JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2021, 22(8), 111–122
https://doi.org/10.12911/22998993/140264
ISSN 2299-8993, License CC-BY 4.0

Received: 2021.06.16
Accepted: 2021.07.24
Published: 2021.08.06

Hydrochemical Indicators Dynamic in Surface Water

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ABSTRACT

On the basis of the analysis of wide temporal monitoring data, a forecast of the integrated hydrochemical indicators of the waters of the Inhul river (Ukraine) was carried out. The performed analysis was also the basis for the determination of a mathematical model of natural fluctuations of the indicators studied. The determined sinusoidal dependence of the integrated water quality indicators allowed determining the average time of fluctuations concerning the processes of self-organisation of river waters. In practice, the developed mathematical models may constitute a valuable support and supplement to the existing models in the field of prediction of self-organization processes of river waters. They may also contribute to even more effective minimization of undesirable effects of anthropogenic impact on aquatic ecosystems.

Keywords: surface water quality, water security, hydrochemical indicators, regression analysis, mathematical modeling, the forecast of the environment state, Inhul river.

INTRODUCTION

The problems of surface water quality is one of the key challenges of humanity. Following the goals of sustainable development for Ukraine, where more than 70% of all water use is surface water, the issues of assessing the state of water resources, their monitoring are very relevant [Mitryasova et al., 2017; Jepson et al., 2017; Mitryasova et al., 2018; Chugai et al., 2020]. Surface water monitoring is the basis for forecast of the state of aquatic ecosystems, prevention of environmental crises, sustainable use of water resources to achieve the sustainable development goals [Fernandez et al., 2012; Mitryasova and Pohrebennyk, 2017; Meyer et al., 2019; Schickele et al., 2020]. In turn, the global water security challenges are primarily are a careful study of the patterns of climate change impact on water resources, rational integrated water management, etc. Among the 17 global sustainable development goals, two are directly related to water security [Gersonius et al., 2013; NRDC, 2013; Butler et al., 2016; Pohrebennyk et al., 2016; Staddon et al., 2017; Ward et al., 2019; Mitryasova et al., 2020]. The growth of anthropogenic activity leads to excessive pollution of water resources [Mitryasova et al., 2017; Wang et al., 2018; Petrov et al., 2020]. Assessment of the surface water quality takes into account the state of the water body in time and space, which allows identifying the trends in water quality, helps to determine the anthropogenic pressure and the consequences of water conservation measures [Barakat et al., 2011; Abbasi et al., 2012; Casal-Campos et al., 2015; De Haan et al., 2015; Bezsonov et al., 2017, Byrne et al., 2017, Ishchenko et al., 2019; Cieśla et al., 2020]. A negative factor limiting the use of water resources is the deterioration of water quality due to the discharge of wastewater into water bodies, as a result of which water is polluted, loses its useful qualities, and often becomes unusable [O'Hare et al., 2018; Soboleva et al., 2020; Birk et al., 2021; Trus et al., 2021].

The main problems regarding the rational use and protection of water resources of Ukraine are pollution of water bodies with harmful emissions as well as insufficiently treated industrial and domestic wastewater; aging of fixed assets for water supply and water protection purposes, low productivity of treatment facilities; insufficient self-healing and self-cleaning ability of aquatic ecosystems; unbalanced management system, characterized by high volumes of water resources in the economy and high water content of products [Charis et al., 2010, Yurasov et al., 2012; Vasenko et al., 2017; Mitryasova et al., 2020]. A significant problem of the reservoirs of the Mykolaiv area (Ukraine) is dumping of the polluted sewage. Sewage is discharged by 66% of water users, 40% of whom discharge contaminated wastewater [Shakhman et al., 2017; Lykhovyd et al., 2018; Bashynska, 2018; Mitryasova et al., 2021; Shakhman and Bystrintseva, 2021]. The Black Sea river basin covers about 60% of the area of all river basins in the region and currently the Regional office of water resources monitor the water bodies condition, assesses irrigated lands, agricultural lands and settlements that are flooded, as well as hydrochemical and radiological control of border water bodies by agreement between the governments of neighboring countries [Farrelly and Brown, 2011; Vlasov and Hryshchankava, 2014; Ignatowicz, 2020].

The feature of this study is the temporal analysis of the dependences of the integrated hydrochemical parameters of the Inhul River on temperature, which allows for creating forecasts of long-term dynamics and a detailed study of the relationships between chemicals and temperature changes. The main purpose of the work was assessment of the state of the Inhul River by integrated hydrochemical parameters and their regression analysis. In order to achieve the goal, there was a need for a detailed study of the characteristics of the Inhul River. On the basis of the regression analysis, mathematical models of fluctuations of the studied waters indicators of the Inhul River during 2008–2020 were created.

STUDY AREA

The object of this research was established based on integrated hydrochemical indicators of the state of water of the river Inhul at the observation point Sofiyivske reservoir (drinking water intake of Novy Buh) during 2008−2020. The Inhul River is the largest tributary of the Southern Buh, flowing through the Kirovohrad and Mykolaiv regions. Inhul reaches 354 kilometers in length, its slope is 0.4 m/km, and the power pool has an area of 9890 square meters (Fig. 1).

RESEARCH METHODS

During the research, the following methods were used: the method of analysis as a method of scientific research, which allows dividing the

Figure 1. Scheme of the Inhul river basin on the territory of Ukraine

subject into parts in order to study it in detail; cartographic, where the map provides an opportunity to present the object of study in space, and mathematical modeling through the use of regression analysis. The latter 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.

In order to assess the adequacy of the model used the criterion of significance, or Fisher (equation 1). 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) are used to determine the significance of the function coefficients.

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

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

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

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

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

Table 1. Chaddock 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 method of estimating the correlation level involves the possibility of directly using the determination coefficient as a number describing the degree of deviation of the estimated values from the values of the function, then the qualitative analysis of the correlation degree was carried out in Table 1.

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

$$S = \sqrt{\frac{1 - R^2}{n - 2}} \quad (3)$$

In order to assess and forecast the state of the aquatic ecosystem, 4 hydrochemical indicators were analyzed, as well as the water temperature indicator over time. The integrated indicators of sanitary nature were selected, namely pH; dissolved oxygen; suspended solids and BOD_5.

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

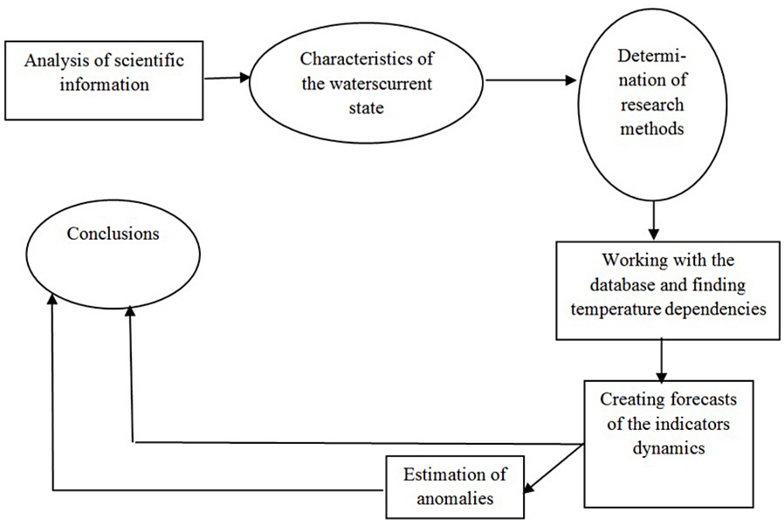

Figure 2. Stages of the research

monitoring of the Regional Office of Water Resources of 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. 2).

RESULTS AND DISCUSSION

The study of water quality is important in terms of assessing the aquatic ecosystem and sustainable water use. In order to comprehensively characterize the dynamics of the state of the waters of the Inhul River, the results of anomalous values were analyzed, which will allow us to determine large-scale episodic discharges. Mathematical interpretation of long-term and seasonal fluctuations of indicators allows estimating a natural background and sources of constant pollution of waters of the Inhul river.

The main indicator, around which the analysis was carried out, is the water temperature. This factor directly affects the biological and chemical processes, as well as the solubility of substances. The 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.

The red line indicates the maximum values of measurements, blue – the average, and yellow – the minimum. For the maximum measured data (red line), the peak values in 30 °C fall in 2010 and 2013, and the minimum 23 °C – in 2019. For the minimum values (yellow line) the stable mark in 0 °C remains, except for 2009 and the period from 2012 to 2015, when the minimum values were 1 °C. For average values, which are taken as a basis for further calculations, the peak values fall on 2010 (14.18 °C), 2012 (14.08 °C) and 2014 (14.25 °C). The graph shows that 2010 was the warmest, while temperature fluctuations in 2012 gave high values of average (14.08 °C) and minimum (1 °C) temperatures, but low for maximum temperature (26 °C). 2013 and 2014 were more balanced in this respect and 2014 saw the middle of the decline in maximum temperatures (28 °C) and the peak for the growth of averages (14.25 °C). The gradual decline of maximum (from 30–26 to 26–23 °C), average (from 13–14 °C to 12–13 °C) and minimum temperatures (from 1 to 0 °C) may indicate both a drop in temperature and fluctuations, as part of the cycle. In order to determine whether this decline was due to cooling or part of a multi-year cycle, a regression analysis of the mean temperature (blue line) of the research year was performed on the measured 12-year interval. Approximating the obtained data by average temperatures, a sinusoidal graph with a regression coefficient of 0.81 and a period of oscillation of about 6 years was obtained. The obtained function is determined by equation (4) and demonstrates harmonic temperature fluctuations.

$$T = 12.97 + 0.958\cos(0.427N - 1.843) \quad (4)$$

where: N – research year number, starting from 2008.

In the process of constructing regression dependence, their numbering was adopted, where 2008 is the first year of the study, 2009 is the second, and so on by 2020, which is the twelfth. The same principle is used in subsequent Curve Expert graphs, as it better conveys the sequence of processes. Deviations were recorded only of the maximum temperatures of 2010 and 2013. The values of average temperatures have been predicted for the next 10 years (Fig. 4).

In the research, the dynamics of change of the hydrogen index (pH) as one of the main

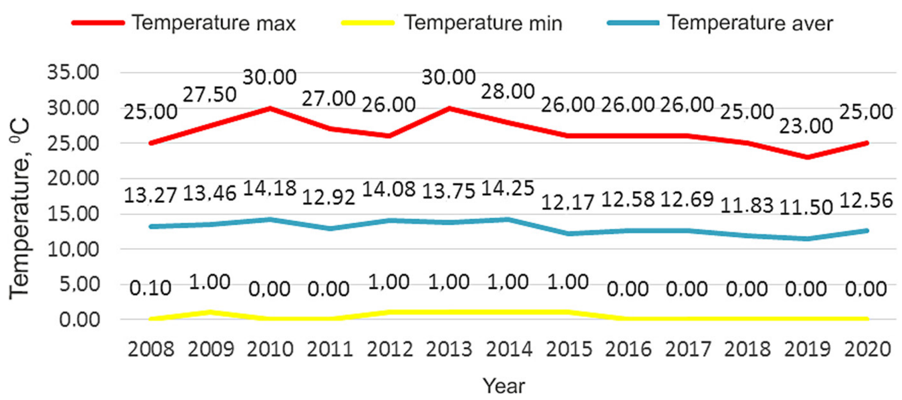

Figure 3. Dynamics of water temperature

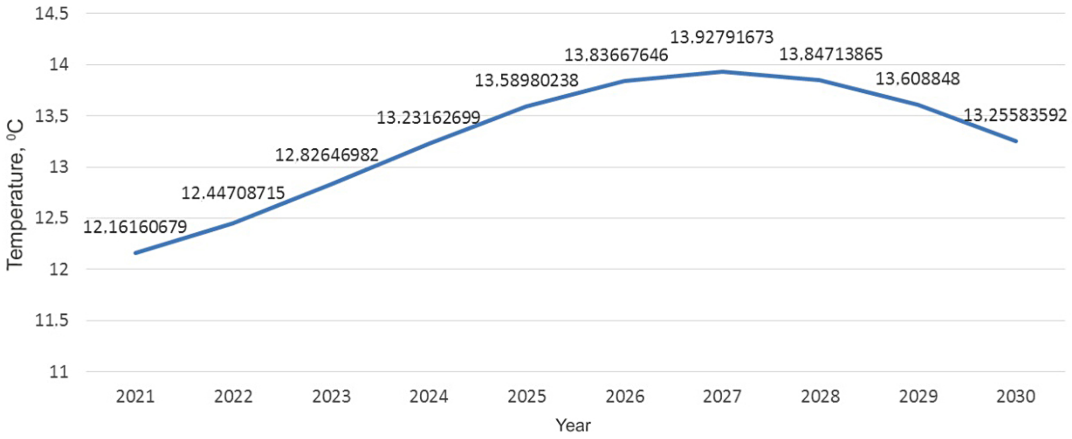

Figure 4. Water temperature forecast for 2021–2030 years

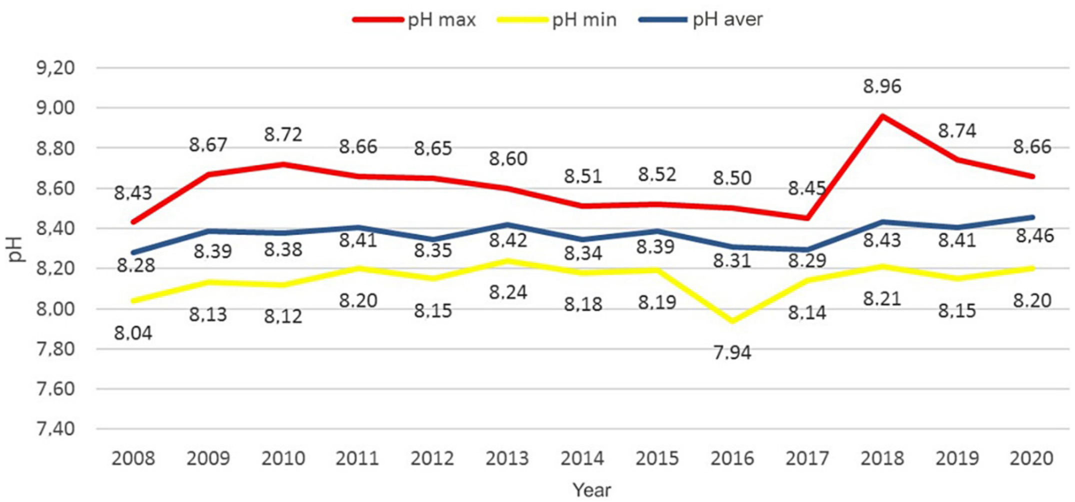

Figure 5. Dynamics of pH change

integrated factors was analyzed (Fig. 5). The value of this indicator is influenced by all physicochemical parameters of the aquatic environment. The minimum was observed in 2016 (7.94), possibly due to precipitation, or due to acid contaminants. The maximum was 8.96 in 2018 when due to the gradual increase during the year, the maximum concentration limit was exceeded (6.5–8.5) and the water became alkaline. Moreover, the excess of the MPC (maximum permissible concentration) by a small amount of 0.1 was observed from 2009 to 2014.

The approximation of the obtained data (Fig. 6) shows the same harmonic fluctuations as temperature, but with a lower regression coefficient. The values from 2008 to 2020 studies show a sufficient level of correlation with the regression coefficient R = 0.68. The obtained function (equation 5) allows predicting fluctuations during the 6 years of a sinusoid. The following forecast data were obtained (Fig. 7).

$$T = 8.37 + 0.0508\cos(0.756N - 3.486) \quad (5)$$

In the analysis of these oscillations (Fig. 8) it is determined that due to the curvature of the annual sinusoid, the maximum step at which it does not affect the sinusoid of seasonal oscillations is 32 quarters, i.e. 8 years.

Oxygen dissolved in water (Fig. 9) is a key indicator for the activity of aerobic living organisms. There is no maximum concentration limit for this indicator, but at least 4 mg/dm^3 of oxygen is required for the survival of living organisms. The minimum figure of 2.8 mg/dm^3, recorded in 2020. This figure is below the subsistence level and well below the summer norm of 6 mg/dm^3. It is caused, apparently, by the purification of the river waters due to discharges of utilities. Which, in turn, led to the mass slaughter of fish in rivers.

The analysis of the obtained function by averages (Fig. 10) shows a similar sinusoid

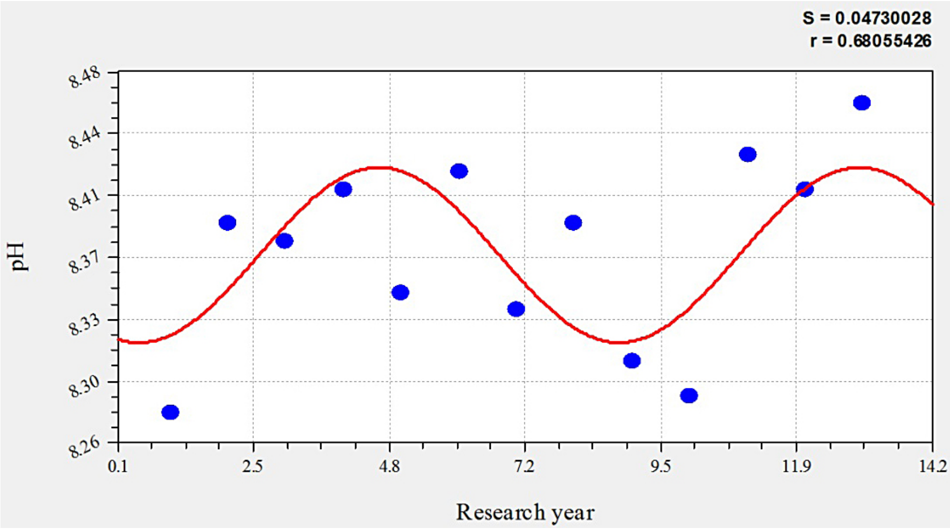

Figure 6. Harmonic pH fluctuations during 2008–2020

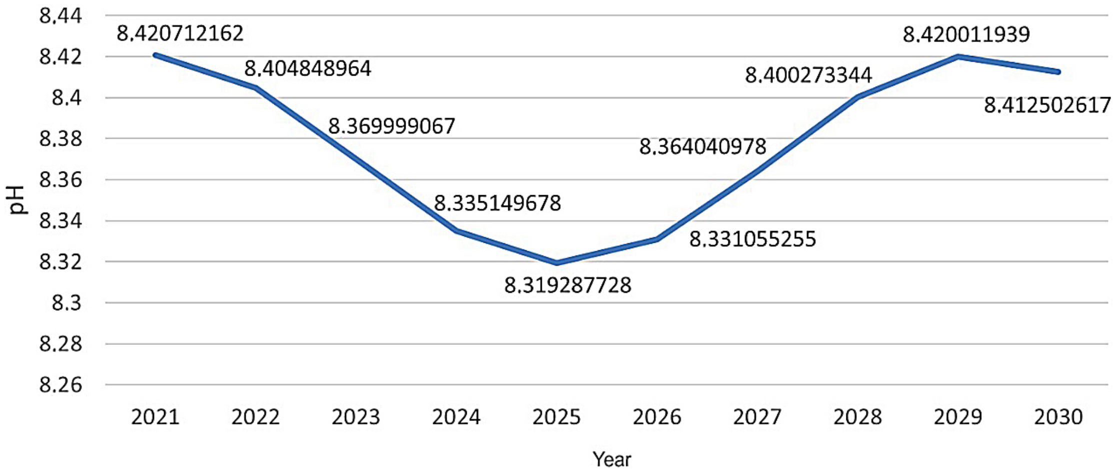

Figure 7. Forecast of the pH level for 2021–2030 years

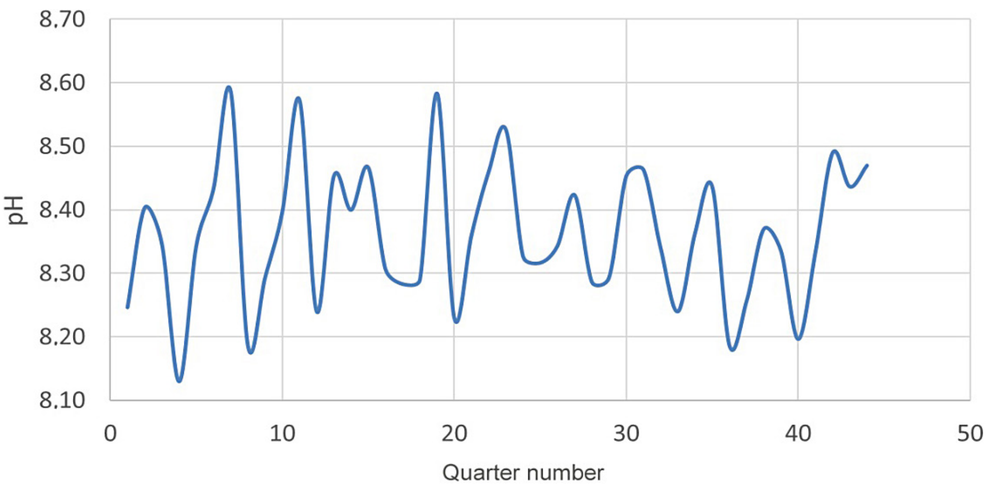

Figure 8. Fluctuations of average pH on a quarterly basis

(equation 6), as in the case of pH, which means the preservation of a multi-year cycle. However, the step in this cycle is about 3 years.

$$T = 12.5 + 0.81\cos(1.81N - 0.01044) \quad (6)$$

The content of soluble oxygen is important for assessing the environmental and sanitary condition of the river ecosystem. The oxygen content must be at a sufficient level necessary for the respiratory processes of aquatic organisms.

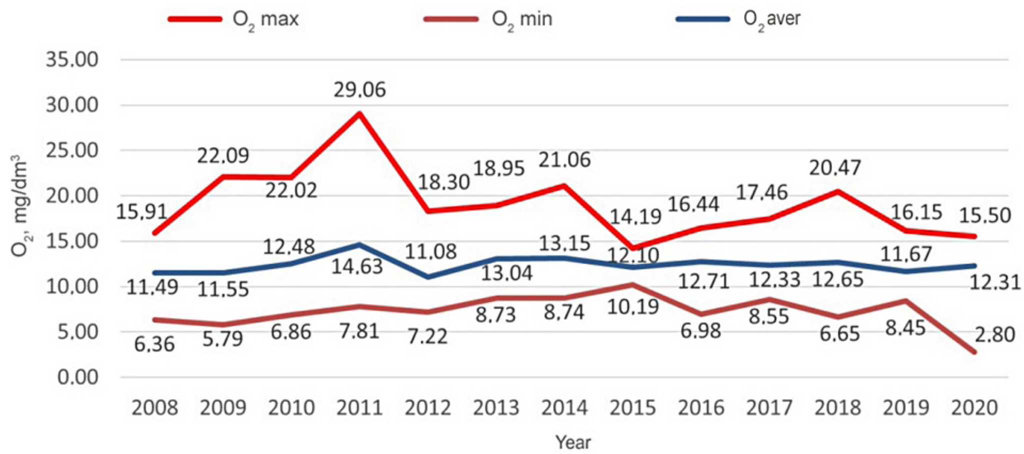

Figure 9. Dynamics of dissolved oxygen concentration

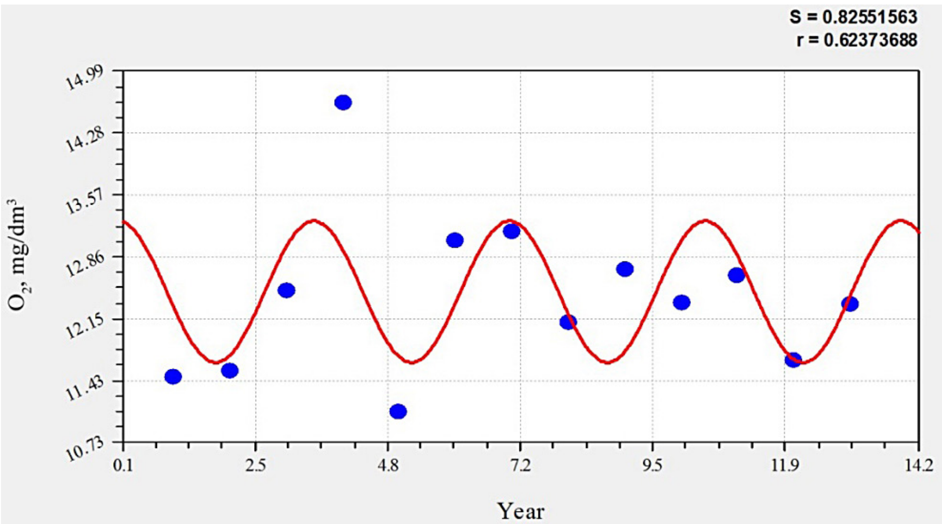

Figure 10. Sinusoid of annual dynamics of dissolved oxygen concentration

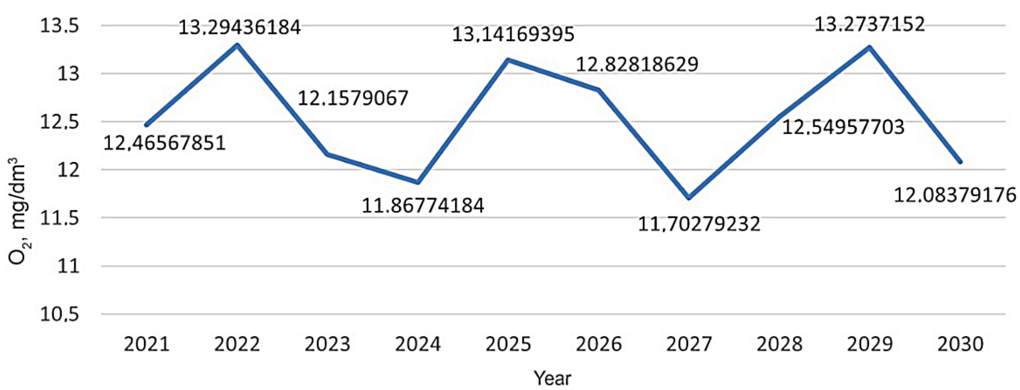

Figure 11. Forecast of dissolved oxygen concentration

Soluble oxygen is also necessary for the processes of self-purification of reservoirs, as it participates in redox reactions of organic and mineral substances. The decrease in the concentration of soluble oxygen indicates a change in hydrobiological, hydrochemical processes, the pollution of the reservoir, primarily organic matter [Stephenson and Shabman, 2017; Lintern et al., 2020; Kovacs and Zavadsky, 2021]. The supply of oxygen to the reservoir occurs through the processes of adsorption, photosynthesis, as well as rainwater, and meltwater. The oxygen content is affected by atmospheric pressure, precipitation, mineralization, temperature. The concentration of dissolved oxygen in the Inhul River during the study period fluctuated from 2.8 mg/dm^3 to 29.06 mg/dm^3 and is subject to seasonal and daily changes. Reducing the oxygen concentration to 3 mg/dm^3 causes the mass death of aquatic organisms [Mitryasova et al., 2021]. For the natural functioning of the aquatic ecosystem, the oxygen content must be at least 4 mg/dm^3, and for fish ponds – 6 mg/dm^3. In general, the oxygen content is a very unstable component of the chemical composition of water. The forecast results are presented in Fig. 11.

BOD_5 determines the consumption of oxygen for the oxidation of organic pollutants present in the reservoir. This is one of the most important integrated indicators of water purity. The possible organic pollutants may include phenols, aromatic compounds, petroleum and petroleum products, sulfur-containing organic compounds. Some organic compounds have a toxic effect. The natural sources of such organic compounds may be the remains of living organisms, but the bulk of organic compounds are the result of anthropogenic activity. The MPC for this indicator is 3 mg/dm^3. The dynamics of change of BOD_5 are given in Figure 12.

Figure 12 shows the peak exceedances of the MPC in 2011, 2017 and 2020. The year 2020 was anomalous in this respect. If the anomaly of 2020 is removed, the usual sine wave with a period of 2 years is obtained. The function of this sinusoid (equation 7) has a regression coefficient of 0.66.

$$T = 2.75 + 0.406\cos(2.43N - 2.42) \quad (7)$$

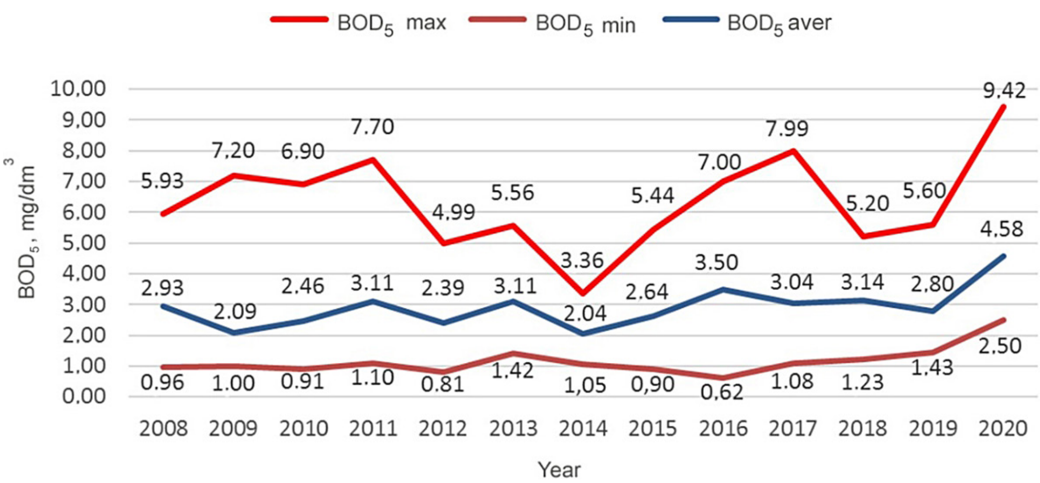

Figure 12. Dynamics of BOD_5

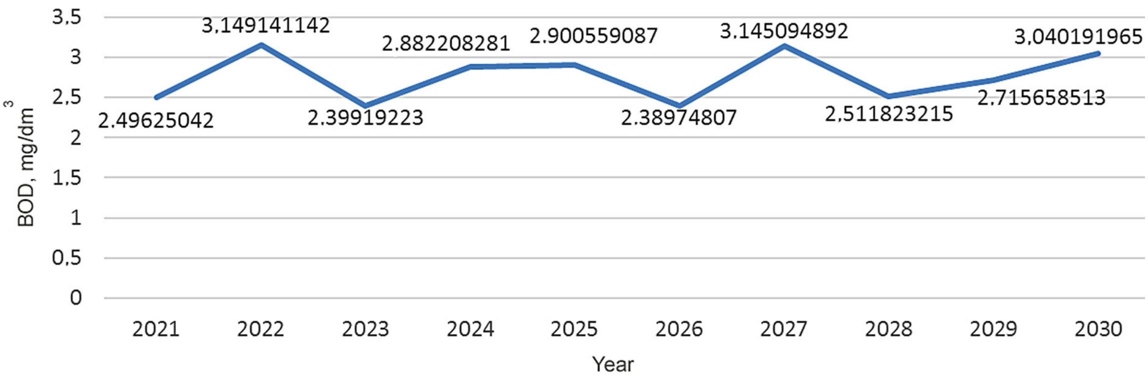

Figure 13. Forecast of natural dynamics of BOD_5

Exceeding the indicator of 3 mg/dm^3 indicates the presence of significant anthropogenic impact from utilities, agricultural production, and river transport. Peak values of 3.3–3.5 are higher than the MPC, which means strong organic pollution of the Inhul River. Applying this function (equation 7), a forecast (Fig. 13) for the next 10 years is obtained.

The content of suspended solids should not exceed 500 mg/dm^3. However, there is also a norm of wastewater treatment. Wastewater is considered if the content of suspended particles does not exceed 60 mg/dm^3. The dynamics of the content of suspended solids over 12 years are shown in Figure 14.

Regression analysis indicates a period of sinusoids (equation 8) of 10 years. A significant deviation in the direction of decline in 2017 falls somewhat out of these statistics, which gives a regression coefficient of 0.73 instead of close to 1.

$$T = 12.05 + 2.21\cos(0.399N - 0.407) \quad (8)$$

The forecast on the basis of this function gives the dynamics (Fig. 15) of the content of suspended particles for the next 10 years.

CONCLUSIONS

The dynamics of change of the main integrated indicators of surface water quality of the Inhul river (Mykolaiv region, Ukraine) for more than 10 years was analyzed. A regression analysis of the dynamics of the studied indicators over time, included: temperature, pH, suspended solids, dissolved oxygen, BOD_5.

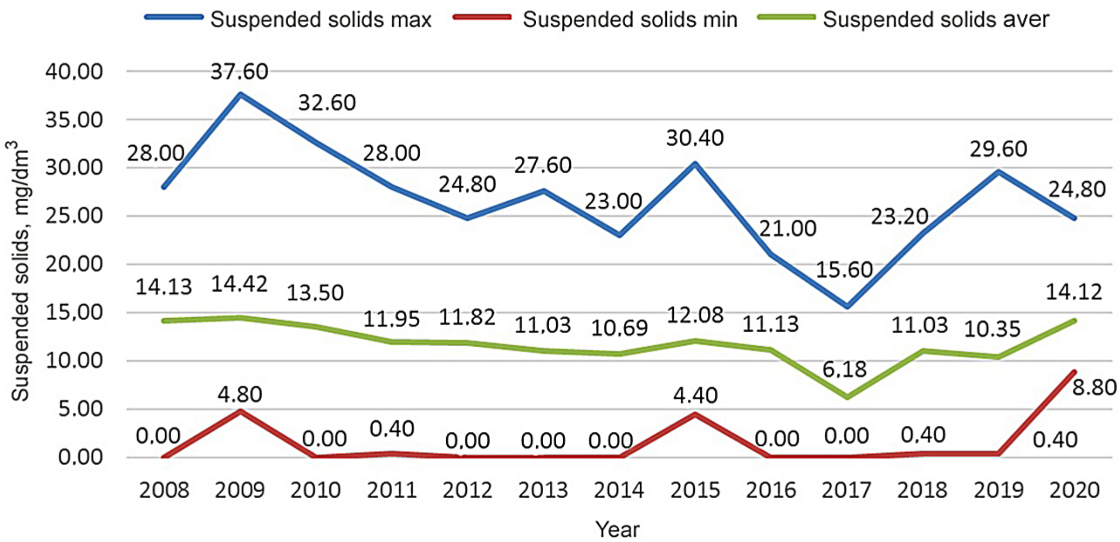

Figure 14. Dynamics of suspended solids content

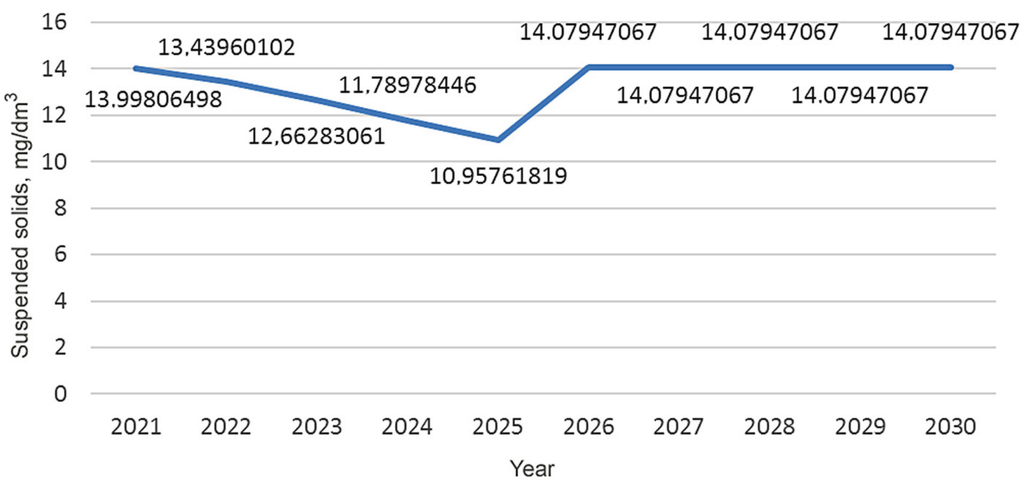

Figure 15. Forecast of the dynamics of the suspended solids content

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), the periodic nature of changes in hydrochemical parameters was shown. On the basis of the obtained functions, the forecasts for 2021−2030 on average annual averages were developed. The obtained forecasts are the basis for analysis for deviations from the natural background, but their accuracy is higher in the case of approximation of seasonal dynamics functions through annual functions.

The main anomalous values of measurements of 2008–2020, as deviations from the specified function, were determined and the causes of such anomalies, which have anthropogenic origin due to the activity of communal and agricultural sectors of the economy, were determined. The study is also the basis for determining the mathematical model of natural fluctuations of the studied indicators. The determined sinusoidal dependences of the integrated indicators of water quality allowed indicating the average time of fluctuations in relation to the processes of self-organization of river waters, which is about 6 years, and confirms the theory of "waves of life".

Acknowledgements

We would like to thank the Regional office of water resources in the Mykolaiv region for creative collaboration during the research, for the opportunity to conduct the experimental work and for collaboration with colleagues from the Rzeszow University of Technology and Maria Curie-Sklodowska University (Poland).

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