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Analysis of Trends and Impacts of Anthropogenic Factors on Groundwater Quality

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ABSTRACT

The study is dedicated the dynamics of groundwater quality in the Mykolaiv region (Ukraine) during the period from 2021 to 2024. It was determined that the concentration of chlorides, sulfates and mineralization in water in 2022 increased by 2–3 times (1190 mg/dm^3) compared to 2021 (453 mg/dm^3), which is due to the use of sea water in the central water supply and the consequences of a man-made disaster that arose under the influence of military operations. Trends in changes in water quality depending on the season and the influence of various factors on the geochemical composition of underground water resources are analyzed. The results obtained indicate a change in groundwater quality. According to the water quality classification according to the water pollution index (WPI), the observed trend indicates a transition from water of quality class II, characterized as "clean water", to water of quality class III, which reflects a moderate level of pollution.

Keywords: groundwater, water quality, pollution dynamics, hydrochemical indicators; water pollution index.

INTRODUCTION

Among the strategic goals of sustainable development, the goal of high-quality drinking water is one of the main priorities (The Sustainable Development Goals; Bezsonov et al., 2017; Mitryasova et al., 2020). An important issue is the search for sources of clean drinking water and the implementation of monitoring studies of its quality, the study of water security and water insecurity (Pohrebennyk et al., 2016; Ishchenko et al., 2019; Mitryasova et al., 2021; Bernatska et al., 2023). The study of groundwater geochemistry strengthens the understanding of complex processes occurring in hydrogeological systems (law of Ukraine "On Environmental Protection", 1991). Groundwater geochemistry investigates the chemical composition of water located in the depths of the earth's crust, as well as the dynamics of changes in this composition under the influence of various factors (Smith and Johnson, 2019; Brown and Patel, 2020; Mitryasova et al., 2021). The purpose of the research is studying the groundwater geochemistry to find out their impact on hydrogeological processes and aquatic ecosystems. To achieve the goal, the following tasks were solved:

- analysis of the chemical composition of groundwater under certain hydrogeological conditions;
- establishing links between the geochemical composition of water and the hydrogeological parameters of the region;
- assessment of the impact of anthropogenic impact on the geochemical characteristics of groundwater;
- identification of potential risks to the quality of groundwater and water systems.

The results of groundwater research and their analysis will contribute to a better understanding of the functioning of hydrogeological systems, will allow the development of effective measures for the control and protection of water resources from pollutions, as well as contribute to improving the efficiency of water systems management in order to preserve the environmental sustainability of natural environments.

The object of the study is groundwater of the Mykolaiv region (Ukraine). The subject of the study is the mineral composition, integrated indicators, namely, pH, hardness, as well as chemical parameters that belong to the crisis (total iron, phosphates, nitrates, nitrites, ammonium ions). The subject of groundwater geochemistry is understandsing the relationships between the chemical composition of water and hydrogeological conditions, such as the hydrological regime, hydrogeological relief, geological composition of rocks, as well as the influence of anthropogenic factors, such as pollution of water bodies by industrial and agricultural emissions.

Understanding the geochemical properties of groundwater is key to many aspects of hydrogeology and hydrology. This helps to determine the sources of groundwater movement, predict their quality, identify water flows, develop measures to control and protect water resources from pollution and the transfer of harmful substances. Water are important components of ecosystems and geological processes, and understanding the geochemical properties of groundwater is essential for many aspects of hydrogeology and hydrology. This includes identifying the sources and routes of groundwater flow, predicting the quality of water resources, detecting water flows, and developing measures to control and protect water systems from pollutions and the transfer of substances (Jones and Smith, 2017; Garcia and Martinez, 2018; Martinez and Sanchez, 2019; Mitryasova et al., 2021).

In this context, the study of groundwater geochemistry is important to ensure the sustainable using of water resources, the effective management of water systems and the environmental sustainability. Therefore, this research is aimed at reviewing the results of groundwater geochemistry studies in order to gain an in-depth understanding of their impact on hydrogeological processes and water systems. The Mykolaiv region is located in the basins of three main rivers: the Southern Buh (59.5%), the Dnieper (23.5%) and the rivers of the Black Sea region (17%). There are 121 rivers and gullies in this area, which have a total length of 3619.84 km. Among them, there is one large river - the Southern Buh, and six medium-sized rivers, such as Kodyma, Synyukha, Chornyi Tashlyk, Chichikleya, Inhul and Inhulets. The area of surface water bodies is 150.5 thousand hectares, which is 6.1% of the total area of the region (State report, 2021; Chepurenko and Kolisnyk, 2020).

Hydrogeological characteristics of Mykolaiv region belong to the Black Sea artesian basin and partly to the Ukrainian crystalline massif. Groundwater is located in sediments of different ages, genesis and lithological composition - from the fractured zone of the crystalline basement to modern (Holocene) and Pleistocene (Mishchenko and Petrov, 2017; Bohdanovych and Kravchenko, 2018; Hrebenyuk and Kovalenko, 2019). The prognostic groundwater resources of the main aquifers in the Mykolaiv region are 441.6 thousand cubic meters per day. Of these, groundwater with mineralization up to 1.5 g/dm^3 makes up 79.23%, and with mineralization from 1.5 g/dm^3 to 3.0 g/dm^3 − 20.77%.

In terms of the volume of explored reserves of groundwater of drinking quality, the Mykolaiv area is the least provided in Ukraine. Operational groundwater reserves per inhabitant are on average 0.09 cubic meters per day. For example, in comparison with the Odessa region (bordering on the Mykolaiv region), it is 1.5 times less, and with the Kherson region − 34 times less. In general, the available water resources in the region are limited and mainly depend on the inflow from other regions. According to the indicators of water resources per inhabitant, the Mykolaiv region is among the outsiders among other regions of Ukraine. The average annual provision of local runoff per inhabitant of the Mykolaiv region is 0.44 thousand cubic meters per year, which is 2.38 times less than the average for Ukraine

According to geological conditions, the southern part of the Mykolaiv region. It is characterized by a deep crystalline basement and is composed mainly of sedimentary rocks: limestones, marls, sands and clays. Within the Black Sea basin, the surface of Precambrian rocks is lowered to the height of the depression. From north to south, the thickness of the sedimentary layer increases. The Southern Buh River is one of the major rivers of the Black Sea in the Mykolaiv region. The Southern Buh is represented by the lower part, which is about a quarter of the entire length of the river. The Southern Buh flows from northwest to southeast and flows into the Buh estuary, connected to the Black Sea at absolute elevations of 0.2 m above sea level. The average slope of the water surface is 0.4 %. In accordance with the geological structure, aquifers lie in the Quaternary sediments of the Sarmatian stage. Water-containing rocks are interlayered with water-resistant clays, but they form a single aquifer complex with a common water-dynamic and hydrochemical regime. The horizon is fed by precipitation, as well as pressure waters below the underlying Upper Cretaceous formations.

Water-containing rocks are limestones, marls, sands and, less commonly, sandstones. The thickness of water-containing rocks is 0.55–30 m. The depth of the aquifer reaches 100 m and more. The waters of the Sarmatian aquifer are mainly pressure, the head height varies from 0.8 to 30 m, in some cases it reaches 100 m. Salinity of Sarmatian waters usually does not exceed 2 g × dm^{-3}. According to the salt composition, the waters are mixed: from hydrocarbonate-sulfate to chloride-sulfate and chloride. The total hardness ranges from 2.4–68.7 mEq/100 g.

MATERIALS AND METHODS

The methodology for the study of groundwater geochemistry includes several stages, which are the selection of the study wells, sampling and analysis, chemical and geochemical methods of analysis (Regulations on state sanitary supervision, 2016). Choosing a research well. When choosing the research well, it is necessary to take into account the geological structure of the region, the presence of aquifers, the features of the hydrogeological regime and potential anthropogenic activity. Areas with different hydrogeological conditions are usually selected to obtain representative data.

Sample collection and analysis. Groundwater samples are usually collected from springs, artesian wells or other sources of interest for research. Samples are collected taking into account the depth, geological composition and other characteristics of the aquifers. After that, laboratory analysis of samples is carried out to determine the chemical composition, level of mineralization, pH and other parameters of water. Chemical and geochemical methods of analysis. Various methods are used for this, namely: spectral analysis, chromatography, atomic absorption spectroscopy and other chemical and geochemical methods.

The use of these methods of analysis allows obtaining detailed information about the geochemical composition of groundwater and its properties, which is important for understanding hydrogeological processes and rational use of water resources. A certain area of the Mykolaiv region with different hydrogeological conditions in the territory where hostilities took place was selected for the study, which will allow obtaining representative data. Such a choice of the study site will allow to research the influence of the geological composition on the chemical composition of groundwater.Armed conflicts are always accompanied not only by socio-economic and political consequences, but also by impacts on the environment. In particular, the environmental consequences of such conflicts can have long-term and unpredictable consequences, especially for the geological environment (Smyrnov et al., 2023).

Mykolaiv region is located in a strategically important region of Ukraine, which is and has been affected by the consequences of military operations. Activities related to the movement of military equipment, the use of various types of weapons and other military operations can have a tangible impact on the geological environment. During the study, five wells located in the war zone were examined (Fig. 1 and Table 1). The results of the geochemical composition of groundwater were obtained according to the plan:

1. Planning a sampling route – first, it is necessary to develop a route plan for sample collection that covers different hydrogeological conditions and points of interest. This can include different types of aquifers, river systems, as well as areas with possible anthropogenic impacts.
2. Sampling – after planning the route, groundwater samples are collected. Samples are usually collected using special drills or pumps from deep wells or sources.
3. Preservation and preparation of samples – once the samples have been collected, they must be properly secured and stored for laboratory analysis. The samples were stored in special containers with low oxygen content.
4. Monitoring – monitoring includes the determination of the chemical composition of water, namely: the level of mineralization, pH, the content of chlorides, sulfates, phosphates, nitrates, ammonium nitrogen, hardness, iron total.
5. Processing and analysis of results – once the laboratory analysis is completed, the results are processed and analyzed in order to establish relationships between the geochemical composition of the water and the hydrogeological conditions of the region.

Table 1. Groundwater sampling points

Markings on maps	Location	Depth, m	Aquifer
W1	Mykolaiv, Korabelnyi district	48.5	Neogene aquifer complex
W2	Lymany village, Mykolaiv district	47.0	Neogene aquifer complex
W3	Halitsynovo village, Mykolaiv district	49.0	Neogene aquifer complex
W4	Shevchenkovo village, Mykolaiv district	52.3	Neogene aquifer complex
W5	Luparevo village, Mykolaiv district	53.6	Neogene aquifer complex

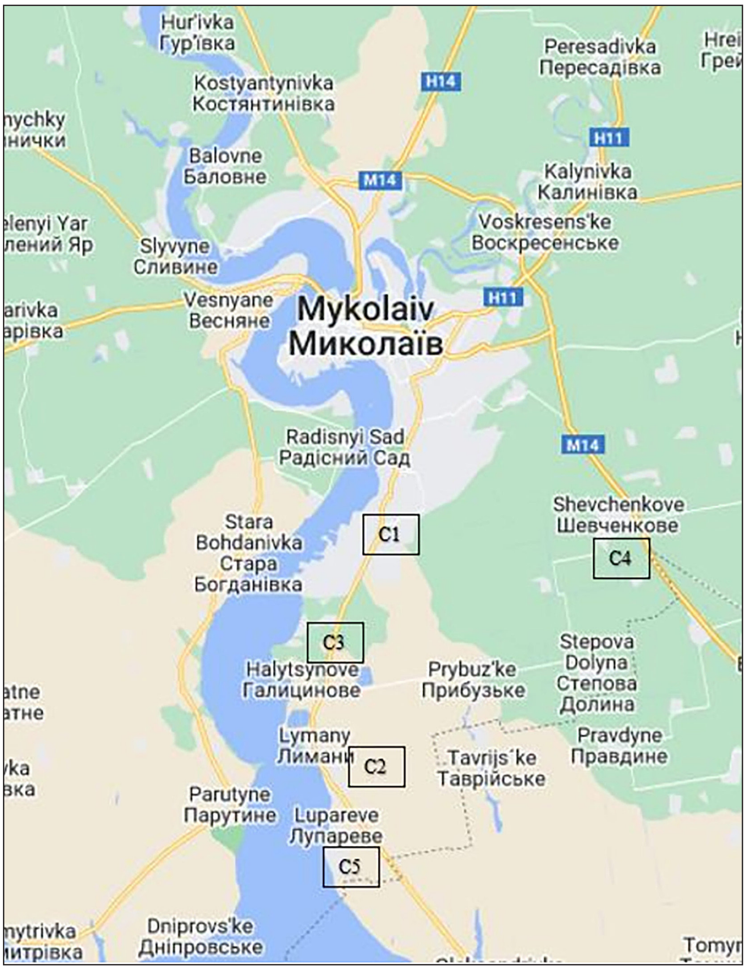

Figure 1. Groundwater sampling map of the Mykolaiv region territory: W1 – Mykolayiv, Korabelnyi district (46.891318; 32022755); W2 – Lymany village, Mykolaiv district (46.726027; 31.972495); W3 – Halitsynovo village, Mykolaiv district (46.804909; 31.966290); W4 - Shevchenkovo village, Mykolaiv distric (46.866606; 32,20904; W5 – Luparevo village, Mykolaiv district, (46.692226; 31.979944)

RESULTS AND DISCUSSION

Taking into account the analysis of the study performed, it is important to emphasize the results for understanding the dynamics of groundwater quality in the Mykolaiv region. The results presented in the main part reflect significant changes in the geochemical composition of water and their impact on the quality of groundwater in the region under consideration during the analyzed period. Now let's move on to the generalized conclusions based on these results to highlight the key findings and recommendations for further action in this area of research in Table 2.

The obtained results made it possible to determine the regularities that are presented in Fig. 2. It was determined that the content of chlorides, sulfates and mineralization in water in 2022 increased by 2–3 times (1190 mg/dm^3) compared to 2021 (453 mg/dm^3). This change is related to the use of

Table 2. Results of the chemical composition analysis of groundwater in the territory of hostilities Mykolaiv Region (Ukraine)

Name of the substance	Chemical concentration, $mg \cdot dm^{-3}$					Maximum permissible concentration of drinking water*
	W1	W2	W3	W4	W5	
Iron total	0.05–0.16 0.11	0.03–0.12 0.1	0.07–0.13 0.1	0.07–0.13 0.09	0.06–0.09 0.07	0.2
pH	7.0–7.5 7.2	7.0–7.5 7.3	7.0–7.4 7.2	7.0–7.8 7.3	7.2–7.6 7.4	6.5–8.5
Chlorides	453–1190 832	316–1105 757	220–850 592	103–989 419	459–1520 951	350
Sulfates	115–780 372	208–805 474	151–215 187	67–620 327	420–1230 615	500
Phosphates	0.1–0.38 0.25	0.04–0.25 0.16	0.23–0.39 0.29	0.03–0.59 10.1	0.03–0.67 0.27	0.5
Nitrites	0.01–0.05 0.03	0.01–0.08 0.04	0.01–0.08 0.05	0.02–0.07 0.04	0.02–0.23 0.08	3.3
Nitrates	0.94–32.5 8.2	2.4–16.5 7.6	4.1–6.8 5.58	3.91–25.6 10.1	5.6–28.4 14.8	50
Ammonium nitrogen	0.05–0.47 0.21	0.05–0.38 0.26	0.05–0.51 0.22	0.08–0.18 0.14	0.14–0.36 0.24	2.6
Mineralization	756–1511 1131	556–1235 886	756–1156 1020	748–1120 939	1087–1870 1313	1500
Hardness	3.4–11.9 8.4	3.8–11.9 8.8	3.8–7.6 5.2	4.3–11.7 6.6	7.2–17.5 11	no more 10

Note: the results are presented in the following sequence: numerator, minimum and maximum value, denominator, average value. *Hygienic Standards. water quality of water bodies to meet the drinking, household and other needs of the population, Order of the Ministry of Health of Ukraine May 2, 2022 No. 721.

sea water in the central water supply of the Mykolaiv city. In other words, salt water entered aquifers through bursts in the aqueduct system. In the summer of 2023, there was a downward trend in the concentration of these ions to 2021 levels. This is due to the fact that as a result of hostilities during the ongoing war in Ukraine, the Kakhovka hydroelectric power plant was damaged, and a large volume of fresh water mixed with the waters of the Dnieper and the Buh estuary, which led to the dilution of fresh water from reservoirs. It was determined that in the winter period of 2023, with a decrease in the impact of the Kakhovka reservoir on the aquifer balance of southern Ukraine, there was an increase in the concentration of salts in the water to the level of 2022. From this we can conclude that the sea water of estuaries plays an important role in the formation of the geochemical composition of groundwater in the Mykolaiv region.

The high content of sulfates, chlorides and mineralization in water can have serious consequences for public health as well as for technical devices. Here are some of the most typical consequences:

- chlorides – high concentrations of chlorides in water can lead to depletion of the body in a variety of ways. Excessive chloride intake can cause diarrhea, high blood pressure, and kidney problems.
- sulfates – high sulfates in water can lead to a laxative effect, triggering frequent cases of diarrhea and gastrointestinal upset.
- mineralization – too much water mineralization can lead to bladder stones.

A high mineralization content can cause scale build-up on heating and hot water elements, which can lead to a decrease in the efficiency of the devices and an increase in the cost of their maintenance and repair. High mineralization can lead to scale build-up in the water supply systems of these appliances, which may reduce their efficiency and require more frequent cleaning or repair. Overall, it is important to regularly check the quality of the water and take steps to purify it of unwanted substances in order to ensure safety and effectiveness for both human health and household appliances.

Assessment of the state of groundwater by the WPI

One of the most commonly used approaches in the system for assessing the quality of natural waters is the hydrochemical WPI. This index

Figure 2. Regularities of changes in the concentration of sulfates, chlorides, mineralization of groundwater on the territory of hostilities of the Mykolaiv region

provides a generalized numerical assessment of water quality, taking into account the main indicators and types of water use. WPI is the average value of exceeding the maximum permissible concentrations (MPC) for individual pollution indicators (usually there are six of them).

Water indices are formalized indicators that summarize various groups of natural indicators of pollution. They take into account various aspects of a water body, allowing for a comprehensive assessment of its quality and use. Water indices allow for a simplified assessment of the degree of pollution of the aquatic environment, taking into account various parameters such as the concentration of various chemicals, the content of organic compounds, as well as the physicochemical properties of water. It is important to ensure water quality for various purposes, such as drinking water, industrial use, and maintaining ecological balance in natural water ecosystems. Some indices take into account not only the concentration of substances in the water, but also their effects on wildlife, such as toxicity to fish or other aquatic life. This makes it possible to more accurately determine the real threat to ecosystems and the health of people who use

Table 3. Water quality classes

Water quality class	Characteristics (text description)	Value of WPI
I	Very clean	WPI ≤ 0.3
II	Clean	0.3 < WPI ≤ 1
III	Moderately polluted	1 < WPI ≤ 2.5
IV	Contaminated	2.5 < WPI ≤ 4
V	Dirty	4 < WPI ≤ 6
VI	Very dirty	6 < WPI ≤ 10
VII	Extremely dirty	WPI > 10

Table 4. Assessment of the groundwater state of the WPI

WPI	The number of the well with the assessment of the water quality class									
	W1	Water quality class	W2	Water quality class	W3	Water quality class	W4	Water quality class	W5	Water quality class
WPI 2021 year	0.5	II	0.7	II	0.4	II	0.5	II	1.0	II
WPI 2024 year	1.2	III	1.2	III	0.6	II	1.0	II	2.0	III
Average	0.9	II	0.8	II	0.7	II	0.7	II	1.1	III

these water resources. The use of water indices is an important tool for monitoring and controlling the quality of water resources, which helps in the development and implementation of effective strategies for the conservation and protection of aquatic ecosystems. According to the values of the calculated WPI, water quality is assessed. At the same time, there are seven quality classes – from very clean (I class) to extremely dirty (VII class) (Table 3)

The first class includes waters that are least affected by anthropogenic load. The value of their hydrochemical and hydrobiological indicators is close to the natural values in the region. Waters of the second class are characterized by certain changes in comparison with natural ones, but these changes do not disturb the ecological balance. The third class includes waters that are under significant anthropogenic impact, the level of which is close to the limit of ecosystem stability.

Waters of IV−VII classes are waters with disturbed ecological parameters, their ecological state is assessed as ecological regression. Thus, the calculated WPI makes it possible to assess the overall quality of water based on the collected and processed data on the levels of water pollution. This assessment can be used to make decisions in order to improve the state of aquatic ecosystems and provide water resources in accordance with established standards and regulations.

The results of the WPI assessment were summarized and presented in the Table 4. The water quality assessment was carried out compared to the state of water before the start of Russian aggression in 2021 and after the consequences of a man-made disaster as a result of hostilities in southern Ukraine in 2024. The results obtained indicate a recent change in groundwater quality. According to the water quality classification according to the WPI, the observed trend indicates a transition from water of class II quality, characterized as “clean water”, to water of class III quality, which reflects a moderate level of pollution. In addition, the analysis shows that the water quality in the well (W5) has a pollution index of 2. This suggests that the water in this region, although it has not reached levels of significant pollution, is already exposed to higher concentrations of pollutants, indicating a potential threat to water quality and consumer health. The obtained data reflect unfavorable trends in the state of groundwater resources and require attention to the development and implementation of measures to monitor, conserve and improve water quality to ensure sustainable use of water resources in the future.

The overall approach to assessing water quality included analyzing the concentration of various pollutants and using appropriate measurement and analysis methods. It was found that the water quality deteriorated after the consequences of the man-made disaster that arose as a result of military operations compared to the water state in 2021. This conclusion is based on a comparative analysis of the concentration of various pollutants in water and their compliance with the maximum permissible standards. This approach makes it possible to objectively assess changes in water quality and determine the consequences of a man-made disaster on the long-term environmental stability of water resources.

CONCLUSIONS

Assessment of groundwater quality in the region of Mykolaiv region shows significant changes during the period under review. Comparing the data for 2021 and 2024, an increase in the concentration of chlorides, sulfates and mineralization in water was found, especially in 2022. This trend is the result of the sea water using in the central water supply of the Mykolaiv city, as well as the negative impact of bursts in the water supply system.

In the summer of 2023, there was a slight improvement in the situation, when the concentration of these ions decreased to 2021 levels. However, this was due to a man-made disaster as a result of military operations, when the damaged Kakhovka hydroelectric power plant caused the mixing of fresh water with the waters of the Dnipro and the Buh Estuary. In the winter period of 2023, with a decrease in the impact of the Kakhovka reservoir on the aquifer balance, there was an increase in the concentration of salts in the water to the level of 2022. This testifies to the important role of sea water of estuaries in the geochemical composition formation of groundwater in the Mykolaiv region.

According to the WPI classification, the observed trends indicate a transition from water of the II class of quality to water of the III class. This means a certain level of pollution, which requires attention and measures to monitor and conserve water resources. The data obtained confirm unfavorable trends in the state of groundwater resources, which requires the development and implementation of effective strategies to improve water quality and ensure sustainable using of water resources in the future. WPI is an important tool for objectively assessing the state of aquatic ecosystems and taking appropriate measures.

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