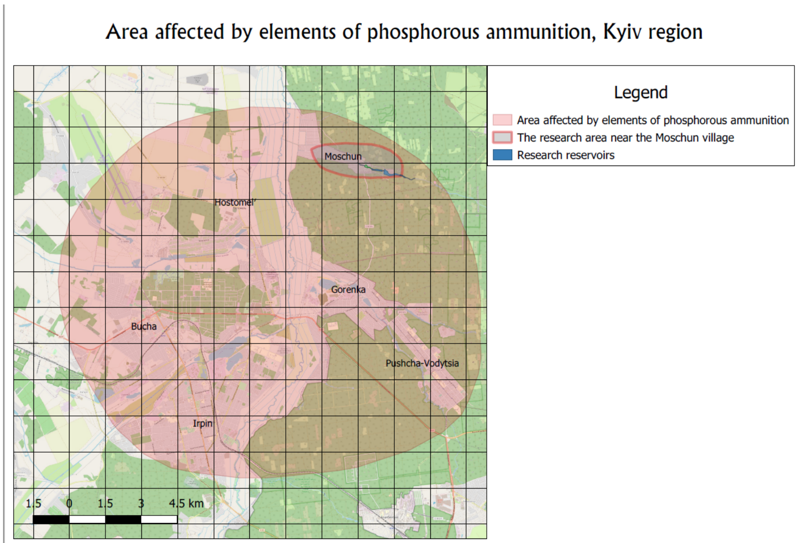

Figure 2 *Destruction zone caused by the phosphorous ammunition elements, Kyiv region on 23 March, 2022 according to the data of the General Staff of the Ukrainian Armed Force on 17 July, 2022*

The use of such weapons against civilians is a crime against humanity and a violation of the Geneva Conventions. Military equipment has same effect as the shell fragments, which means that metal impurities can pollute ground and water. Ammunition residues can contaminate both edaphotope and hydrotop with non-essential (trace) heavy metals. The hydrobionts toxicity is affected by other compounds, like the form of the test substance, water hardness, light and temperature conditions, oxygen concentration, ph, flow rate, lighting, the complexing agents, synergy and condition of biological objects. Toxicity can be determined by the ability of metals to concentrate (*Aleekseev*, 1981; *Vyskushenko*, 2002; *Handziura*, 2021; *Yanovych*, 2017; *Ion Arch Malacea,* 2003).

Metals in the animal body affect many vital organs, tissues, and structures, including the gills. These toxicants alter the function of the blood; the hearts of aquatic animals, damage the effect on the gills, disrupt biochemical processes. All this is reflected in the general functional state of hydrobionts and their respiration (*Romanenko*, 2001).
Heavy metals such as Hg are classified as non-essential chemical elements Hg^{2+}, Cd^{2+}, Pb^{2+}, Bi^{3+}, As^{2+}, which are known as highly toxic, thus it is they that cause negative changes in the vital activity of organisms at the production, energy and substance levels at very low concentrations, and their biological role has not been determined (*Yevtushenko*, 2018).
A further essential feature of interest is added by the fact that two reservoirs originate from the same cascade of artificially created lakes and have different types of significance for the studied territory, namely, one lake is exclusively fishery, and the other is defined as recreational.
Sulfate content ranges from 11 mg/ dm^3 up to 14 mg / dm^3 within the normal range. Water samples contain polyphosphates of 1.21 mg /dm^3 in a recreational reservoir and 0.86 mg / dm^3 in the fishing lake. The content of sodium, potassium, fluorides, manganese, calcium, and magnesium in water samples during the research did not exceed the standard values of these indicators.
The content of iron and aluminum differs from the standard value. But the presence of cuprous compounds has the greatest excess of 50 times in the fishing and 40 times in the recreational reservoir.

Table 1 *Cationic water content of HM in hydrotopes studied in Moshchun's reservoirs*

Water	**Average heavy metals content**			
	Fe^{2+}	*Mn^{2+}*	*Cu^{2+}*	*Al^{3+}*
MAC*	**≤0,1**	**≤0,01**	**≤0,001**	**≤0,04**
Fishery	0,2±0,002400	0,015±0,000084	0,05±0,000190	0,06±0,000480
Recreational	0,15±0,001800	0,001±0,000006	0,04±0,000152	0,02±0,000160

** - the standard values are given in accordance with NS: SER 4630-88 and "Generalized list of maximum acceptable concentrations (MAC) and Tentative Safe Exposure Level (TSEL) of harmful substances for the water of fishery reservoirs"*

One of the most objective and reliable indicators of the water quality and the overall level of man-made load is the content of pollutants in bottom sediments. They are formed as a result of a suspended material sedimentation in water and its interaction with the water phase and accumulate salts of pollutants carried out by surface waters, products of the wind erosion, heavy compounds formed in the surface atmosphere, as well as the solid phase of industrial and domestic wastewater.
Therefore, any changes in the anthropogenic load within water catchments that lead to the transformation of ecosystem relations and cause irreversible changes in the structure and composition of bottom sediments are an important component in the region's environmental safety system and an indicator of the anthropogenic dynamics.
On the one hand, this process conduces water purification, including a set of trace elements with accumulation of ecotoxicant, on the other hand, it is a subordinate source of the reservoirs contamination and an indicator of the anthropogenic dynamics and the level of environmental safety of the region, since it is bottom sediments that reflect changes in the long-term supply of trace elements to aquatic ecosystems (*Arsan*, 2010).
The HM distribution in the bottom sediments of the studied water bodies in Moshchun (except Al^{3+} and Fe^{2+}). The content of cadmium, manganese and lead does not exceed the established standards of maximum permissible concentrations: Cd^{2+} 0.23 mg / kg in a recreational reservoir and 0.063 mg / kg in a fishing lake, Mn^{2+} 15.99 mg / kg and 10.46 mg / kg, Pb^{2+} 3.34 mg/kg and 2.03 mg / kg, accordingly.
According to the results of the study, iron (total) 466.5 mg/kg in a recreational reservoir and 360.5 mg/kg in a fishing lake, chromium, copper, zinc, nickel, aluminum and cobalt were found in bottom

sediments. Also, in comparison with the amount of other HM compounds, the amount of aluminum in both cases is large, namely in a recreational reservoir 298.0 mg/kg, a fishery – 237.00 mg/kg. However, even due to the significant amount of aluminum and zinc, the content of these indicators in bottom sediments is not normalized.

Table. 2. *Cationic composition of HM in the bottom sediments of the studied reservoirs in Moshchun*

Water	Fe^{2+}	Mn^{2+}	$Cr^{2+/3+}$	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Al^{3+}	Co^{3+}	Pb^{2+}
	Average HM content, mg/kg									
Fishery	360,5 ± 4,326	10,46 ± 0,059	1,513 ± 0,004	0,86 ± 0,001	6,6 ± 0,079	0,063 ± 0,001	2,58 ± 0,031	237 ± 1,896	0,625 ± 0,016	2,03 ± 0,037
Recreational reservoir	466,5 ± 5,600	15,99 ± 0,090	1,864 ± 0,005	3,1 ± 0,040	9,5 ± 0,100	0,23 ± 0,005	2,41 ± 0,030	298 ± 2,380	0,789 ± 0,019	3,34 ± 0,060

Conclusions

1. Analysis of the chemical elements distribution shows contamination both the aquatic environment and bottom sediments with heavy metals.
2. Essential heavy metals were found in the aquatic environment of fishing lakes and recreational reservoirs Fe^{2+}, Mn^{2+}, Cu^{2+}, Al.^{3} There are significant exceeding $MAC_{fishery./reservoir}$, the fishing lake turned out to be more contaminated.
3. Despite the lack of the heavy metal content normalization in the bottom sediments, a significant qualitative cationic composition was found, namely 10 heavy metals. Among them the largest number is defined by Al^{3+} (at the fisheries 237±1,896 mg/kg, and at the recreational – 298±2,380 mg / kg) and Fe^{2+} (at the fisheries 360.5±4.326 mg/kg, and at the recreational – 466.5±5.6 mg/kg. Among the entire cationic composition in the bottom sediments, there are not just heavy metal compounds, but non-essential and trace ones, which have a pronounced toxic effect and disrupt the homeostasis and enantiostasis of ecosystems.

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