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Spatial-temporal characteristics of surface water quality

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ABSTRACT

The development of hydrochemical passports for rivers represents a key step toward better understanding and managing water resources in Ukraine. The objective of this research is to assess the state of surface waters and forecast changes in the water area of the city of Mykolaiv. This is achieved by determining sampling points within the water area of the Buzky Estuary, the Southern Buh and Inhul rivers, and within the districts of Mykolaiv. The analysis includes examining integrated hydrochemical indicators and investigating the temporal and spatial changes in water quality. The research focuses on the regularities of changes in water quality over time and space and includes surface waters of the Buzky Estuary, the Southern Buh River, and the Inhul River within Mykolaiv. Photometric method for determining water quality indicators using the eXact Strip Micro 20 long-wave photometric system. Mathematical methods include statistical data processing, the method of average values in determining the level of surface water pollution, and graphical reflection of data for qualitative visual evaluation of results using MS Excel software. The level of mineralization varies between different observation points, but the general trends remain similar. The data indicate a significant excess of the maximum permissible concentration at all observation points, which is a serious reason not to use these waters as a source of technical and even more so drinking water supply. Alkalinity significantly exceeds the maximum permissible concentration in all months considered, which indicates a consistently high level of this indicator in water. There is an increase in alkalinity from December to March, after which there is a sharp drop in April, and in May it rises again. The regression analysis found that annual hydrochemical indicators dynamics correspond to the sine wave of long-term fluctuations. The resulting function has made it possible to predict fluctuations over 6 years of a sine wave.

Keywords: hydrochemical indicators; surface water; state of water resources; water quality.

INTRODUCTION

Water is not only a natural resource but also an integral part of the existence of all life on the planet. The share of water suitable for use by the population and industry is very limited – only 3% of the total water resources. Moreover, only 0.3% of fresh water is concentrated in the most accessible surface water bodies, such as lakes and rivers. Therefore, the issue of providing humanity with clean fresh water is urgent. The problem of water resources suitable for drinking was included in the list of major issues of the World Economic Forum in Davos as one of the biggest global risks for the future. Ensuring equal access to high-quality and safe drinking water for human health is a strategic objective of the Water Strategy of Ukraine until 2050 (World Economic Forum in Davos 2024; Water Strategy of Ukraine for the period until 2050, 2022).

Globally, the assessment of surface water quality is crucial for ensuring the sustainability of water resources. One of the most widely recognized systems is the Water Framework Directive (WFD), adopted by the European Union in 2000. The WFD aims to achieve "good status" for all water bodies across Europe by establishing a framework for the protection and management of water resources. The directive requires member states to monitor, assess, and report the ecological and chemical status of their waters. The WFD uses a comprehensive approach by classifying water bodies based on biological, chemical, and hydromorphological criteria. It emphasizes the importance of reducing pollution from agricultural run-off, industrial discharges, and urban wastewater, which are common sources of contamination for surface waters in Europe (European Commission, 2000).

In addition to the WFD, the European Environment Agency (EEA) regularly monitors and assesses surface water quality across European countries. The EEA's reports help inform policy decisions aimed at improving water quality. The agency emphasizes the importance of using integrated water management practices to tackle issues such as eutrophication, pollution from hazardous substances, and the impacts of climate change on water quality. One notable initiative is the European Water Information System (WISE), which gathers and presents data on water quality across member states, enabling better decision-making and public access to information (EEA, 2023).

Globally, organizations like the World Health Organization (WHO) and the United Nations Environment Programme (UNEP) also play a significant role in establishing guidelines and best practices for water quality assessment. The WHO sets international standards for safe drinking water and provides guidelines for managing the health risks associated with contaminated surface waters. For instance, the WHO's Guidelines for Drinking-water Quality are an essential reference for countries in assessing the safety of water sources, including surface waters (WHO, 2017). The UNEP Global Environment Monitoring System for Water (GEMS/Water) is another key initiative that supports global efforts to monitor water quality, providing data and tools for countries to assess their surface water resources and address pollution (UNEP, 2022).

Many countries also adopt national standards and monitoring programs that align with international practices. For example, in the United States, the Clean Water Act of 1972 established the legal framework for reducing pollution in surface waters and improving water quality through monitoring and regulatory measures. The U.S. Environmental Protection Agency (EPA) plays a central role in implementing water quality standards and regularly publishes reports on the state of the nation's waters (EPA, 2020).

These global and European practices underscore the importance of regular monitoring, international cooperation, and integrated management approaches to ensure that surface waters remain safe and sustainable for both human use and the environment.

The scientific works of many foreign scientists acquired significant scientific importance in the study of environmental problems related to the growing consumption of natural resources, water resources management, anthropogenic influence on the state of water bodies (Staddon, 2016; Meyer et al., 2019; Obolewski et al., 2018; Kapelewska et al., 2018).

In Ukraine, the assessment of surface water quality is primarily regulated by national water legislation, including the Water Code of Ukraine and various environmental standards (Water Code of Ukraine, 1995). Ukrainian scientists play a significant role in developing methodologies for water quality monitoring, often adapting international practices to the local context (Bernatska et al., 2023; Bezsonov et al., 2021; Ishchenko et al., 2019; Pohrebennyk et al., 2017; 10. Malyushevskaya et al., 2023; Mitryasova et al., 2018, 2020, 2021). So, researchers have conducted extensive studies on the ecological state of rivers and reservoirs across the country, using the average annual values of hydrochemical parameters to assess water quality (Gopchak et al., 2020; [1]Mitryasova et al., 2021).

The Ukrainian Hydrometeorological Institute also contributes to water quality monitoring through its network of observation stations, which regularly collect data on water temperature, pH levels, and concentrations of pollutants like heavy metals and nutrients. Ukrainian scientists frequently collaborate with international organizations such as the UNEP and the European Union under initiatives like the Danube River Protection Convention to align Ukraine's water monitoring practices with European standards.

The development of hydrochemical passports for major rivers, including the Dnipro and the Southern Buh, represents a key step toward better understanding and managing water resources in Ukraine (Khilchevskyi et al., 2016; Sherstyuk, N. 2016. Shevchuk et al., 2021). Currently, the quality of surface waters, which serve as a drinking water source for 80% of Ukraine's population, is unsatisfactory and characterized by increased levels of anthropogenic pollutants. Groundwater, in most cases, is marked by increased hardness, mineralization, and an excessive content of organic substances, among other issues. Most river basins and reservoirs in Ukraine, which provide for the water needs of the population, cannot be considered ecologically safe. In southern Ukraine, particularly in the Northern

Black Sea region, water quality deviations from the norm reach 70–80%. Thus, research on the state of surface waters has become particularly relevant and important for the safety of people and society.

Water composition quality indicators are among the most decisive in assessing the state of water resources, especially during military conflicts that have occurred throughout human history. The water issue is also critical for the city of Mykolaiv, which has been left without a stable centralized water supply system since April 12, 2022, due to the ongoing war.

The study was carried out as part of a collaboration agreement between Petro Mohyla Black Sea National University and Department of Ecology and Natural Resources of the Mykolaiv Regional Military Administration.

The objective of this research is to assess the state of surface waters and forecast changes in the water area of the city of Mykolaiv. This is achieved through determining sampling points within the water area of the Buzky Estuary, the Southern Buh and Inhul rivers, and within the districts of Mykolaiv. The analysis includes an examination of integrated hydrochemical indicators and an investigation into the temporal and spatial changes in water quality.

The objects of the research include surface waters of the Buzky Estuary, the Southern Buh River, and the Inhul River within Mykolaiv. The subject of the research focuses on the regularities of changes in water quality over time and space.

The Buzky Estuary is a large brackish water body located in southern Ukraine, where the Southern Buh River flows into the Black Sea. It stretches from the city of Mykolaiv to its opening near the village of Parutyne. The estuary is approximately 47 km in length and varies in width from 3 to 5 km. Its borders are marked by steep cliffs and rolling hills, providing a scenic yet rugged appearance. The estuary is shallow, with depths rarely exceeding 10 meters, and is characterized by a mixture of fresh and saline water due to river inflows and sea tides. The Buzky Estuary is an ecologically significant area, supporting various species of fish and birds, and is a key fishing and shipping route. Its location places it at the confluence of diverse ecosystems – riverine, marine, and wetland environments.

The Buzky Estuary also plays a crucial role in the region's economic development, serving as a vital waterway for shipping, trade, and the fishing industry. Its proximity to major cities like Mykolaiv enhances its strategic importance for maritime logistics and industrial activities. Ensuring water quality in the estuary is essential, especially during armed conflicts, when infrastructure is often compromised. Clean and accessible water is critical for sustaining the health and well-being of the population and maintaining essential services. Monitoring and protecting the estuary's water quality during such times are key to preventing waterborne diseases and ensuring regional stability.

MATERIALS AND METHODS

Photometric method for determining water quality indicators using the eXact Strip Micro 20 long-wave photometric system. Mathematical methods include statistical data processing, the method of average values in determining the level of surface water pollution, and graphical reflection of data for qualitative visual evaluation of results using MS Excel software. For the mathematical interpretation of the data, the CurveExpert software package was also used. To assess the adequacy of the model, the Fisher significance criterion (Equation 1) is used.

$$F = \frac{R^2}{1-R^2} \cdot \frac{\text{n}-\text{m}-1}{\text{m}} \quad (1)$$

where: R is the coefficient of regression (determination), n is the number of observations, and m is the number of factors in the regression equation.

In this case, the regression (determination) coefficient is the proportion of variance of the dependent indicator, which is explained by the resulting function (Equation 2).

$$R^2 = 1 - \frac{\sigma^2}{\sigma(y)^2} \quad (2)$$

where: $\sigma^2(y) = D[y]$ – variance of a random variable obtained during measurements;
$\sigma^2 = D[y|x]$ – conditional variance as a function of exponent x in the function for which the regression coefficient is located.

Materials for research were also taken from reports on the state of the environment (National Report, 2023). Observation points are shown in Figure 1. There are the surface waters of the Buh Estuary, the Southern Buh River, the Inhul River (General plan of Mykolaiv city):

- GC "Lazurne", Vesnyanska Territorial Community (46.991186, 31.876144);
- Microdistrict. Nizhnyaya Naberezna (46.980002, 31.985235);
- Microdistrict. Yacht Club (46.977016, 31.960774);
- Microdistrict. Namyv (46.947273, 31.932793).

Surface water quality indicators: pH; total alkalinity; calcium hardness; sulfates; sulfites; phosphates; nitrates; nitrites; cyanide; ammonium; common iron; copper(II); metals(II).

RESULTS AND DISCUSSION

Data on water mineralization by month, expressed in mg/dm³, are shown in Figure 2. The values are compared with the maximum permissible concentration (MPC), which is 1000 mg/dm³. The mineralization of water significantly exceeds the maximum permissible concentration (1000 mg/dm³) during the entire observation period. The highest values are observed in November (3610 mg/dm³) and December (3070 mg/dm³). The downward trend in mineralization begins after November, reaching its lowest level in April (1560 mg/dm³), followed by an increase to 2410 mg/dm³ again in May. This indicates seasonal fluctuations in mineralization, which remains significantly higher than the permissible norms throughout the entire period. The correlation coefficient between the period of the year and mineralization is approximately -0.81. This indicates a strong negative correlation, that is, as we approach spring, mineralization decreases and then partially increases in May.

In accordance with the data obtained, regularities have been determined. The temperature of the air and water corresponds to natural seasonal changes. The pH values remain between 7.3 and 8.1, indicating a slightly alkaline environment. This is the normal range for natural water.

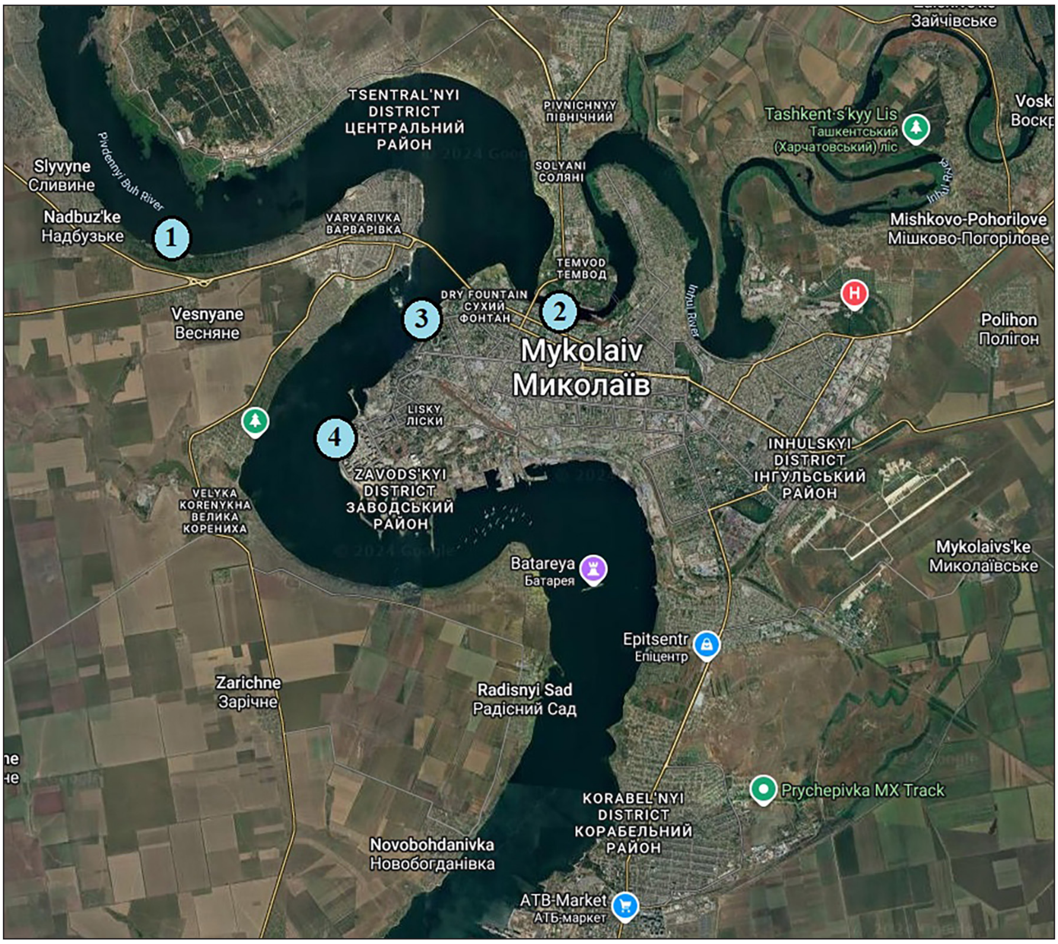

Figure 1. Sampling map 1. GC "Lazurne", Vesnyanska Territorial Community (46.991186, 31.876144); 2. Microdistrict. Nizhnyaya Naberezna (46.980002, 31.985235); 3. Microdistrict. Yacht Club (46.977016, 31.960774); 4. Microdistrict. Namyv (46.947273, 31.932793).

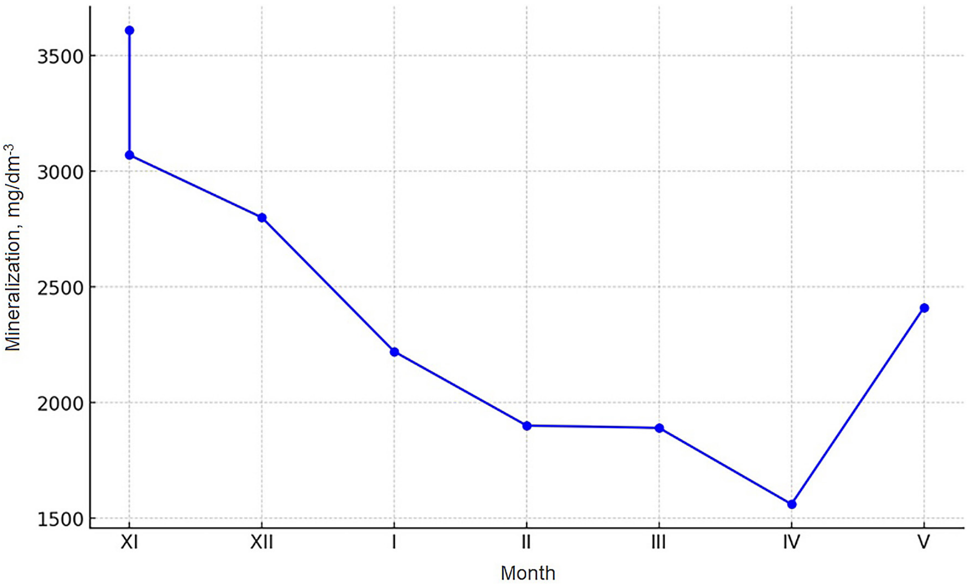

Figure 2. Dynamics of water mineralization.

Alkalinity increases significantly during the winter months (January, February), which may be due to freezing processes and limited water mixing. Hardness increases significantly in February (up to 4200 mg/dm^3), which is an abnormal figure compared to other months. Mineralization remains at a high level throughout the period, with slight fluctuations. Sulfate indicators exceed the maximum permissible concentration in all months, which is associated with high mineralization. Iron levels in November and March are higher than in other months, which may indicate local pollution or natural sources. The turbidity varies from month to month, which can indicate natural processes.

Therefore, a significant deviation in hardness in February and high rates of mineralization and sulfates indicate the need for further research. The patterns found, such as the increase in alkalinity, are consistent with natural processes.

Alkalinity significantly exceeds the maximum permissible concentration in all months considered, which indicates a consistently high level of this indicator in water (Fig. 3). There is an increase in alkalinity from December to March, after which there is a sharp drop in April, and in May it rises again. This may be due to seasonal processes or external influences that affect the chemical composition of the water. Alkalinity in the months of November and December is kept at a relatively stable level. A significant increase in alkalinity is observed during the winter months (January and February), which may be due to lower temperatures and less water mixing. An unusual drop in April may indicate a change in water exchange, possible water discharge, or the influence of other factors. The P-value for the correlation of alkalinity over time is approximately 0.274. This value is quite high, indicating that there is no statistically significant correlation between alkalinity and time (months). Changes in alkalinity probably do not have a linear relationship with time, and, in general, alkalinity has a wave-like relationship with peak values in early spring. The increase in alkalinity in spring for natural waters can be due to several natural processes:

- snow melting and spring floods, during which a large amount of meltwater enters the reservoir, which can be saturated with various dissolved substances, including bicarbonates;
- activation of biological processes, such as photosynthesis in algae and other aquatic plants. In the process of photosynthesis, carbon dioxide from water is converted into organic matter, reducing the concentration of free CO_2 in the water, which leads to an increase in pH and, accordingly, alkalinity;
- decomposition of organic matter accumulated over the winter begins to decompose under the influence of microorganisms. This can cause the release of bicarbonates into the water, increasing its alkalinity;
- changes in the chemical composition of water due to increased surface runoff, which contains minerals from the soil, can increase the overall salinity and alkalinity of the water.

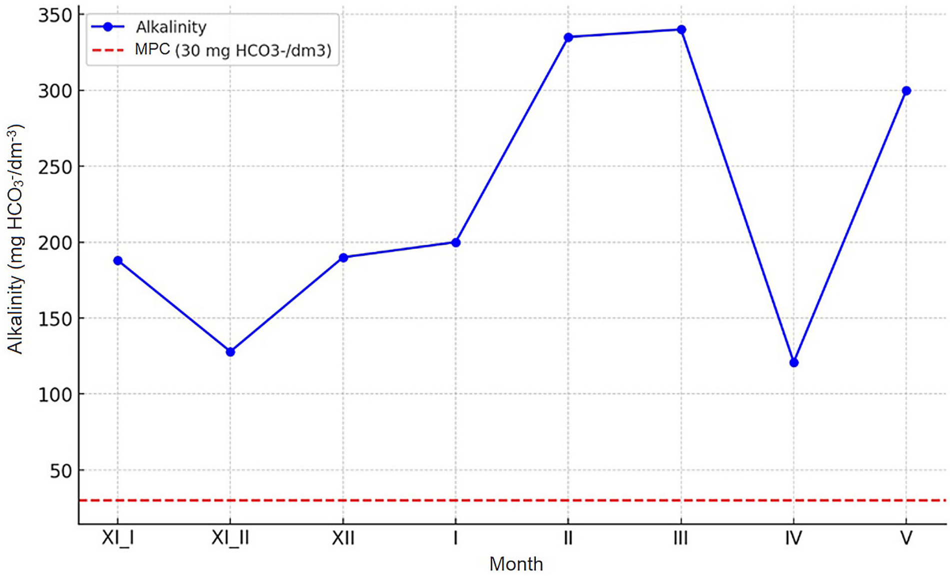

Figure 3. Dynamics of water alkalinity (Observation point №4)

Therefore, these factors can lead to an increase in alkalinity in the spring, when there is an active water exchange and changes in the physical and chemical characteristics of water bodies.

Analyzing the graph of water mineralization by observation points (Fig. 4), the following regularities can be detected: all values of mineralization at different stages of observations exceed the maximum permissible concentration (1000 mg/dm^3). This is indicative of sustainable natural processes. There is a general downward trend in the level of mineralization from November to April and May in most points. This may be due to seasonal changes, such as an increase in the water content of rivers in winter due to melting snow and ice, which leads to the dilution of salts. The level of mineralization varies between different observation points, but the general trends remain similar. In point 4, the level of mineralization remains relatively stable. This may indicate the stable nature of the influence of natural factors, which are less prone to changes in winter. In April, there is a sharp decrease in the level of mineralization, which may be due to a significant influx of fresh water.

Thus, the data indicate a significant excess of the maximum permissible concentration at all observation points, which is a serious reason not to use these waters as a source of technical and even more so drinking water supply. There is a decrease in mineralization in winter and early spring. Further monitoring is necessary for a

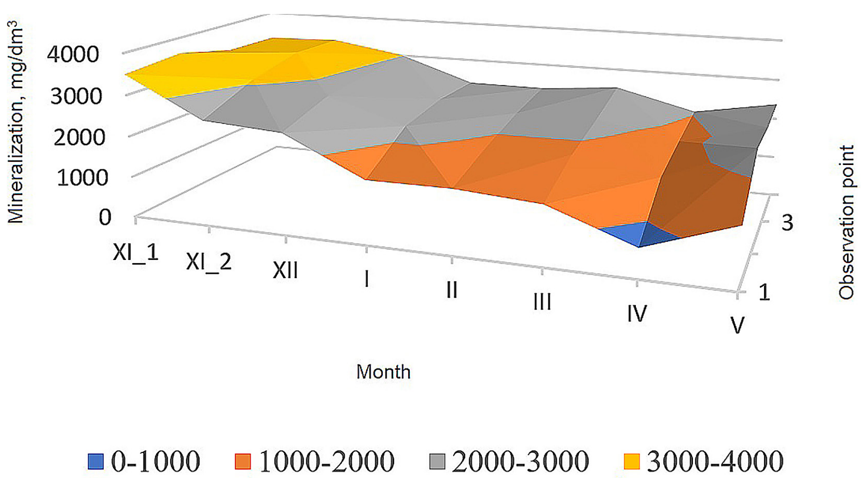

Figure 4. Dynamics of water mineralization during by observation points.

more detailed understanding of natural and anthropogenic processes. Average mineralization by observation points:

- Point 1 (farthest from mouth): 1882.63 mg/dm³;
- Point 2: 2432.50 mg/dm³;
- Point 3: 2554.38 mg/dm³;
- Point 4 (closest to mouth): 2658.75 mg/dm³.

Mineralization gradually increases towards the mouth of the river. This is due to the accumulation of salts and other solutes in the water closer to the mouth. The highest mineralization is observed in November, gradually decreasing in winter and spring. This is due to hydrological and weather conditions, in particular the increase in water flow in winter and spring, which reduces the concentration of solutes. Consequently, as the distance to the mouth decreases, there is an increase in mineralization. In addition, during the year, mineralization decreases from autumn to spring, which is due to climatic and hydrological changes.

To consider the oscillation season we have used the example of the pH indicator, which is integrated, since its value is influenced by a number of hydrochemical and hydrobiological factors, as well as temperature. Working hypothesis: seasonal fluctuations will be sinusoidal functions, which will allow you to accurately predict their natural levels and interpret deviations as anomalous phenomena.

During the regression analysis, it was found that the annual pH dynamics corresponds to the sine wave of long-term fluctuations. The approximation of the obtained data (Fig. 5) demonstrates the same harmonic oscillations.

The pH values from 2008 to 2024 of the studies show a sufficient level of correlation with the regression coefficient R = 0.78. The resulting function (Equation 3) makes it possible to predict fluctuations over a 6-year period of a sine wave. We obtain the following prognosis data (Fig. 6).

$$T = 8.37 + 0.0508cos0.756N - 3.486. \quad (3)$$

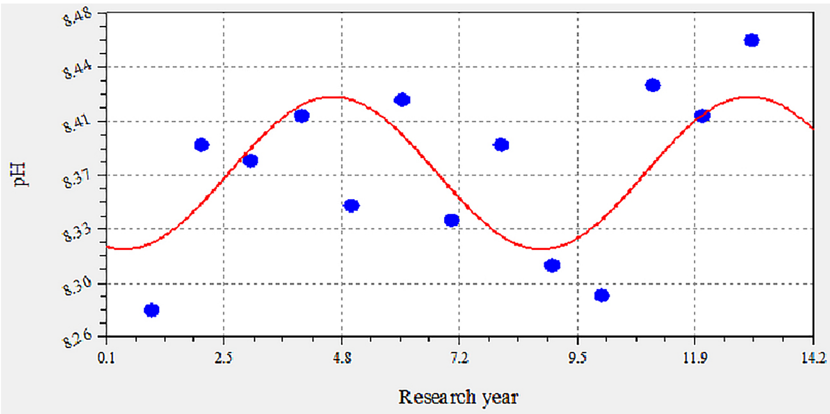

Figure 5. Harmonic pH oscillations from 2008 to 2024

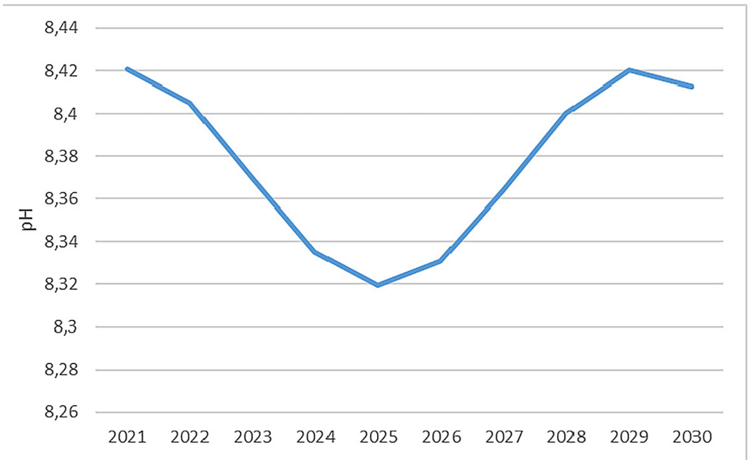

Figure 6. Prognosis of pH level up to a year.

Similar relationships were obtained for other hydrochemical parameters. All the resulting graphical dependencies are sine waves with different oscillation periods. It has been determined that seasonal fluctuations are sinusoids, on average corresponding to a six-year period of oscillations, which, in principle, confirms the theory of "Waves of Life" and the ability of natural ecosystems to self-regulate.

CONCLUSIONS

The study of spatial-temporal characteristics of surface water quality of the Buzky Estuary within the water area of the city of Mykolaiv, Ukraine made it possible to reach the following conclusions:

1. The level of mineralization varies between different observation points, but the general trends remain similar. The data indicate a significant excess of the maximum permissible concentration at all observation points, which is a serious reason not to use these waters as a source of technical and even more so drinking water supply. There is a decrease in mineralization in winter and early spring.
2. Alkalinity significantly exceeds the maximum permissible concentration in all months considered, which indicates a consistently high level of this indicator in water. There is an increase in alkalinity from December to March, after which there is a sharp drop in April, and in May it rises again. This may be due to seasonal processes or external influences that affect the chemical composition of the water.
3. During the regression analysis, it was found that the annual hydrochemical indicators dynamics correspond to the sine wave of long-term fluctuations. The approximation of the obtained data has demonstrated the same harmonic oscillations. The resulting function have made it possible to predict fluctuations over a 6-year period of a sine wave.

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