CORRELATION ANALYSIS OF THE WATER QUALITY INDICATORS ON THE SMALL RIVER

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Abstract. *Small rivers form the water resources of medium and large rivers, hydrochemical water quality and creating lands large areas.*

Purpose is determination of interdependencies between hydrochemical indicators of surface water quality on the example of a small river as a limiting factor of formation of aquatic ecosystem of territories.

Correlation analysis of the studied indicators of water quality were conducted on an average value of each indicator (pH, phosphates, nitrates, BOD_5, COD, soluble oxygen) for the period from 2007 to 2021. Found a significant increase in phosphates with time. Positive changes are founded in water object that is related to a decrease in the value of BOD_5. This is due to a decrease in the number of use of oxygen on oxidation of inorganic and organic substances. In general, the use of river runoff of the river above normal, and the overall environmental state of river basin is defined as "extremely poor".

Periods were determined with exceeding the MPC for hydrochemical indicators of water quality; the sources of the input of pollutants into the water object were identified and analyzed. Weak correlations between BOD_5, COD and nitrates, phosphates were determined. These confirm the fact of increasing BOD_5 and COD due to non-oxine-containing forms of phosphorus and nitrogen compounds. A further perspective is to study ways to reduce the supply of phosphates to the water body.

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Introduction. Environmental monitoring is one of the country's priorities towards achieving the goals of sustainable development. The one is the goal of the roadmap for the implementation of environmental policy in Ukraine, as a country that has set a course for European integration in terms of implementing programmes aimed at national security and sustainable development of society. Environmental issues outlined in the legislation and regulations of the European Union, namely: Millennium Development Goals (Millennium Development Goals, 2015); Objectives of 2050 of the Seventh Environment Action Programme (7th Environment Action Programme, 2013; Ishchenko et al, 2019), Water Framework Directive 2000/60/EC (Directive 2000/60/EC of the European Parliament and of the Council, 2000; Charis and Galanakis, 2010); Industrial Pollution Directive 2010 /75/EU (Directive 2010/75/EU of the European Parliament and of the Council, 2010); Water Code of Ukraine (Water Code of Ukraine,1995.

The scientific works of scientists have acquired significant scientific significance in the study of environmental problems related to water resources management and anthropogenic impact on the state of water bodies. Staddon C. et al. study the socio-economic issues of water resources management, the structure of water consumption in different countries (Staddon, 2016).

Meyer A.M., Klein C., Fünfrocken E., Kautenburger R., Beck H.P. et al. study the correlations between chemical components, as well as the patterns of distribution of pollutants in the aquatic environment, study the problems of pollution of small rivers (Meyer et al., 2019; Mitryasova and Pohrebennyk, 2017; Mitryasova et al., 2020).

Obolewski K., Glinska -Lewczuk K., Szymanska M., Astel A., Lew S. study the issues of green chemistry of water bodies, search for patterns between the content of chemical components of the aquatic environment and its biological component (Obolewski et al., 2018).

Issues of assessing the impact of industrial enterprises on the water resources state present in the works Kapelewska J. et al. (Kapelewska. et al., 2019). Schickele A. et al. investigate the influence of temperature on the morphological composition of water bodies (Schickele et al., 2020).

The works of Snizhko S. et al. became especially important issue - multifactorial impact on surface water quality (Snizhko, 2004); Grebin V. et al. - regional landscape-hydrological analysis of the modern water regime of the rivers of Ukraine (Grebin and Khilchevskyi, 2016). Thus, the study of Grebin V. and Khilchevsky V., in accordance with the requirements of the Water Framework Directive developed a method of hydrographic zoning of rivers of Ukraine, assessment of aquatic ecosystems.

Vasenko O. et al. develop methods of comprehensive assessment of water bodies taking into account the factors of degradation processes, carry out scientific research to improve the methodology for establishing environmental standards of surface water quality, taking into account landscape and geographical features of aquatic ecosystems, ranking of observation points (Vasenko et al., 2016; Bezsonov et al., 2017; Pohrebennyk et al., 2019; Mitryasova and Pohrebennyk, 2020a).

However, a comprehensive analysis of water resources from the standpoint of assessing the state of small rivers for effective integrated management for sustainable development of the region and achieving proper environmental status of water bodies, in accordance with Ukrainian legislation and the Water Framework Directive, processes of adaptation to EU environmental policy.

Small rivers are an important component of the natural environment. Small rivers form the hydrochemical conditions of water resources and water quality of medium-sized and large rivers, creating landscapes large areas. An important feature of small rivers in the fact that they are the starting point of the river network, and any changes that occur in their mode, marked on the hydrological chain (Tanriverdi et al, 2010; Pohrebennyk et al., 2016; Zeinalzadeh and Rezaei, 2017; Zhang et al. 2018; Alifujiang et al., 2021; Thuy et al., 2021; Mitryasova et al., 2021b; McBean et al., 2022; Tha et al., 2022; Ward, 2021). Water resources of small rivers are part of the shared water resources and are often the main and sometimes the only one source of local water. Small rivers have a number of features that need to be considered when developing environmental management measures (Petrov et al., 2020). The first is the dependence of water content, hydrological regime and water quality of small rivers on the state of the catchment. The second is climatic and weather factors (Mazlum et al., 1999; Mitryasova et al., 2021a; Arndt et al. 2022).

The object of the research is a small river Mertvovod in Mykolaiv region (Ukraine).

The length of the river is 114 km, the area of the drainage basin is 1820 km². The river valley is predominantly trapezoidal, width up to 3 km, depth up to 40 -50 m. The floodplain is 200-300 m wide, up to 1-1,5 km below the ground. The generator is twisted; its average width in the lower reaches is up to 20 m. The slope of the river is 1,8 m/km (Southen Bug River Basin Management in Mykolaiv Region, 2021).

Monitoring studies are conducted by Southern Buh River Basin Management in Mykolaiv region at the point of monitoring near Voznesensk (Mykolaiv region, Ukraine) (fig. 1)

Fig. 1. The sampling point location on the Mertvovod River.

Materials and Methods. The study methods were used: observation; comparisons and analogies; analysis; synthesis; generalization. Also we have used for the research: Google Maps, Microsoft Excel, Origin software. Calculations are made using the correlation formulas 1 and 2 (Buda and Jarynowski, 2010; Kupalova, 2008; Mitryasova et al., 2021):

$$r = \frac{\sum(x-\bar{x})(y-\bar{y})}{\sqrt{\sum(x-\bar{x})^2\sum(y-\bar{y})^2}} \quad (1)$$

r = -1; +1

where x, y are the numeric values of the variables, which set the correlation connection; where $\bar{x}, \bar{y}$ – – average arithmetic value.

$$R = \sqrt{1-(1-r^2_{yx1})(1-r^2_{yx2/x1})} \quad (2)$$

r = 0; +1

where r_{yx1} – doubles correlation coefficient;

$r_{yx2/x1}$ – partial correlation coefficient.

To describe the magnitude of the correlation coefficient are the following, which are presented in table 1.

Table 1

Correlation coefficient interpretation

Value	The correlation coefficient interpretation
≤ 0,2	very weak
≤ 0,5	weak
≤ 0,7	average
≤ 0,9	high
≥ 0,9	very high

Correlation analysis was used to find quantitative relationships between natural water quality indicators (pH, phosphates, nitrates, COD (chemical oxygen demand), O_2). Trend analysis using the Shapiro-Wilk test in the Origin program allowed to determine changes in the water body.

To study the relationship between the indicators of surface water quality on the small river example, three integrated indicators were selected, namely soluble oxygen, pH, COD, BOD_5 (biochemical oxygen demand) as well as hydrochemical parameters that fall into the risk zone are: nitrates, phosphates and ammonium for the period from 2007 to 2021.

The value of pH characterizes the active acidity, its value is influenced by the following factors:

- the content of carbon dioxide and oxygen in the water;
- content of humic acids;
- the presence of heavy metal ions;
- temperature regime of the reservoir.

The content of hydrogen ions of natural reservoirs is determined by the quantitative ratio of carboxylic acid and its ions by chemical equation 1:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (1)$$

The formation of bicarbonates occurs due to the dissociation processes of equations 2 and 3:

$$Ca(HCO_3)_2 \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (2)$$

$$Mg\,(HCO_3)_2 \leftrightarrow Mg^{2+} + 2HCO_3^-. \quad (3)$$

Due to the hydrolysis of bicarbonates, the pH increases according to the chemical equation 4:

$$HCO_3^- + H_2O \leftrightarrow CO_2 + OH^- \quad (4)$$

Surface waters with low carbon dioxide content have a slightly alkaline reaction medium; the pH≤7 with large amounts of CO_2. pH values are closely related to the processes of photosynthesis due to the consumption of carbon dioxide by aquatic vegetation. The source of hydrogen ions is also humic acids, which are contained in soils.

During the hydrolysis of heavy metal salts, strongly acidic waters with pH≤3 are formed (chemical equation 5):

$$FeSO_4 + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^+ + SO_4^{2-} \quad (5)$$

Such waters are formed when significant amounts of iron, aluminum, copper and many other heavy metals ions enter the water. A similar process of oxidation of heavy metal sulfides occurs during the discharge of mine water by chemical equations 6 and 7:

$$2FeS_2 + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (6)$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (7)$$

The sources of hydrogen ions are humic acids. Acidic, weakly acidic waters (pH = 3 -6.5) are formed during the decomposition of organic compounds, as well as the influx of carbon dioxide and sulfonic acids. Therefore, the pH value of natural waters depends on the content of carbon dioxide, humic and other organic acids, as well as the content of cations of weak bases (ammonium ions, aluminum, iron, organic bases). In these cases, the pH is not below 4.5.

High values of COD and BOD_5 in natural waters are due to a number of indicators, namely the high content of inorganic and organic pollutants, humic substances, hydrogen sulfide, sulfites, sulfides, nitrites, ammonium nitrogen.

Results and Discussions

The correlation nexus between COD, phosphates and nitrates.

Phosphates and nitrates, as the main forms of the most important nutrients of Phosphorus and Nitrogen, often limit the development of water productivity. Therefore, the inflow of excess phosphorus and nitrogen compounds from the catchment (in the form of mineral fertilizers with surface runoff from fields (for example, from a hectare of irrigated land is taken out 0 4-0.6 kg of phosphorus), with runoff from farms (0.01-0.05 kg/day per animal), with untreated or untreated domestic wastewater (0.003-0.006 kg/day per capita), as well as with some industrial waste leads to a sharp uncontrolled increase in plant biomass of the water body (This is especially true for stagnant and low-flowing reservoirs.) There is a so-called change in the trophic status of the reservoir, accompanied by the restructuring of the entire water community and most importantly to the predominance of putrefactive processes.

The presence of nitrates 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 and runoff 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 oxygen to oxidize organic matter.

In surface waters, nitrates are in 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.

The value of COD in all investigated samples exceeded the maximum permissible concentration, minimum value – 15,24 mgO_2/dm^3 and maximum – 68,6 mgO_2/dm^3 (MPC < 15 mgO_2/dm^3).

Exceeding the maximum permissible concentrations by phosphates and nitrates were observed. Exceeding the maximum permissible concentration of COD is associated with oxidation of organic substances which fall into natural water from surface runoff and dumping sewage. There was a weak correlation between indicators (fig. 2). This confirms the fact that high COD values may be due to oxygen-free compounds of nitrogen and phosphorus, such as ammonium phosphide forms. So, with the increase of phosphates COD vice versa decreases, which is typical. The increase of phosphates is caused with deterioration of the river water quality due to the discharge of domestic sewage.

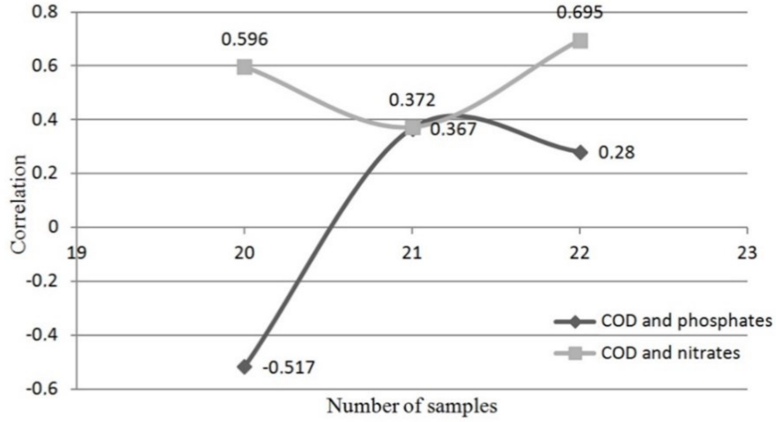

Fig. 2. The nexus between COD and phosphates, and nitrates.

The correlation nexus between soluble oxygen, nitrates and pH.

The values of soluble oxygen in the water were in the norms and were > 4.00 mgO_2/dm^3. The values of nitrates were in the norms and not exceeded MPC. Value of pH were in the rules in not all the samples and was up 8.74 (MPC of pH = 6.5–8.5).

The smallest dependence observed between O_2, nitrates and pH (fig. 3.) Correlation coefficient equals about 0.36, that is, there is a weak dependence between parameters. In the period the soluble oxygen (O_2) decreases, and nitrates on the contrary increase that is typical of data indicators and associated with the maximum increase of COD in the given period that makes up 52.47 mgO_2/dm^3 (MPC < 15 mgO_2/dm^3).

Such excess, allow the claim about water pollution by organic and inorganic substances. Oxidation -reduction process of conversion of nitrogen-containing compounds into nitrates occurs.

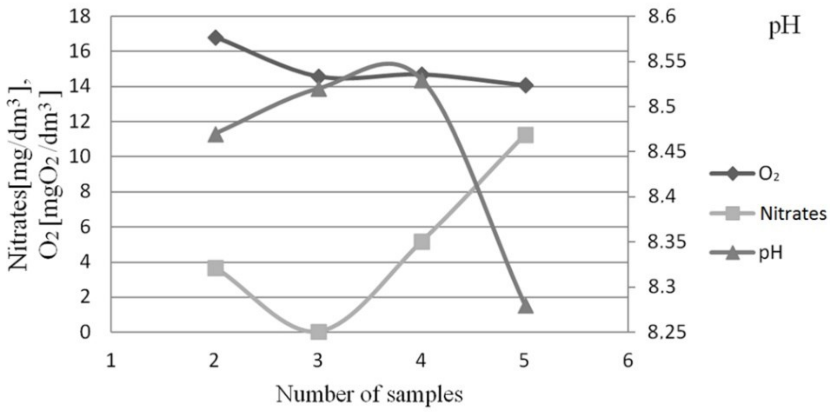

Fig. 3. The nexus between by soluble oxygen, nitrates and pH.

The correlation nexus between BOD_5, phosphates and nitrates.

In the studied period there was observed exceeding of MPC by BOD_5, the maximum value of which was 20.4 mgO_2/dm^3 (MPC < 3 mgO_2 $/dm^3$). The correlation changes in most cases from 0.6 to 1.0 which indicating on close functional connection.

Excess value of BOD_5 confirms receipt of the organic substances of plant and animal origin. With a high content of organic matter in the water, aerobic bacteria multiply rapidly, which require oxygen to function. This can lead to a decrease in the content of dissolved oxygen, create hypoxic conditions and the death of certain species of organisms that live permanently in the aquatic environment. The smallest correlation is observed between BOD_5, phosphates and nitrates (r = 0.31) that is weak link between indicators. Also this confirms the fact that high BOD_5 values may be due to oxygen-free compounds of nitrogen and phosphorus, such as ammonium phosphide forms. So, with the increase of phosphates BOD_5 vice versa decreases, which is typical also.

A sharp increase of nitrates is observed, which is 25.6 mg/dm^3 (with MPC=45 mg/dm^3) (fig. 4). The concentration of nitrates is subject to seasonal variations: the minimum is in the growing season, the maximum is in autumn, when the organic substances decay and nitrogen compounds transition from organic forms in the mineral. Nitrates come mainly from surface runoff, which contains residues of used nitrogen fertilizers. Another source of no-waste is groundwater, which can have fairly high concentrations (up to 100 mg/dm^3) and increase the content of nitrates in the areas of discharge into surface waters. Groundwater is the main source of nitrates in the limited period, when the supply of surface water is mainly due to groundwater runoff. There are also a significant number of other sources of nitrates in surface waters: surface runoff from landfills, urban areas, wastewater from animal complexes, urban waste water. In the research period, the maximum concentration of nitrates was observed in autumn. The amplitude of seasonal fluctuations of the nitrates is an indicator of the eutrophication of the water object.

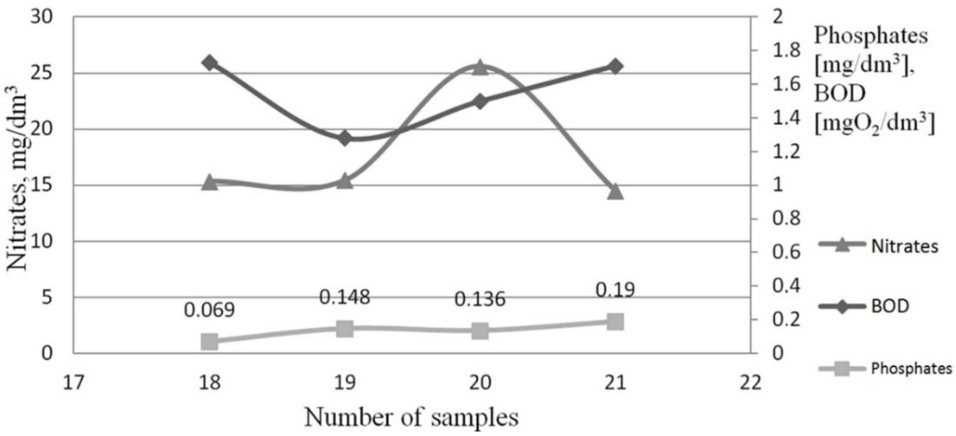

Fig. 4. The nexus between BOD_5, phosphates and nitrates.

The correlation nexus between pH, ammonium and soluble oxygen.

There is excess of MPC on pH that is 8.74 (MPC = 6.5-8.5), exceeding by ammonium, which is 0.84 mg/dm^3 (MPC = 0.39 mg/dm^3), the value of dissolved oxygen is normal and is 4.00 > mgO_2/dm^3. The smallest dependence between parameters observed in the sample №15 and the coefficient of multiple correlation is weak 0.223 (fig. 5).

At the all test period the highest concentration of ammonium is 0.84 mg/dm^3 (MPC = 0.39 mg/dm^3) and meets the sample №17. A sharp increase of ammonium is associated with agricultural ranges, growing downpours the day before sampling.

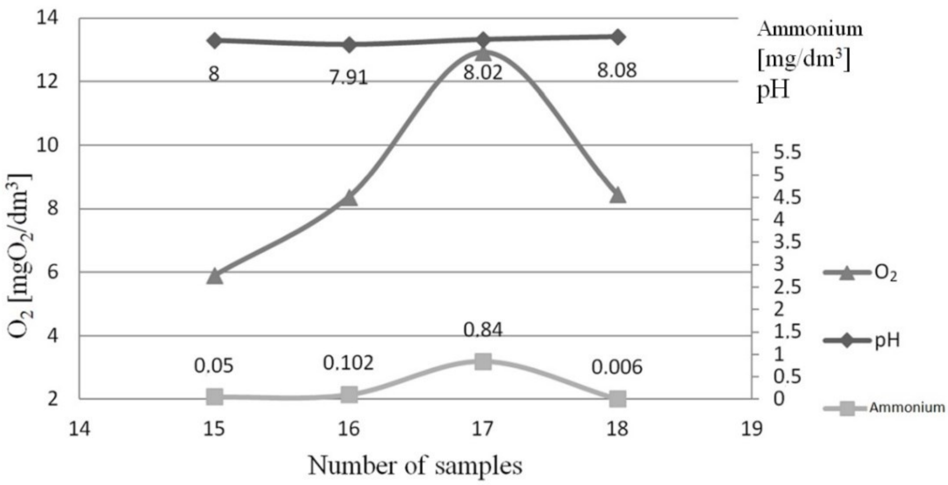

Fig. 5. The nexus between pH, ammonium and soluble oxygen.

Conclusions. The status of the small river is an indicator of the water security of natural surface water. Correlation analysis of dependences between COD, phosphates and nitrates; and also soluble oxygen, nitrates and pH; BOD_5, phosphates and nitrates; pH, ammonium and dissolved oxygen show stable links between chemical components that are caused by chemical interconversions, the influence of external factors (weather conditions, the hydrological regime of the river, the anthropogenic factor).

As a result of the environmental analysis of the river Mertvovod identified periods of excess the MPC by hydrochemical indicators of water quality. The sources of pollutants in the water are discovered and analyzed.

Using of correlation analysis gave a clear idea about weak correlations between BOD_5, COD and nitrates, phosphates. These confirm the fact of increasing BOD_5 and COD due to non-oxine-containing forms of phosphorus and nitrogen compounds. A significant increase by phosphates is detected, which is associated with the collection of cleansers with domestic waters and more with the lack of quality sewer facilities. A significant reduction of COD over the years is detected.

A further perspective is to study ways to reduce the supply of phosphates to the water body. It is also relevant to further study the dependencies between water quality indicators, as well as their interpretation.

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