УДК 504.4.054

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PROGNOSIS MODELS OF NITRATES AND ORTHOPHOSPHATES CONTENT IN SURFACE WATERS

Abstract. *The dynamics of hydrochemical parameters such as nitrates, and orthophosphates of surface waters were analyzed. Based on the analysis of wide temporal monitoring data, of prognosis nitrates and orthophosphates of the surface waters were carried out.*
The purpose is an assessment of the state of the surface water by nitrates and orthophosphates hydrochemical parameters and their regression analysis.
The object of research – was to determine nitrates and orthophosphates indicators of the river water state during 12 years.
The regression analysis method using the Windows Excel CurveExpert software was used to determine the empirical dependencies and search for connections.
Against the background of high regulation of the Inhul river basin (the presence of 770 ponds and an irrigation system on 33 hectares, water use is carried out by more than 20 enterprises) showed the periodic nature of changes in hydrochemical parameters. Based on the obtained functions, prognoses to 2030 on annual averages were developed. The study is the basis for determining the mathematical model of natural fluctuations of the research indicators. Regression analysis allows obtaining a sinusoidal dependence on the orthophosphates content, which demonstrates 13 years fluctuation (R = 0.90). We have an 11-year sinusoidal wave with a period of 10 years and fairly high representativeness (R = 0.85) for nitrate content. The determined sinusoidal dependences of the integrated indicators of water quality allowed determining the average time of fluctuations concerning the processes of self-organization of river waters, which is about 11 years, and confirms the theory of "waves of life". The surface waters of the river are capable of self-renewal and their hydrochemical status has not yet reached a critical point, after which irreversible changes in the river ecosystem may occur.
Keywords: *nitrates; phosphates; prognosis models; water security; the prognosis of the environment state*
DOI: https://doi.org/10.32347/2411-4049.2022.4.30-43

Introduction

In 2015, within the framework of the 70th session of the UN General Assembly was held in New York UN Sustainable Development Summit and the adoption of the

Agenda, which approved new development guidelines. The final document of the Summit "Transformation of our world: the agenda in the field of sustainable development by 2030" 17 Sustainable Development Goals and 169 tasks were approved. One of the strategic goals of sustainable development is related to clean water, quality of water resources. The problem of surface water is one of the key challenges of humanity. In 2018, the International Decade for Action in the Field of Water Resources for Sustainable Development was launched. Water resources are a source of industrial and domestic water supply, and therefore play a crucial role in economic development and human life [1−7].

International experts from the World Health Organization have found that more than 60% of the world's diseases are caused by consumption of poor water. So today, water is regarded not only as a natural resource, it has a pronounced social significance. The regulatory framework for water quality assessment is formed based on general requirements for the composition and properties of water and the values of maximum permissible concentrations of substances in the water of water bodies. The general requirements determine the permissible composition and properties of water, which are assessed by the most important physical, bacteriological and chemical indicators [8−12].

Two indicators of water quality from the sanitary-toxicological group were selected for the study. These are nitrates and orthophosphates. We chose these indicators for the study because Nitrogen and Phosphorus are one of the main biogenic elements, they are the main elements of plant nutrition.

The presence of nitrate ions, NO_3^-, in natural waters is associated with:

- internal processes in the reservoir – nitrification of ammonium ions with the participation of oxygen under the action of nitrifying bacteria;
- atmospheric precipitation, which absorbs oxides of nitrogen formed during atmospheric electric discharges (the concentration of nitrates in precipitation reaches 0.9-1 mg);
- industrial and domestic wastewater, especially after biological treatment, when the concentration reaches 50 mg/dm^3;
- runoff from agricultural lands from irrigated fields where nitrogen fertilizers are applied.

The main processes aimed at reducing the concentration of nitrates are their consumption by denitrifying bacteria and phytoplankton, which in the absence of oxygen use nitrate oxygenat to oxidize organic matter.

In surface waters, nitrates are in a dissolved form. The concentration of nitrates in surface waters is subject to seasonal fluctuations: minimal in the growing season, it increases in autumn and reaches a maximum in winter when the minimum consumption of nitrogen is the decomposition of organic matter and the transition of nitrogen from organic to mineral forms. The amplitude of seasonal fluctuations can be one of the indicators of eutrophication of a water body [13, 14, 15].

Orthophosphates, PO_4^{3-}, exist in three forms: orthophosphate, metaphosphate (or polyphosphate P_2O_5) and organically bound phosphate. Orthophosphates are used on agricultural land as fertilizers. They enter surface waters during rains or melting snow. Polyphosphates are used in laundry detergents and synthetic detergents. In water, they are converted to orthophosphate and are available for absorption by plants. Organic phosphate is phosphate that is bound in plant tissue, solid waste, or other organic material. Phosphates are present in clean water bodies in very small quantities. It is an essential element for plant life, but when too much in the water, it can accelerate the eutrophication of rivers and lakes (a reduction in dissolved oxygen in water bodies caused by the effect of algal blooms). The increased content of phosphates in water is a consequence of its pollution. Natural unpolluted water bodies have a phosphate concentration of less than 0.1 mg/dm^3, and sometimes even less than 0.03 mg/dm^3. Phosphate concentrations in the water above 0.3 mg/dm^3 indicate obvious contamination. Phosphorus enters the water in both urban and agricultural environments. Orthophosphate forms are formed by natural processes, but the main sources are influenced by humans.

In recent years, phosphorus compounds have become one of the most dangerous water pollutants, which enter aquatic ecosystems with wastewater from cities, industrial production and agricultural mineral fertilizers. Municipal wastewater (containing detergents and organic waste) is discharged into rivers. Even after mechanical and biological treatment of water in purification plants, a large amount of phosphates enters the water. According to some reports, up to 75% of the total amount of phosphorus discharged into water bodies is brought by municipal wastewater. Another source of phosphates is various industrial wastes from chemical production, processing of vegetables and fruits, pulp and paper industry, etc. The contribution of the industrial group of effluents to the total amount of discharged phosphorus reaches 20%. Phosphorus is a common ingredient in agricultural fertilizers. In turn, grain crops are fed to farm animals, which produce manure rich in orthophosphates. Applying chemical fertilizers to soil already saturated with orthophosphates and applying excessive manure results in orthophosphate runoff during heavy rainfall and contamination of nearby water sources [16, 17, 18, 19, 20].

The purpose of this study is an assessment of the state of the surface water by nitrates and orthophosphates hydrochemical parameters and their regression analysis.

The object of research: nitrates and orthophosphates indicators of the river water state at the observation point Sofiyivske reservoir (drinking water intake of Novy Buh) during 2008–2020.

Study area and methods. The natural surface waters of the Inhul river, which is river of the Northern Black Sea Coast, Ukraine, were chosen as the object of the study. The Inhul river is the largest tributary of the Southern Buh, flowing through the Kirovohrad and Mykolaiv regions, Ukraine. The length of the Ingul River is 354 km, the slope of its flow is 0.4 m/km, and the feeding basin has an area of 9890 km^2 (Fig. 1).

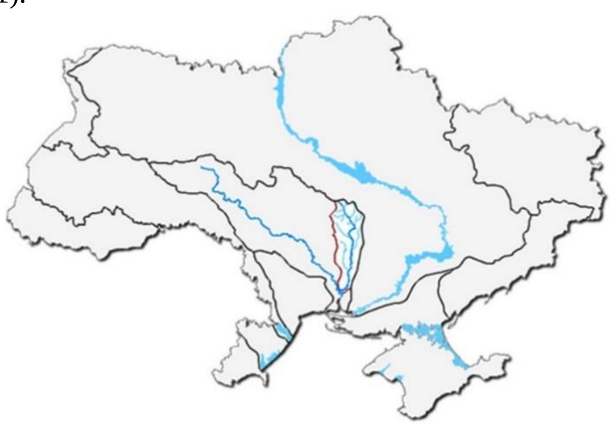

Fig. 1. The Inhul river basin is on the territory of Ukraine [21]

Long-term monitoring of certain parameters allows building mathematical models for forecasting the evolution of surface waters to maintain sustainable use of water resources and prevent environmental crises [22−27]. Increased anthropogenic activity leads to excessive pollution of water resources [28−31].

One of the main problems of water resources of the Mykolaiv region (Ukraine) is the high over-regulation of rivers (dams, artificial ponds), and the discharge of polluted wastewater from industrial facilities and agricultural production. Sewage is discharged by 66% of water users, of which 40% discharges contaminated wastewater [32−35].

The specificity of this study is the temporal analysis of the dependences of nitrates and orthophosphates in the surface waters of the Inhul river on temperature. This allowed us to study the relationships between hydrochemical parameters and temperature changes, as well as to form predictive mathematical models of long-term dynamics. The main problem of water resources in Ukraine is the pollution of water bodies with insufficiently treated industrial and domestic wastewater; moral aging of fixed assets for water supply and water protection purposes, low productivity of treatment facilities.

Research methods. We used the following methods for our study: the method of analysis; cartographic, where the map provides an opportunity to present the object of study in space; mathematical modeling through the use of regression analysis. The regression analysis was used through the Windows Excel software of the multifunctional system CurveExpert to determine the empirical dependencies and find the links found in the regression function.

We have used the criterion of significance, or Fisher (formula 1) to assess the adequacy of the model. Also we have used Fisher distribution tables (a = 0.10, a = 0.05) for 120 degrees of freedom and critical Fisher distribution points for 12−17 degrees of freedom (a = 0.01, a = 0.05) to determine the significance of the function coefficients.

$$F = \frac{R^2}{1-R^2} \cdot \frac{\mathrm{n-m-1}}{\mathrm{m}} \quad , \tag{1}$$

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

The regression coefficient (determination) is a fraction of the variance of the dependent indicator, which is explained by the function (formula 2).

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

where $\sigma^2(y)$ = D[y] – the variance of the random variable obtained from the measurements;
σ^2 = D[y|x] – conditional variance depending on the exponent *x* in the function for which the regression coefficient is located.

The method of estimating the correlation level involves the possibility of direct use of the determination coefficient as a number describing the degree of deviation of the values from the values of the function, and then the qualitative analysis of the correlation degree is carried out by a table 1.

Table 1. Scale of the regression coefficient (determination)

Value	Interpretation
R < 0	Inverse correlation
0 < R < 0.2	Very weak
0.2 < R < 0.5	Weak
0.5 < R < 0.7	Average
0.7 < R < 0.9	High
0.9 < R	Very high

The quantification also determines the level of the standard error of rank correlation (formula 3) and builds a balance chart, which in the CurveExpert software package occurs automatically.

$$S = \sqrt{\frac{1-R^2}{\mathrm{n}-2}}. \tag{3}$$

Results

By the nature, features and consequences of the influence on the chemical composition formation of natural waters are influenced by the following factors: physical and geographical (relief, climate, weathering, soil cover); geological (rock composition, hydrogeological conditions); physico-chemical (chemical properties of elements, acid-base conditions, water mixing, ion exchange); biological (vital activity of living organisms in the aquatic environment and in catchment areas); anthropogenic (all factors associated with human activities). Conditions for the formation of the chemical composition of natural waters of different types depending on the ratio and sequence of manifestation of these factors [36–46].

Climate change, which is now a major topic for discussion and research, also has a direct impact on the hydrological and hydrochemical and hydrobiological regimes of the river. We investigated changes in river temperature for more than 10 years (Fig. 2).

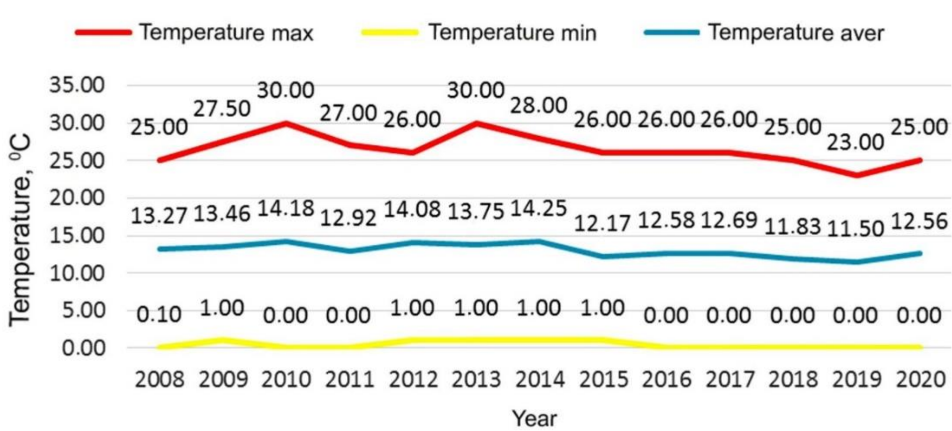

Fig. 2. Average water temperature changes

So, water temperature is the main indicator around which the analysis was carried out. This factor directly affects the hydrobiological and hydrochemical processes, and the solubility of substances. During the study, a regression analysis of the dynamics of annual averages and their seasonal quarterly dynamics during 2002–2020 was performed (data from the laboratory of water and soil monitoring of the Regional Office of Water Resources of the Mykolaiv region (Ukraine) (Law of Ukraine, Regional report). The recurrence of the studied indicators indicates the cyclical nature of natural and man-made processes that generate them (Fig. 3). Analysis of changes in water temperature (Fig. 3), despite the well-known facts of global warming, shows harmonic periodic fluctuations and even some decrease in temperature [21].

The red line indicates the maximum values of measurements, the blue − the average, the yellow − the minimum. The maximum measured data (red line) the peak values in 30^{0}C were fixed in 2010 and 2013, and the minimum 23^{0}C – in 2019. For the minimum values (yellow line) the stable mark in 0^{0}C remains. except for 2009 and the period from 2012 to 2015, when the minimum values were 1^{0}C. For average values, which are taken as a basis for further calculations, the peak values fall on 2010 (14,18^{0}C), 2012 (14,08^{0}C) and 2014 (14,25^{0}C). Deviations were recorded only of the maximum temperatures for 2010 and 2013. The values of average temperatures were predicted for the next 10 years. The predictive mathematical model demonstrates the oscillatory (sinusoidal) nature of temperature change, despite all current claims about the impact of global warming on water resources.

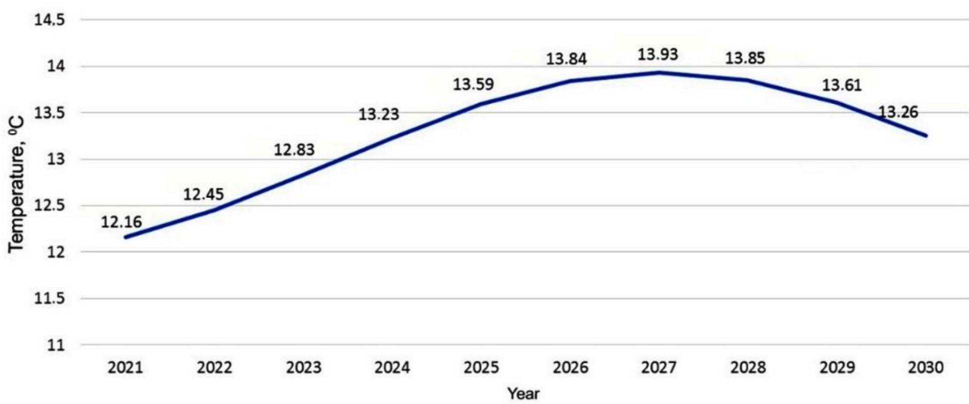

Fig. 3. Water temperature prognosis

Orthophosphates. According to the State Agency for Water Resources, there are two main MPC standards for orthophosphates: for household use and fisheries. Both are currently 3.5 mg/dm^3 (Regional office of water resources). It was determined that the maximum values do not exceed the MPC when analyzing the dynamics of orthophosphates concentrations (Fig. 4)

Regression analysis allowed obtaining a sinusoidal dependence on the orthophosphates content, which demonstrated the period of fluctuation of 13 years. However, the period under study here also falls in the area of decline and growth until 2020 (Fig. 5.) Free state phosphorus is not found in natural conditions. In waters phosphorus is in organic and inorganic forms. The base mass of Phosphorus is suspended. Phosphorus compounds enter into natural water as a result of reservoir processes, weathering and dissolution of rocks, exchange with bottom sediments and anthropogenic sources. The content of various phosphorus forms is influenced by the processes of its circle. In contrast to Nitrogen, the circle of phosphorus is unbalanced, which determines its lower content in water, so Phosphorus is a biogenic element whose content is limited.

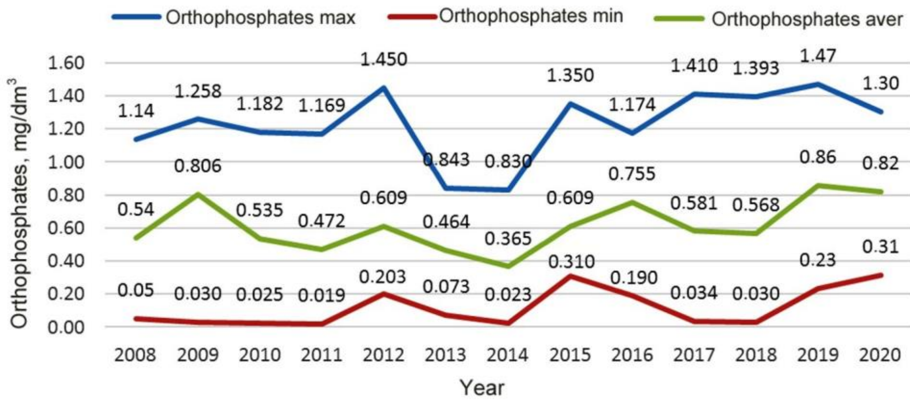

Fig. 4. Dynamics of the orthophosphates

The chemical composition of natural waters is influenced by direct and indirect factors. The direct factors are: atmospheric precipitation; soils, rocks, plants, groundwater, sewage (industrial, agricultural, household sources).

Indirect factors are: climate; relief, vegetation, water regime. Orthophosphates (PO_4^{3-}) are the main cause of eutrophication, as well as an important indicator of diffuse and point sources of pollution. Eutrophication is the result of the natural aging of reservoirs, as well as the consequence of anthropogenic action. The last factor is overwhelming.

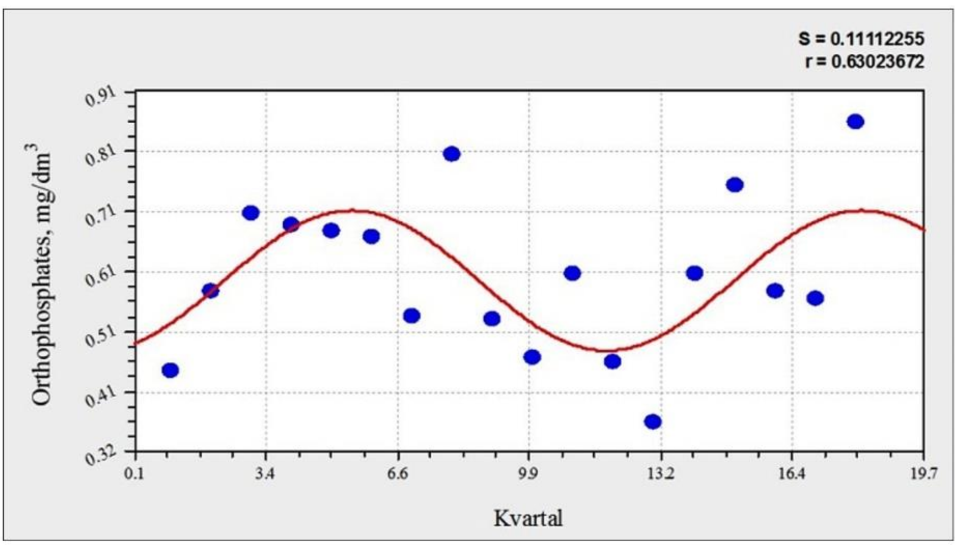

Fig. 5. A sinusoidal wave of orthophosphates content during 2002–2020

When forecasting, it is proposed to use the function (formula 4) as a more complete.

$$T = 0.598 + 0.116\, cos(0.496N - 2.714). \qquad (4)$$

The obtained graph (Fig. 6) allows predicting natural fluctuations of phosphate content in the surface waters of the Inhul River. The prognosis, developed based on this function is highly reliable, due to the high regression coefficient of the function.

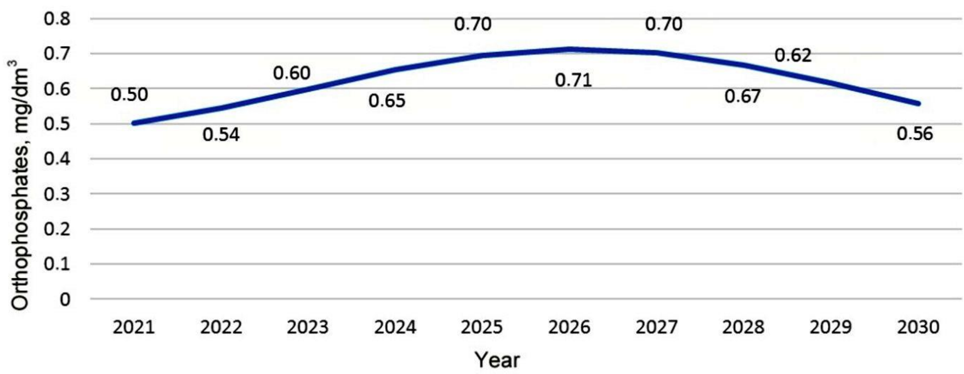

Fig. 6. Prognosis of orthophosphates content by 2030

Nitrates. Analysis of the dynamics of the content of nitrates as the main compounds of nitrogen, as a biogenic element, shows a significant excess of the MPC (45 mg/dm^3) to 70.49 mg/dm^3 in 2008 (Fig. 7). Nitrates indicators eutrophication and an important indicator of diffuse pollution by fertilizers (leaching from the soil), as the characteristics of the sewage works.

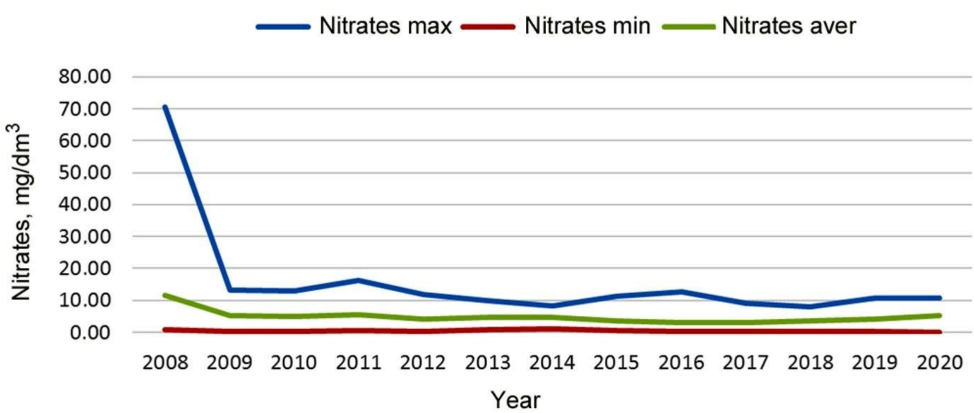

Fig. 7. Dynamics of the nitrates

Due to the anomaly of 2008 caused by mass accidental emissions of Galician treatment plants, which affected the entire river area, we have the highest representativeness for the growth function (Saturation Growth-Rate Model, Fig. 8).

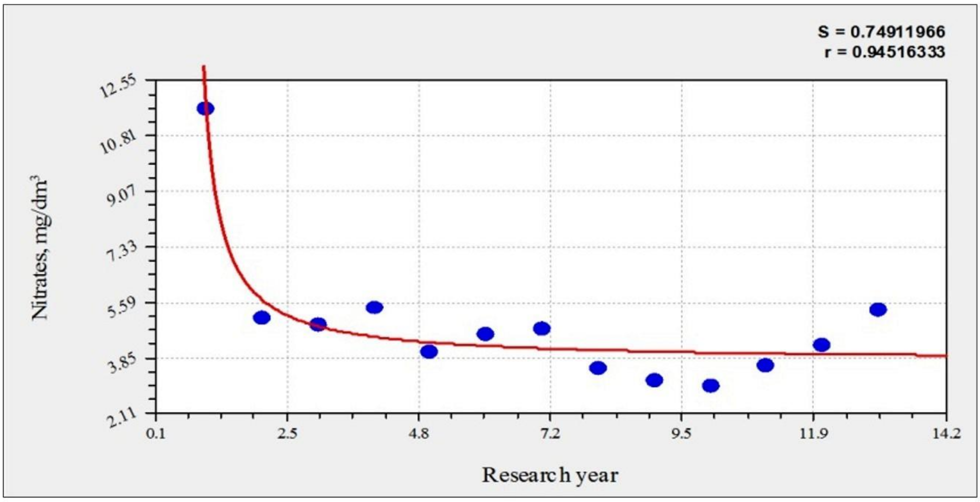

Fig. 8. The function of the nitrates concentration changes

However, although its regression coefficient of the function (formula 5) is high (0.95), we consider it necessary to note that the value of 2008 is the result of artificial pollution, not seasonal dynamics, so the forecast must be built without taking it into account.

$$T = \frac{3.75N}{N - 0.68} \quad . \tag{5}$$

So if we exclude this anomaly, we get an 11-year sinusoidal wave (Fig. 9) with a period of 10 years and fairly high representativeness (R = 0.85).

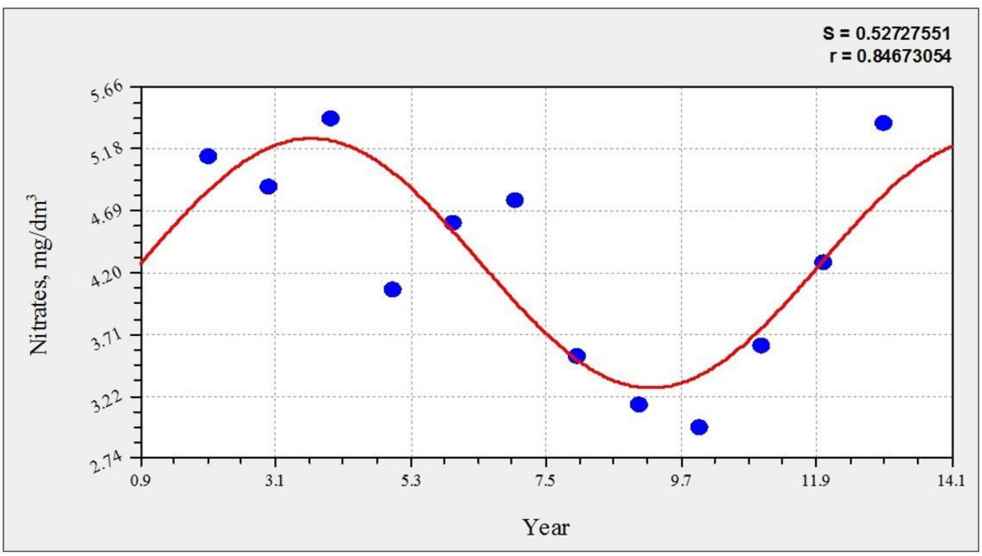

Fig. 9. A sinusoidal wave of nitrate content

The function (formula 6) determines the entry into the study period of the stage of decreasing values.

$$T = 4.28 + 0.985\, cos(0.568N - 2.081). \quad (6)$$

The prognosis (Fig. 10) shows stable natural dynamics of nitrate content in surface water.

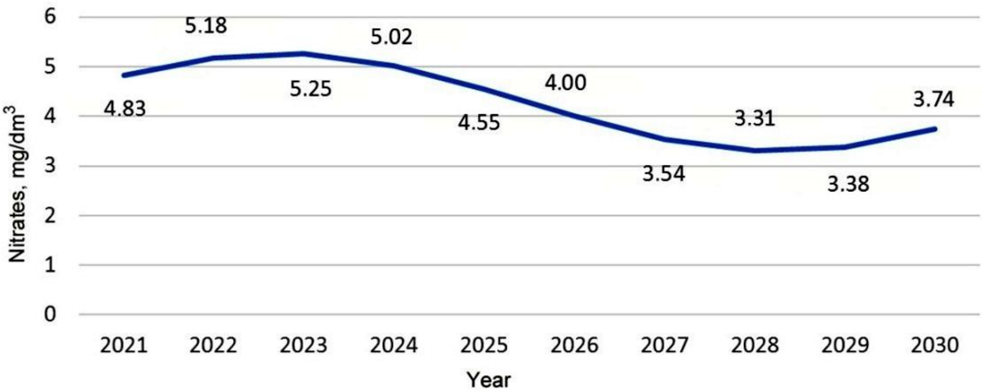

Fig. 10. Prognosis of nitrate content until 2030

Conclusions

The dynamics of the studied indicators over time, namely: temperature, nitrates and orthophosphates were presented as a regression analysis. Against the background of high regulation of the Inhul river basin (the presence of 770 ponds and an irrigation system on 33 hectares, water use is carried out by more than 20 enterprises) has shown the periodic nature of changes in hydrochemical parameters. Based on the obtained functions, prognoses for 2021–2030 on average annual averages have been developed. Regression analysis allows obtaining a sinusoidal dependence on the orthophosphates content, which demonstrates the period of fluctuation of 13 years. The study is the basis for determining the mathematical model of natural fluctuations of the studied indicators. Regression analysis allows obtaining a sinusoidal dependence on the orthophosphates content, which demonstrates the period of fluctuation of 13 years ($R = 0.90$). We have an 11-year sinusoidal wave with a period of 10 years and fairly high representativeness ($R = 0.85$) for nitrates content. The determined sinusoidal dependences of the integrated indicators of water quality allowed determining the average time of fluctuations concerning the processes of self-organization of river waters, which is about 11 years, and confirms the theory of "waves of life". Currently, the surface waters of the river are capable of self-renewal and their hydrochemical status has not yet reached a critical point, after which irreversible changes in the river ecosystem may occur.

Acknowledgements

We would like to express our gratitude to the Regional Office of Water Resources in the Mykolaiv region for creative collaboration during the research, for the opportunity to conduct the experimental work also.

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The article was received 03.08.2022 and was accepted after revision 09.11.2022

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ПРОГНОЗНІ МОДЕЛІ ВМІСТУ НІТРАТІВ І ФОСФАТІВ У ПОВЕРХНЕВИХ ВОДАХ

Анотація. Проаналізовано динаміку таких гідрохімічних показників, як нітрати та ортофосфати поверхневих вод. На основі аналізу даних широкого часового моніторингу проведено прогноз нітратів і ортофосфатів поверхневих вод.

Мета – оцінка стану поверхневих вод за гідрохімічними показниками нітратів і ортофосфатів та їх регресійний аналіз.

Мета дослідження – визначення нітратно-ортофосфатних показників стану води річки упродовж 12 років.

Для визначення емпіричних залежностей та пошуку зв’язків використовувався метод регресійного аналізу з використанням програми Windows Excel CurveExpert.

На фоні високої зарегульованості басейну річки Інгул (наявність 770 ставків та зрошувальної системи на 33 га, водокористування здійснюють понад 20 підприємств) показано періодичний характер зміни гідрохімічних показників. На основі отриманих функцій здійснено прогнози до 2030 р. за середньорічними показниками. Дослідження є основою для визначення математичної моделі закономірних коливань досліджуваних показників. Регресійний аналіз дозволив отримати синусоїдальну залежність вмісту ортофосфатів, яка охоплює 13-річне коливання (R = 0,90). Отримано 11-річну синусоїду з періодом 10 років і досить високу репрезентативність (R = 0,85) за вмістом нітратів. Визначені синусоїдальні залежності інтегральних показників якості води дозволили визначити середній час коливань щодо процесів самоорганізації поверхневих вод, який становить близько 11 років і підтверджує теорію «хвиль життя». Поверхневі води річки здатні до самовідновлення, а їх гідрохімічний стан ще не досяг критичної точки, після якої можуть відбутися незворотні зміни в річковій екосистемі.

Ключові слова: нітрати; фосфати; прогнозні моделі; безпека водних ресурсів; прогноз стану довкілля

Стаття надійшла до редакції 03.08.2022 і прийнята до друку після рецензування 09.11.2022

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