

Integrated assessment of the surface source of water supply according to environmental-risk indicators

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Received 07.12.2022; Received in revised form 24.04.2023; Accepted 12.07.2023 Abstract. The risk assessment provides a basis for comparing, ranking and prioritizing risks and assessing environmental impacts as functions of stressors in a river basin. The main sources of pollution of the Dnipro Reservoir are discharge of wastewater into the river without proper treatment; uncontrolled discharges of wastewater; non-compliance with the regime in

bank strips and water-protection zones; and bank erosion. Health-risk assessment includes four main stages: hazard identification, exposure assessment, dose-effect assessment, and risk characterization. We determined that according to all parameters – except BSK5, HSC, and suspended matter – the water meets the regulation standards of the Hygienic Water-Quality Standards of Water Bodies to Meet the Drinking, Household and Other Needs of Population, but does not reach the upper limit of the 1st quality class according to DSTU 4808:2007. Also, the average annual values were significantly above the minimum values of the examined parameters. There was a decrease in the level of BOD, at the checkpoints in the city of Dnipro, indicating invasion of the watercourse (points 4 and 5) by substances that inhibit biochemical processes. The same parameter decreased at the checkpoint where the River leaves the city limits and further downstream, suggesting an influx of organic compounds. The oxygen content was observed to decline in the part of the watercourse located in the city (points 4 - 8) and increase in the middle and lower parts of the reservoir. There was also seen a trend of growth of sulfates, nitrogen compounds, phosphates, synthetic surfactants and COD at the control checkpoints located within the city of Dnipro. As a result of the risk assessment of the impact of anthropogenic activities of the Dnipro agglomeration on the Dnipro Reservoir, we determined that nitrites, nitrates and phosphates and suspended solids are the priority substances in the list. This can impose negative impacts on the health, causing mutagenic and carcinogenic effects, and enhance the eutrophication of the surface water. The Dnipro agglomeration has been causing a negative ecological impact on the Dnipro Reservoir, increasing the risk value from 0.999999206 (checkpoint 3, before the city of Kamianske) to 0.999999924 (checkpoint 6, where the River leaves the city limits).

Key words: ecological safety of surface water, ecological risk, water-quality indicators.

Інтегральна оцінка поверхневого джерела водопостачання за показниками екологічного ризику

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Анотація. Оцінка ризику дає основу для порівняння, ранжування та визначення пріоритетів ризиків та оцінки впливу на довкілля як функції впливу стресу у басейні річки. Основними джерелами забруднення Дніпровського водосховища є: скиди

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стічних вод у річку без належної обробки; самовільне скидання стічних вод; недотримання режиму в прибережних смугах і водоохоронних зонах; ерозія узбережжя. Оцінка ризику для здоров'я включає в себе виконання чотирьох основних етапів: ідентифікація небезпеки, оцінка експозиції, оцінка дози-ефекту, характеристика ризику. Встановлено, що вода за усіма показниками крім БСК, ХСК та завислі речовини відповідає нормам, встановленим Гігієнічними нормативами якості води водних об'єктів для задоволення питних, господарсько-побутових та інших потреб населення, але не відповідає верхній межі 1 класу якості за ДСТУ 4808:2007. Також середньорічні значення в рази перевищують мінімальні значення досліджуваних показників. Спостерігається зниження рівня БСК, на постах в м. Дніпро, що свідчить про надходження до водотоку речовин, що пригнічують біохімічні процеси, (т.4 та т.5) та поступове збільшення цього показника на виході з міста та далі вниз за течією, що свідчить про надходження органічних речовин. Вміст кисню знижується на ділянці водотоку, розташованій у місті (т4 – тб) та збільшується у середній та нижній частині водосховища. Також спостерігається тенденція зростання сульфатів, сполук азоту, фосфатів СПАР та ХСК для точок контролю, які знаходяться в межах м. Дніпро. В результаті оцінки ризику впливу антропогенної діяльності Дніпровської агломерації на Дніпровське водосховище, визначено, що в перелік пріоритетних речовин на перший план виходить нітрити, нітрати та фосфати і завислі речовини. Це може спричинити негативний вплив на здоров'я, спричиняючи мутагенну та канцерогенну дію, також прискорює евтрофікацію поверхневого водного об'єкту. Спостерігається негативний вплив Дніпровської агломерації на екологічний стан Дніпровського водосховища - збільшення величини ризику з 0,999999206 (т.3, перед м. Камя'нське) до 0,999999924 (т. 6, на виході з м. Дніпро).

Ключові слова: екологічна безпека поверхневих вод, екологічний ризик, показники якості води.

Introduction

Growing anthropogenic loading on the territories of drainage basins following relaxed water-protecting measures promotes pollution of surface-water objects. As a result, the problem of pollution of surface water exacerbates for the country in general. Polluted water bodies and watercourses become unsuitable for drinking, and sometimes for technical water as well, lose fishing potential, and become unsuitable for agrarian purposes. The modern concept of risk assessment is considered the main decision-making mechanism in the management in almost all countries at both regional and state levels, in cases of potential source of environmental pollution and an individual production. Ecological risk comprises natural risks associated with natural threats and technogenic risks related to technical objects and processes. Ecological risk is defined as a risk associated with changes in the environment, caused by consequences of technogenic or natural emergencies. By assessing risks, we mean ranking, comparing, identifying priority risks, and assessing impact on the environment as functions of stress factors on a river basin. The final stage of assessment of ecological risk generalizes reactions to stress and profiles of influence to estimate likelihood of a stressor having unfavorable effects on the environemt. The main part of the assessment is determining acceptable risk. Water resources are aquatic objects that directly or indirectly affect the life of population and development, and are a basis for anthropogenic activity. Due to growing rates of urbanization and industrial and agrarian development, the aquatic environment has been subjected to various influences of human activity. Contaminants of water bodies and watercourses, which are discharged as a result of anthropogenic activity, are mainly general

nitrogen, general phosphorus, and biochemical oxygen demand. Those contaminants increase risks for the aquatic environment, and this has become a large problem for ecological and social systems. Those enhanced risks can be detrimental to the health of population, promoting morbidity and mortality. Risk, as a quantitative threat value, is broadly used in the international practice for purposes of a substantiated comparison of threats from various types of work, economy spheres, argumentation of social advantages, assessment of realization of various unsatisfactory consequences, etc. (Bezsonnyi, 2021; Green, 2013; Kuzmin, 2017; Buts, 2020; Khumarova & Krivenceva, 2022).

Therefore, evaluation of ecological danger to the surface-water objects due to an existing anthropogenic factor is a relevant and important issue

A number of studies have been focused on the risks from «new contaminants», which have not been studied well enough and are not regulated by ecological standards – illegal drugs, pharmaceutics, personal-hygiene means, etc. Those contaminants are quite common in water bodies and are mainly introduced into the aquatic environment with discharged poorly treated water. They raise concern due to a possible direct or indirect ecological effect on the environmental biota (for example, endocrine disorders). Those compounds are usually uncontrolled and can enter the environment and cause a negative impact on the ecology and health of the population. According to the data of the NORMAN network, around 700 compounds have been identified in the aquatic environment of Europe, classified into 20 classes. The main goal of risk assessments is the protection of ecological systems in the aquatic environment and health of population. There is a need of new methods of assessing total risks posed by integral influence of various stress factors, including various new contaminations. Combination of legal and normative requirements and management measures regarding environmental pollutions, and also regarding their manifestation in the environment should be the basis for achieving an effective complex management of aquatic resources (Petrie, 2015; Geissen; 2015, Beyer, 2014; Krukov, 2020).

A large number of studies focused on assessment of contaminations and health risks from heavy metals. Heavy-metal environmental contamination is a serious global problem, the reasons of which being toxicity of heavy metals, large variety of sources, and the ability to accumulate. While studying the influence of heavy metals on the condition of water, risk for the human health was assessed using the methods of statistical analysis, and index of water quality, danger index, danger coefficient, modeling of Monte-Carlo, and carcinogenic risk (Mastroianni, 2016; Zhou, 2019; Osorio, 2016; Asotskyi, 2018).

Pesticides are typical contaminants of surface water in developed countries (Silva, 2015; Tsaboula, 2016; Haregeweyn, 2017; Bezsonnyi, 2021; Brooks, 2016; Rasmussen, 2015; Wood, 2017; Munz, 2017). An approach to identifying pesticides has been developed and applied to the river basin of the Pineios (Central Greece). It accounts for the level of ecological risk, contains data regarding frequency of manifestation of a pesticide above the ecological norms, intensity of the manifestation, spatial distribution, and data about the behavior of pesticides in the environment, and harmful effect on the human health (Silva, 2015). Countries of the European community have committed to carry out monitoring of priority chemical compounds, determined as those of concern at the level of the European Union and basin/national levels respectively, in surface-water objects, and also to inform about excesses of the ecological norms of quality with the purpose of maintaining proper chemical and ecological conditions. That is why standards for specific contaminants of the aquatic basin should be established at the national level.

The studies (Liu, 2016; Feng, 2016) analyzed assessments of ecological risk to the human health from polycyclic aromatic hydrocarbons (PAHs). The proposed methods of assessing ecological risk included calculation of danger coefficient, zones of overlapping areas of probability density curves, and were employed to assess combined risks of PAHs to aquatic ecosystems. The result of assessment of danger coefficient indicates that the risk coefficient for mollusks and zooplankton was above 0.1, indicating high potential risk. As with cancer risk for humans and non-carcinogenic danger in the study area, the assessments were made based on additional risk from PAHs throughout life.

An individual direction of the research is quantitative assessment of risks to aquatic micro- and nanoplankton (Besseling, 2019; Everaert, 2018; Koelmans, 2017). There was conducted a large-scale monitoring of methods of modeling, influence, occurrence, behavior, measurement, effects, and threshold values of microplastic in aquatic objects. There was performed evaluation of ecological risk posed by microplastic (<5 mm) in the marine environment, assessing the order of magnitude of past, present and future concentrations based on the data of global production of plastic. Up to year 2100, there will be 9.6 to 48.8 particles per m⁻³ in the global ocean, and this would be 50 times greater than the current concentration.

A study (Balachuk, 2013) proposed a new approach to assessment of an expected ecological risk to an end area of a ramified river, which, unlike the existing methods, accounted for effects of discharges and water quality in the river tributaries in areas up the stream in the basin of that river. The main existing approaches to assessing ecological risks have been examined. The study formalized coding of ecological risk to the river-end area, providing an example of assessment of an expected ecological risk. The proposed approach can be used not only for a river but also for other natural systems that may be presented as informational models with geometrical networks. Also, possible use of the approach for ecological networks or modeling of ecological risks from air contamination allows for more accurate assessment of expected ecological risks.

We should note the studies (Rybalova, 2017; Bezsonnyi, 2021; Bezsonnyi, 2022) presenting a procedure of assessing risk of deterioration of a watercourse status. The procedure was based on identifying ecological quality standards of surface water, taking into account the landscape-geographic peculiarities of river basins. To assess risks of degradation of ecological condition of the aquatic environment, there were used data complexes from systems of monitoring surface-water quality. This method allows automating the process of estimating an ecological risk. Measuring risk of decline in ecological condition of an aquatic object would promote introduction of an adaptive system of management of water quality, which would account for variable social-economic and ecological conditions. The proposed method of assessing ecological risk of disturbance of aquatic systems was based on the normative-legal grounds, methods, and approaches to ecological assessment of surface water, adopted in the EU and Ukraine.

The analyzed reports and studies and risk assessments suggest that the general ecological risk can be divided into two types:

- Risk to health of population, possible negative impacts on health.

- Risk of deterioration of sustainability of the ecological systems as a result of potential and actual environmental contamination.

Risk is also a combination of likelihood of harm and severity of this harm (DSTU, 2014). Magnitude of likelihood was assessed for a certain temporal interval or several temporal intervals (1 year, 2 years, 5 years, etc). Such assessments can also be made for certain types of economic use of aquatic resources. Likelihood value is in the interval between 0 (no risk) to 1 (risk is the highest).

As the presented analysis demonstrates, an issue of identification and assessment of risk of pollution of aquatic resources is a subject of many studies, and it has to be noted that in economically developed countries, the problem of risk assessments is focusing on new types of contaminants, including pharmaceutical drugs, narcotics, and microplastic. Nonetheless, assessment of risk from anthropogenic activity is still relevant.

The objective of the study was to characterize the ecological condition of water of the Dnipro Reservoir according to the ecological-risk indicators.

Materials and methods

The main sources of contamination of the Dnipro Reservoir are untreated-water discharges to the river; uncontrolled discharge of wastewater; non-adherence to the regime in bank lines and protected water zones; and bank erosion (National report, 2022; Bezsonnyi, 2022). Therefore, anthropogenic factor has the greatest effect on the functioning of the river ecosystem, disturbing the natural condition of the watercourse and introducing irregular components that worsen the water quality in the Dnipro River and the Dnipro Reservoir. Influx of contaminants with wastewater into the Dnipro complicates the process of water treatment and requires energy expenditures. Therefore, it is important to identify reasons, sources, and scales of contamination of surface water in this river and its tributaries, because even discharges of water that had been processed according to the standard scheme into small streams are accompanied by steep decrease in the water quality, jeopardizing health of a population. Monitoring of ecological condition of surface water that is a source of drinking water is a crucial task in the nature protection.

For this purpose, in our study, we used the open data of the State Agency of Aquatic Resources of Ukraine (for the period of 2003 - 2022; <u>https://data.gov.ua/dataset/surface-water-monitoring</u>) according to the Order of Performing the State Monitoring of Water, approved by the Order of the State Agency of Water Resources of Ukraine No 587 as of 6/24/2020.

Control of surface water of the examined object was carried out at the laboratory of monitoring of water and soil of the Regional Office of Aquatic Resources in Dnipropetrovsk Oblast in permanent checkpoints of monitoring of flows of the surface water (Table 1). The monitoring points are located in areas of drinking-water drainage.

Estimating ecological risk allows for ranking by individual parameters so as to identify priority contaminants, those requiring neutralization the most, in order to rehabilitate an aquatic ecosystem.

Assessment of risk to health includes performing four main stages: identification of danger, evaluation of exposure, assessment of dose-effect, and risk characteristic (MR, 2007).

At the stage of identifying danger, there are detected chemical compounds present in drinking water of a studied zone (region) which can cause unfavorable

Table 1. Control checkpoints of water quality

| Check- point № | Checkpoint ID | Checkpoint name |
|-------------------|------------------|---|
| p1 | 27063 | Dnipro-Donbass Canal, 0.5 km, Shulhivka village, near the Dnipro-Donbass HVK |
| p2 | 27047 | Dnipro River, 476 km, Verhniodniprovsk, drinking-water drainage |
| p3 | 27048 | Dnipro River, 462 km, Auly urban-type settlement, drinking-water drainage in cities Dnipro and Kamianske |
| p4 | 27071 | Dnipro River, 420 km, the city of Dnipro, right bank, Kaidaky drinking-water drainage |
| p5 | 27072 | Dnipro River, 420 km, the city of Dnipro, left bank, Lomovskyi drinking-water drainage |
| р6 | 27073 | Dnipro River, 404 km, the city of Dnipro, the Dniproenerho Prydniprovska Thermal Power Plant, drinking-water drainage |
| p7 | 27074 | Dnipro River, 372 km, Voronove village, drinking-water drainage of the Dnipro-West- ern-Donbass State Sewer and Water Communication Enterprise |
| p8 | 27075 | Dnipro River, 365 km, Viiskove village, Solone-District drinking-water drainage |



Fig. 1. Locations of the control checkpoints of water quality. OpenStreetMap view.

consequences for health. At this stage, it is practical to carry out a random screening study of this water in order to determine threats that could be unaccounted for when developing control programs. It has to be noted that at this stage of assessing risks, the analysis is conducted at a quality level. The obtained ranking values of the danger indices should be used for mutual comparison and identification of priority compounds in a studied territory or an object.

Assessing the source of water and choosing priority indicators require data of monitoring of possible sources of contamination, and also results of analyzes of discharges and water in the surface-water object.

Assessment of ecological risk includes identification of likelihood that aquatic ecosystems would be disturbed by anthropogenic, natural, and military factors. Therefore, when assessing risk of disturbance of surface water, it is important to determine ecological standards. At the first stage, assessment of the ecological risk of deterioration of surface water, there is determined a list of contaminants that exceed the values of the ecological standards. It is believed that those compounds promote degradation processes in the aquatic ecosystem. The next stage is assessing total ecological risk of deterioration of aquatic objects. Risk associated with sanitary-toxicological properties of water is estimated based on the equation (Rybalova, 2017; Bezsonnyi, 2021):

$$Risk = \left(\frac{1}{\sqrt{2\pi}}\right) \times \int_{-\infty}^{\Pr ob} e^{\frac{-t^2}{2}} dt, \quad (1)$$

where $-\pi = 3, 14;$

e – basis of natural logarithm;

t – confidence coefficient.

Prob – conditional logarithmic indicator that is described by the following equation

$$Prob = -2 + 3,32 \cdot lg(C/C_{m}),$$
(2)

where C_i – concentration of *i* substance in aquatic object;

 $C_{e\mu}$ – ecological normative for aquatic objects.

Total ecological risk of deterioration of the condition of surface water of aquatic objects is determined according to the rule of multiplying possibilities, where multiplier is not a risk value but a value that characterizes likelihood of its absence (Rybalova, 2017):

$$ER = 1 - \prod_{i=1}^{n} (1 - ER_i).$$
(3)

Where *ER* is the total ecological risk of deterioration of surface-water objects; $ER_1, ..., ER_n$ – ecological risk of each contaminant.

| Class of ecologi- | Characteristic of the water resources | | | | |
|--------------------|---|-----------|--|--|--|
| cal status of sur- | | | | | |
| face water | | value | | | |
| I. Excellent | Water objects in natural condition are usually oligotrophic, water is transparent or | | | | |
| | with a small content of humus. Water objects are suitable for all types of use. | | | | |
| II Good | Water objects close to the natural condition or slighty eutrophicated. Water is suit- able for all types of use. | | | | |
| II. 000u | | | | | |
| | Water objects are subject to low impact of wastewater, surface contamination sourc- | | | | |
| III. Satisfactory | es or other types of impact. Quality usually corresponds to requirements of most | | | | |
| | types of water use. | | | | |
| | Water is significantly contaminated by wastewater, surface runoff, and is subject to | | | | |
| IV. Unsatisfactory | other factors. Aquatic objects are suitable only for types of use for which lower eco- | | | | |
| | logical standards of surface water are established. | | | | |
| V Deen | Water objects are significantly polluted by wastewater, surface runoff or have de- | | | | |
| v. Poor | graded as a result of other factors. | 0,9 - 1,0 | | | |

| Table 2. Dependence | of quality of surface | water on ecological-risk value |
|---------------------|-----------------------|--------------------------------|
|---------------------|-----------------------|--------------------------------|

Obtained values of ecological risk are proposed to be interpreted using a ranking scale (Table 2) (Bezsonnyi, 2021).

$$R = -ln(P), \tag{4}$$

A study (Cui, 2021) proposed estimating risk for surface-water object according to the formula (4):

$$R = -ln(P), \qquad (4)$$
where $P = \sum n/N,$
where $\sum n = \sum (C/\Gamma/U)$

where $\sum n_i = \sum (C_i / \Gamma / \mathcal{I} K)$, where C_i is concentration of *i* pollutant that exceeds Maximum Concentration Value, MCV (those compounds that do not exceed the norm are not incorporated into the formula); N – total amount of compound analyzed.

A similar approach to assessing risk using ratio of number of observations with MCV excesses to the overall number of observations has been presented in the study (Rybalova, 2017) that suggests assessing risk of decline in the condition of surface-water objects for each *i* pollutant in *j* range of observations using the following formula:

$$R_{ii} = 1 - ((1 - P_{ii}) \times (1 - S_{ii})), \tag{5}$$

Where P_{ii} is the likelihood of decline in the ecological standard for *i* parameter in *j* range; S_{ii} – parameter of consequences the disturbance of ecological balance in aquatic ecosystem has entailed for *i* parameter in j range.

Possibility of disturbance of ecological normative is estimated according to formula:

$$P_{ij} = \frac{n_{EH_j}^i}{N_{EH_i}^i} \tag{6}$$

Where n_{EHi} is number of observations of ecological condition of the surface-water object for each i pollutant in j range with a violated ecological standard; N_{EHi} is the overall number of observations of ecological condition of a surface-water object for each *i* pollutant in *j* range with identification of ecological standard. For assessments, the authors proposed using data for the entire period of monitoring (over 30 years) from various monitoring subjects - the Ministry of Environment, State Water Agency, State Natural Resource Agency and the State Emergency Service.

Results and Analysis

Below is assessment of a retrospective dynamics in changes of indicators of ecological status of water of the Dnipro Reservoir. Table 3 presents the averaged data of monitoring for the period between 2003 and 2022 for 8 monitoring objects of surface-water areas of the Dnipro Reservoir. To compare, there have been added minimal values of the parameters observed and normative values according to the Hygienic Standards of Water Quality of Aquatic Objects for Satisfying Drinking, Economic-Domestic and Other Needs of Population (Gigien.) (Hihiyenichni normatyvy, 2022) and DSTU 4808:2007 Sources of Centralized Drinking-Water Support. Hygienic and Ecological Requirements to Ecological Condition of Surface Water and Rules for Selection (for the 1st class of quality, D 4808) (DSTU, 2007).

As Table shows, water – according all parameters but BOD, COD and suspended substances - corresponded to the norms established by the Hygienic Standard of Quality of Aquatic Objects for Satisfying Drinking, Economic-Domestic, and Other Needs of Population, but not meets the upper threshold of quality class 1 according to DSTU 4808:2007. Also, mean annual values several times exceed the minimum values of the studied parameters, on average by 5-6 times for suspended substances; by 1.5-2.5 times for sulfates; by thousand times for nitrates; 40-60 times for nitrites; and 5-8 times for phosphates.

| Check- points | BOD5 | Sus- pended | Oxygen | Sulfate | Chloride | Ammoni- um | Nitrate | Nitrite | Phos- phate | Surfac- tants | COD |
|------------------|-------|----------------|--------|---------|----------|---------------|---------|---------|----------------|------------------|--------|
| p1 | 2.726 | 6.979 | 9.608 | 32.85 | 18.58 | 0.289 | 1.347 | 0.044 | 0.345 | 0.022 | 27.000 |
| <i>p2</i> | 2.756 | 6.339 | 9.051 | 33.52 | 25.15 | 0.328 | 1.604 | 0.051 | 0.292 | 0.022 | 28.610 |
| р3 | 2.295 | 4.408 | 8.916 | 31.87 | 24.86 | 0.313 | 1.598 | 0.043 | 0.324 | 0.026 | 26.687 |
| <i>p4</i> | 2.309 | 4.764 | 8.849 | 32.91 | 24.36 | 0.315 | 1.881 | 0.057 | 0.305 | 0.026 | 27.157 |
| <i>p5</i> | 2.190 | 5.112 | 8.754 | 37.92 | 26.12 | 0.318 | 1.610 | 0.060 | 0.349 | 0.022 | 27.682 |
| <i>p6</i> | 2.523 | 5.104 | 8.780 | 58.69 | 35.40 | 0.312 | 1.817 | 0.061 | 0.344 | 0.026 | 29.144 |
| <i>p</i> 7 | 2.625 | 5.332 | 9.244 | 55.14 | 32.52 | 0.305 | 1.790 | 0.045 | 0.284 | 0.026 | 29.072 |
| [8 | 2.810 | 5.614 | 9.178 | 45.45 | 30.62 | 0.332 | 1.802 | 0.058 | 0.316 | 0.022 | 29.609 |
| Min. | 0.500 | 1.100 | 21.160 | 21.10 | 11.80 | 0.071 | 0.001 | 0.001 | 0.040 | 0.020 | 0.000 |
| Hygien. | 0.500 | 0.250 | 4.000 | 500.00 | 350.00 | 2.000 | 45.000 | 3.300 | 3.500 | 0.100 | 15.000 |
| D 4808 | 1.300 | | 8.000 | 40.00 | 30.00 | 0.100 | 0.200 | 0.002 | 0.015 | 10.000 | 9.000 |

Table 3. Averaged data of monitoring for 2003 – 2022

Note. Min – minimum value; Ggien. – normative values according to the Hygienic Normatives of water quality of aquatic objects for satisfying drinking, economic-domestic and other needs of the population; D 4808 – normative values according to DSTU 4808:2007 (1st quality class).

To determine the influence of anthropogenic activity of urban ecosystem of the Dnipro agglomeration, we analyzed dynamics of some pollutants (Fig. 2 - Fig. 7) at observation points in the section from the lower part of the Kaminske Reservoir (p2, p3) to the lower part of the Dnipro Reservoir (p7. p8).



Fig.2. Dynamics of BOD5 according to monitoring checkpoints.

We observed decrease in the level of BOD_5 at the checkpoints of the city of Dnipro, indicating ingress of substances to watercourse which inhibit biochemical processes, (p4 and p5) and gradual increase in

this parameter at the checkpoint where the River leaves the city limits and further downstream, indicating influx of organic compounds.



Fig. 3. Dynamics of oxygen at monitoring checkpoints.

Oxygen content decreased in the watercourse areas located in the city (p4 - p6) and increased in the middle and lower parts of the Reservoir. Also, there was observed a tendency towards increase in sulfates, nitrogen compounds, phosphates, synthetic surfactants and COD for the control points within the city of Dnipro (Fig. 4 - Fig. 7).



Fig. 4. Dynamics of sulfates and COD at monitoring checkpoints.



Fig. 5. Dynamics of nitrites and synthetic surfactants at monitoring checkpoints.



Fig. 6. Dynamics of ammonium and phosphate at monitoring checkpoints.



Fig. 7. Dynamics of nitrates at monitoring checkpoints.

When assessing the degradation risk to superficial water, it is important to determine ecological standards. For this study, as a standard, we chose values of the upper threshold of water-quality class 1 in accordance to DSTU 4808:2007.

Results of the estimation of the risk each pollutant poses at each control point and their ranking are presented in Fig. 8 - 11. Results of pollutant ranking of by ecological risk indicate that the list of priority compounds includes nitrites, nitrates and phosphates, and suspended compounds. At the same time, the first three compounds have almost the same values, nitrites have been at the 1st place at all the control points, except 3 and 7, where phosphates have had excesses in third and forth values after the decimal separator.



Fig. 8. Ranking of contaminants at control checkpoints p1 and p2.



Fig. 9. Ranking of contaminants at control checkpoints p3 and p4.



Fig. 10. Ranking of contaminants at control checkpoints p5 and p6.







Fig. 11. Ranking of contaminants at control checkpoints p7 and p8.

The dynamics of general ecological risk, determined by the rule of multiplying likelihoods (3) according to monitoring points is depicted in Fig. 12.

We should note a growing risk at p4, as compared with p3. Also, at p4, there were increases in nitrites (Fig. 5) and nitrates (Fig. 7), decrease in oxygen (Fig. 3), and the ammonium concentration was almost the same. Down to p4 (Kaidak Drinking-Water Drainage), the ecological condition of water has been forming under the influence of a number of factors: the Dnipro Metallurgic Factory and the Dniproazot OJSC, located upstream, also we should not dismiss the influence of densely located upstream community gardens and dacha communities around the cities of Kamianske and Dnipro, i.e. the reason of heightened content of nitrates in the watercourse is their influx from industrial enterprises and with runoff from fields and areas treated with nitrogen-containing fertilizers (ammonium and calcium nitrates). In addition, point 4 is located behind the place where the Oril River falls into the Dnipro, which additionally causes nitrate pollution.

Oxidation of ions by oxygen ammonium solved in water to nitrate ions is one of the reasons the nitrate content has increased. Elevated content of nitrates in water is dangerous for the human health. This is associated with the role of nitrates in the synthesis of nitrosamines and nitrosamides, both in the natural environment (water, water body, soil, plants) and the human body (digestive tract). Nitrosamides and nitrosamines exert mutagenic and carcinogenic effects. Therefore, heightened content of nitrates in water elevates risk of oncogenic morbidity among the population. Moreover, high content of nitrogen compounds promotes eutrophication of a water body.

For p5 and p6, located within the city, we observed increases in sulfates (Fig. 4) and phosphates (Fig. 6). We can confidently state that this has been caused by insufficiently treated wastewater effluent from enterprises of the city of Dnipro. Works of the municipal enterprises of the city entails contamination by phosphates and sulfates. Despite the fact that for systems of centralized water provision, there are regulation standards for phosphate content in waste-



Fig. 12. Dynamics of general ecological risk

water, use of phosphates in domestic detergents remains unregulated.

In general, the Dnipro agglomeration was observed to impose a negative impact on the ecological condition of the Dnipro Reservoir – increase in risk value from 0.999999206 (p3, before Kamianske) to 0.999999924 (p. 6, where the River leaves the city limits), i.e. the value of risk is high, according to the formula (3), becoming 0 to 1. However, this depends on the regulation-standard value, which could be taken higher, but this would not remove the problem of continuous nitrogen-phosphate contamination of watercourse.

The Dnipro River is the main surface source of drinking water in Ukraine. Therefore, we should take into account that the traditional biological treatment allows for a removal of the main mass of organic contaminants but is incapable of substantially removing nitrogen and phosphorus compounds, and also organic compounds (BOD, COD) according to the modern requirements. Over the process of treatment, there occur transformation and partial (20-40%) removal of ammonium nitrogen and phosphorus. Currently, more and more attention is being paid to decline in phosphorus influx because it is believed that control of eutrophication of water bodies mainly depends on reduction of phosphorus. However, of no less importance is the fact that removal of nitrogen compounds from wastewater is much harder (Tretyakov, 2015).

Effectiveness of reduction of phosphorus compounds in wastewater has been improved by using

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mineral coagulants. Over the recent years, there have also been used synthetic flocculants, individually or combined with coagulants (salts of ammonium and iron) and ground limestone (Shevchenko, 2016).

The methods of treatment of wastewater to reduce nitrogen compounds are as follows: physical-chemical, electrochemical, method of ion exchange, and biological. All those methods are utilized in various industrial spheres, but have a number of disadvantages, and therefore cannot be practically applied for reduction of biogenic elements in wastewater in all cases.

Advantages of biological removal of nitrogen are that nitrification results into a necessary level of ammonium removal (if needed, denitrification is performed afterward). Furthermore, such a system can be adapted as an addition to an existing biological treatment (Shevchenko, 2016).

Conclusions

Assessment of risk that anthropogenic activity of the Dnipro agglomeration poses to the Dnipro Reservoir revealed that the list of priority compounds first of all include nitrites, nitrates, phosphates, and suspended compounds. This may have a negative impact on the health, causing mutagenic and carcinogenic effects, and also foster eutrophication of the surface water. There was observed a negative ecological effect of the Dnipro agglomeration on the Dnipro Reservoir – increase in the risk from 0.999999206 (p.3, in front of Kamianske) to 0.999999924 (p. 6, where the River leaves the city limits).

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