UDC 504:556.7
DOI: 10.15587/1729-4061.2021.243058

DEVELOPMENT OF A METHOD OF ASSESSMENT OF ECOLOGICAL RISK OF SURFACE WATER POLLUTION BY NITROGEN COMPOUNDS

Nataliia Loboda
Doctor of Geographical Sciences, Professor
Department of Hydroecology and Water Research
Odessa State Environmental University
Lvivska str., 15, Odessa, Ukraine, 65016

Maria Daus
Corresponding author
PhD, Associate Professor
Department of Life and
Occupational Safety, Ecology and Chemistry
Odessa National Maritime University
Mechnikova str., 34, Odessa, Ukraine, 65029
E-mail: dme2468@gmail.com

A method has been developed for quantitative and qualitative assessment of the risk of surface water pollution by nitrogen compounds based on the use of the indicator of the total content of inorganic nitrogen forms in water (Ninorg), that is, $\left(\mathrm{NH}_4^+ + \mathrm{NO}_2^- + \mathrm{NO}_3^-\right)$. This indicator is considered as the sensitivity coefficient kn. The choice of the indicator is dictated by the need to protect waters from pollution caused by nitrogen compounds during their flow from agricultural sources (Directive 91/676 /EU). The experience of developed countries has shown that nitrogen compounds degrade the quality of water and prevent the achievement of a "good ecological state" of water bodies. For territories with developed agriculture, it is important to establish environmental risks of damage depending on the degree of nitrogen pollution. Quantitative assessments of environmental risk are provided on the basis of a probabilistic approach. The risk was calculated as the product of the probability of a hazardous event occurring multiplied by the consequences of this event. The consequences of river pollution with nitrogen compounds were assessed as the ratio of the total concentration of nitrogen compounds (sensitivity index kn) to its threshold value (50 mg/dm^3 or 11.^{3} mgN/dm^3). In order to develop a scale for qualitative and quantitative risk assessment, relationships were established between the sensitivity indicators kн and the risk indicators R' for individual rivers, and for the study area as a whole, by means of spatio-temporal generalization. The probabilistic characteristics of possible environmental damage were determined on the basis of the obtained regression equations of the form R'=f(kn) and the statistical law of distribution of the risk value R'. The developed method will make it possible to determine the rank of the risk zone and the probability of getting into it, depending on the given sensitivity indicator kn

Keywords: risk of contamination with nitrogen compounds, sensitivity coefficient, risk assessment scale

Received date 21.08.2021
Accepted date 14.10.2021
Published date 29.10.2021

How to Cite: *Loboda, N., Daus, M. (2021). Development of a method of assessment of ecological risk of surface water pollution by nitrogen compounds. Eastern-European Journal of Enterprise Technologies, 5 (10 (113)), 15–25. doi: https://doi.org/10.15587/1729-4061.2021.243058*

1. Introduction

The experience of developed countries has shown that significant concentrations of nutrients, including nitrogen compounds, in surface waters lead to a deterioration in their quality. EU directives aimed at achieving the "good ecological status" of water bodies include the Urban Wastewater Directive, the Drinking Water Directive and the Nitrogen Directive. The Nitrogen Directive provides for measures to help prevent the pollution of surface and groundwater by nitrates from agricultural sources.

Although nitrogen compounds are vital nutrients that promote the growth of plants and crops, their high concentrations are harmful to humans and nature. Almost all nitrates dissolve in water. Contamination of drinking water with these substances can lead to negative health effects. One of the most common consequences of such contamination is methemoglobinemia, various cancers, adverse reproductive consequences (especially fetal neural tube defects), diabetes and thyroid disease [1, 2]. Systematic violation by agricultural producers of agrotechnical and agrochemical farming practices, plowing of floodplain lands to the water's edge causes progressive soil erosion and a decrease in humus content. Excessive use of mineral fertilizers, flushing of waste from livestock farms and pesticides from the surface of watersheds contributes to the deterioration of water quality. Due to high concentrations of nitrogen compounds in river water, there is a risk of failure to achieve environmental goals – "good ecological status of water" [3]. An excessive amount of nitrates in the water promotes the reproduction of algae and cyanobacteria, which gives rise to the process of eutrophication of water bodies. Eutrophication is a global problem that adversely affects freshwater and marine ecosystems.

The agricultural use of nitrates from organic and chemical fertilizers is the main source of water pollution in Europe. In the early 90s (that is, after the adoption of the nitrate Directive 91/676/EU of December 12, 1991), the use of mineral fertilizers began to gradually decline and stabilized in the 2000s. However, agriculture still accounts for more than 50 % of the total nitrogen entering surface waters [4].

The relevance of research on this issue for the present lies in the need to develop methods for assessing the possibility of adverse environmental situations and their consequences as a result of improper agricultural work. A risk event (pollution of surface waters with nitrogen compounds) is considered undesirable, which can harm the environment and human health. Quantitative and qualitative indicators of a risk event (risks) should serve as a basis for identifying negative impacts, controlling and preventing or reducing possible consequences.

2. Literature review and problem statement

Nitrates are the most abundant nitrogen compounds in surface waters. The nitrogen form is one of the mobile and readily soluble compounds, which is easily washed out of the soil during intense precipitation and the formation of slope drainage. The predominance of the nitrate form in nitrogen compounds indicates diffuse (distributed over the territory) pollution [5]. The work [6] emphasizes that the greatest role (74 %) in the formation of emission flows of biogenic compounds is played by agriculture.

In the normative documents on the prevention of nitrate pollution [7], considerable attention is paid to the allocation of vulnerable zones for surface waters through agricultural production and wastewater. These calculations are based on observations of the content of ammonium, nitrate and nitrite nitrogen in surface and groundwater. Based on these data, criteria for sensitivity to nitrogen pollution and a method for identifying vulnerable zones have been developed. But there are still unresolved questions regarding the quantitative and qualitative assessments of the risks of water pollution. The reason for this may be objective difficulties associated with the expert approach, which is determined by the availability of information, the characteristics of the natural environment, the way pollutants enter it. The absence or lack of biological observation data in many countries makes it fundamentally impossible to use assessments of environmental risks, taking into account the damage caused to aquatic organisms.

In [8], the authors linked the physical characteristics of Swansea Bay (temperature, salinity, turbidity, dissolved oxygen, and inorganic nitrogen) with the amount of chlorophyll-a in phytoplankton biomass, which was used as a risk indicator for eutrophication. With this approach, objective difficulties may arise due to the lack of expensive biological observations.

In [9], the risk assessment of groundwater pollution by nitrates was carried out using the DRASTIC model and a geographic information system (GIS). The DRASTIC model uses many specific parameters such as groundwater depth, recharge, aquifer thickness, soil characteristics, topographic data, and the like. It has been shown that nitrate concentrations correlate well with risk indicators [9]. But it is fundamentally impossible to apply the DRASTIC model in territories and catchments, with a sparse network of observation posts and a small amount of information.

The risk factor (HQ or RQ) is defined as the ratio of the concentration of a pollutant in a concentration with a high level of adverse effects (toxicity). For example, when assessing the pollution of rivers with pesticides, the concentration of a substance in the environment is compared with the concentration of pesticides at which 50 % of organisms die (toxic con5 centration) [10]. However, the determination of the toxic concentration may require additional studies if the concentrations with a high level of negative results are not standardized [11].

Surface water pollution indicators are often calculated from stationary hydrochemical observations. The main connection in their determination is the ratio of the actual (average or maximum) concentration of the pollutant to the background or permissible (maximum permissible concentration) value. Pollution index values are used to determine pollution levels. Each level has its own quality characteristic. In [12], the scale of gradations consists of the Miller number 7±2 [13]. Pollution indices can be used as an estimate of the risk of contamination. So, in the case of pollution by several chemical substances, the aggregated pollution index is used in the form of the sum of the excess of a given threshold (maximum permissible concentration MPC). However, to take into account the total impact of pollutants on the considered component of the natural environment, the components of the integral pollution index can be taken into account with different weight coefficients. The weighting factors can be determined by the water content of the rivers[14] or by probabilistic characteristics. For a more accurate risk assessment, probabilistic methods are used, that is, the statistical law of risk distribution is considered. In this case, it is possible to identify the range of possible impacts on the environment and conduct simulation modeling [15].

A variant of overcoming the corresponding difficulties can be the use of a probabilistic risk model based on hydrochemical observation data. It is this approach to risk assessment that was used in [16], but it is not suitable for assessing the risk of water pollution by nitrogen compounds. To solve this problem, it is proposed to apply the research results obtained in the implementation of the provisions of the nitrate directive. The total concentration of mineral forms of nitrogen, presented as a sensitivity coefficient with a theoretically justified threshold of 11.3 mgN/dm^3, forms the basis for further calculations. All this allows to assert that it is expedient to conduct a study devoted to the development of a method for assessing the environmental risks of pollution of surface waters with nitrogen compounds.

3. The aim and objectives of research

The aim of the research is to develop a method for assessing the risk of pollution by nitrogen compounds of surface waters based on the use of data on the total content of inorganic nitrogen forms in water. This will provide an opportunity. improve approaches to assessing water quality due to pollution by nitrogen compounds and will form the prerequisites for making decisions on ensuring man-made and environmental safety.

To achieve the aim, the following objectives were set:

– to identify areas that are sensitive to pollution by nitrogen compounds according to the sensitivity coefficient;

– to establish connections between risk indicators and the coefficient of sensitivity to pollution by nitrogen compounds;

– to establish the boundaries of zones of contamination with nitrogen compounds;

– to develop scales of qualitative and quantitative risk assessment based on the use of the statistical law of distribution of the risk indicator.

4. Materials and methods of research

The work considers the rivers of the south-west of Ukraine, most of them are small, with an area of less than 2000 km^2 [17]. The exceptions are the rivers Kodyma, Kogylnyk, Tyligul, which are medium. The rivers of the study area belong to four basins. The rivers Kuchurgan, Yagorlyk, Okna, Bilochi belong to the Dniester basin. The Kodyma River is located in the Southern Bug basin. The rivers Kyrgyzh-Kytai and Velykyi Yalpug belong to the Danube basin, other rivers belong to the Black Sea basin.

Table 1 shows the hydrographic characteristics of the studied rivers in southwestern Ukraine [18–20]. River basins are plowed up by 60–91 % (Table 1), and river water is used by agricultural enterprises.

Table 1

Hydrographic characteristics of rivers

No.	River	Drainage area, km^2	River length, km	Average slope, ‰	Forestedness, %	Plowing, %
1	Okna	157	27	5.50	23.7	65
2	Bilochi	237	37	5.70	5.50	65
3	Yagorlyk	1590	73	1.70	6.90	65
4	Kuchurgan	2150	109	1.60	0.57	59
5	Baraboy	652	74	1.00	2.36	73.5
6	Kodyma	2470	179	0.73	6.70	75
7	Alkalia	663	67	1.70	–	–
8	Khajider	894	93	1.70	≤1	91
9	Kaplan	276	42	2.60	–	–
10	Sarata	1250	119	1.80	10	65
11	Kogylnyk	3910	243	1.10	16	60
12	Chaga	1270	120	1.10	–	–
13	Kyrgyzh-Kytai	705	63	1.90	–	–
14	Velykyi Yalpug	3280	142	1.10	–	–
15	Malyi Kuyalnyk	1540	89	0.78	0.8	–
16	Velykyi Kuyalnyk	1860	150	0.70	4.87	61.3
17	Tyligul	3550	173	0.90	8	60

The rivers of the Danube-Dniester interfluve (Alkalia, Khajider, Kaplan, Kogylnyk, Chaga, Sarata) originate on the territory of Moldova and flow into Lake Burnas, Lake Khajhider, Lake Sasyk, respectively. Most of the rivers of the Danube-Dniester interfluve in the 80s of the last century were constituent elements of the Danube-Dniester irrigation system.

The Malyi Kuyalnyk, Velykyi Kuyalnyk, Tyligul rivers flow in the Dniester-Southern Bug interfluve and flow into the Khadzhibey, Kuyalnyk and Tyligul estuaries, respectively. The fresh waters of the Tiligul and Bolshoi Kuyalnik rivers affect the formation of water and salt balances in estuaries with the appropriate name [19]. The Baraboy River flows into the Black Sea, its reservoirs are used as receiving waters of the Dniester for irrigation of agricultural lands.

The Water Framework Directive [21] and the Nitrogen Directive [22] have established a threshold value for the content of nitrogen compounds in water (50 mg/dm3 or 11.3 mg N/dm3). In order to quantify the sensitivity of rivers to pollution by nitrogen compounds, the sum of the concentrations of nitrogen ions in water (mg N/dm3) was used. The total concentration value was considered as a sensitivity criterion:

$$k_n = \mathrm{NH}_4^+ + \mathrm{NO}_2^- + \mathrm{NO}_3^-, \tag{1}$$

where k_n – indicator of the sensitivity of the territory to pollution by nitrogen compounds;

NH_4^+ – concentration of ammonium nitrogen, mg N/dm^3;

NO_2^- – concentration of nitrite nitrogen, mg N/dm^3;

NO_3^- –concentration of nitrate nitrogen. mg N/dm^3.

If $k_n > 11.3$ mg N/dm^3, then the considered zone is defined as “sensitive to nitrate pollution”, that is, it belongs to the zone of risk of failure of the water body to achieve “good ecological state”.

Quantitative risk analysis is performed using mathematical and statistical methods, such as: statistical method; a method for assessing the likelihood of expected damage; method of minimizing losses; the method of using a probability tree [23]. The method for assessing the probability of expected damage is based on the fact that the degree of risk is defined as the product of the expected damage by the probability that this damage will occur [24]. A quantitative assessment of environmental risk can be defined as the product of the probability of occurrence of a hazardous environmental event multiplied by the consequences of this event. The environmental risk can be described by natural indicators of damage – the number of victims, the number of destroyed objects, the amount of lost crops, the possible level of pollution of the territory, etc. An indicator of the environmental consequences of river pollution by chemical substances can be the excess of the concentration of substance C over its maximum permissible concentration C_{MPC}: (C/C_{MPC}).

When solving the problems of risk assessment, the R indices were calculated based on the determination of the ratio of the concentrations of the pollutant and its MPC [25]:

$$R \cong C_i > C_{MPCi}, \tag{2}$$

$$R = C_i / C_{MPCi} > 1, \tag{3}$$

$$R = C_{MPCi} / C_i > 1, \tag{4}$$

where R – quantitative indicator of risk;

C_i – concentration level of the i-th pollutant;

C_{MPCi} –maximum permissible concentration for the i-th pollutant. C_{MPCi} is appointed depending on the type of water user.

Taking into account the probability of the occurrence of a risk event, the risk indicator R takes the form

$$R' = \sum_{i=1}^{n} \frac{C_i}{C_{\mathrm{MPC}_i}} \times \frac{N_{ai}}{N_i} > 1, \tag{5}$$

where C_i – concentration of the i-th pollutant;

C_{MPCi} – maximum permissible concentration of the i-th pollutant;

N_{ai} – the number of samples with a chemical indicator when the MPC was exceeded;

N_i – the total number of samples taken.

In this study, the calculation of the risk of contamination with nitrogen compounds was carried out according to the equation, which considers the ratio of the k_n value as the sum of the concentrations of nitrogen compounds up to the threshold value of 11.3 mg N/dm^3, multiplied by the relative frequency of the event:

$$R' = \sum_{i=1}^{n} \frac{k_n}{11.3} \times \frac{N_i}{N}, \tag{6}$$

where N_i – the number of cases when $k_n > 11.3$;

N – the total number of cases.

To characterize the level of the risk situation, let’s investigate the relationship between the risk indicator R` and the indicator of sensitivity to contamination with nitrogen compounds k_n based on the application of regression analysis.

When calculating environmental risks, the assumption is axiomatic that most of the results of economic activities, including those that cause environmental pollution (in particular, the water environment), are random variables and obey a law close to normal [26]. Checking the series k_n, R` according to the Gauss criterion showed that they can be considered as that obey the normal law.

5. Research resutls of depelopment of a method for assessing the risks of surface water pollution by nitrogen compounds

5. 1. Identification of zones sensitive to pollution by nitrogen compounds by the sensitivity coefficient

The basis of calculations is the data of hydrochemical observations of the basin management of water resources of the Black Sea and Lower Danube rivers for the period 2000–2018 (Table 2). The observation was carried out in accordance with the "Program of state environmental monitoring in the system of the State Water Management Agency of Ukraine in terms of monitoring the quality of surface waters by radiological and hydrochemical indicators" (order of the State Water Management Agency No. 125 dated June 14, 2000) and the "Program of State Environmental Monitoring in terms of the implementation of control by the State Water Management Agency quality of surface waters "(order of the State Water Management Agency No. 111 of June 14, 2010).

Table 2

Relative frequency of cases of exceeding the criterion of sensitivity to pollution by nitrogen compounds

No.	River – Post	Observation period, years	Number of measurements	Number of cases of excess	Relative frequency of excess, %
1	Okna – Labushne	2000–2008, 2010–2018	59	29	49
2	Bilochi – Shershentsi	2000–2018	66	0	0
3	Yagorlyk – Artyrivka	2000–2018	67	4	6
4	Kuchurgan – Stepanivka	2000–2018	69	0	0
5	Baraboy – Baraboy	2000–2018	68	0	0
6	Kodyma – Balta	2000–2018	70	5	7
7	Alkalia – Shyroke	2004–2009, 2011–2018	43	0	0
8	Khajider – Serhiivka	2003–2018	61	20	33
9	Kaplan – Krutoyarivka	2007–2018	47	23	49
10	Sarata – Miniailivka	2007–2018	38	2	5
11	Kogylnyk – Serpneve	2007–2018	48	4	9
12	Chaga – Petrivka	2007–2018	46	0	0
13	Kyrgyzh – Kytai Maloyaroslavets	2003–2018	55	11	20
14	Velykyi Yalpug – Tabaky	2003–2018	59	3	5
15	Malyi Kuyalnyk – Baranovo	2000–2008, 2010–2018	49	0	0
16	Velykyi Kuyalnyk – Ruska Slobodka	2000–2006, 2008, 2010–2018	50	1	2
17	Tyligul – Berezivka	2000–2018	63	3	5

The total number of posts at which hydrochemical observations were carried out was 17. Each observation was carried out once a quarter, the total number of observations varied from 38 to 70 over the observation period. The observation gaps are explained by the fact that some rivers were in a dry state.

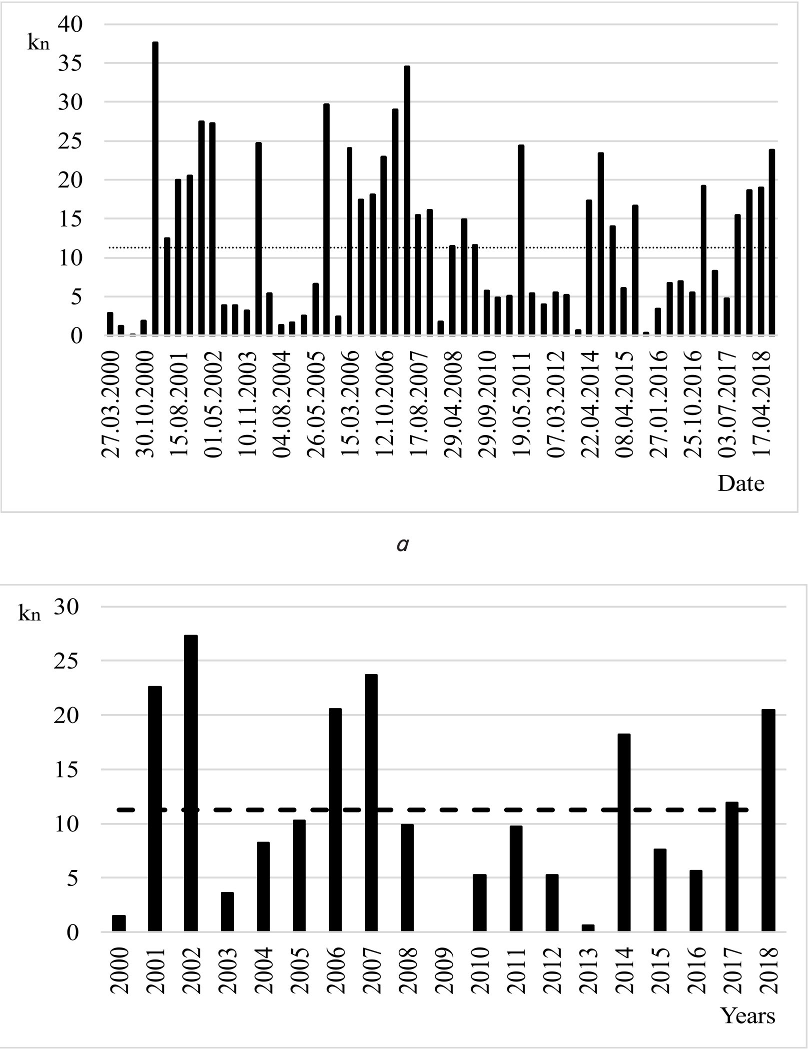
Analysis of observational data on the concentrations of nitrogen compounds showed that exceeding the threshold value k_n=11.3 mg N/dm^3 was observed in 104 cases out of 958, which is about 11 %. It was found that 96 % of these cases were formed due to nitrate nitrogen. This fact indicates the presence of diffuse pollution of the waters of the studied rivers with nitrogen compounds. The most empirical probability (relative frequency of the event) pollution by nitrogen compounds was found on the rivers Okna, Khajider, Kaplan, Kyrgyzh-Kytai (Table 2). It is on these rivers (above the considered sections) that the risk of failure to achieve a good ecological state of waters is established (Table 3). In most cases (60 %), the threshold was exceeded in the first quarter (January, February, March) and the fourth quarter (October, November, December). Winter thaws or spring floods are formed in the first quarter, autumn floods – in the second.

The most significant excess of k_n was found on the Okna river (Fig. 1).

Table 3

Risk zones established by the sensitivity index k_n to pollution by nitrogen compounds (k_n> 11.3 mg N/dm^3), determined according to long-term average data, in parentheses are the maximum and minimum values.

No.	River – Post	Indicator of sensitivity to nitrogen k_n, mg N/dm^3	Conclusions
1	Okna – Labushne	11.8 (37.56–0.03)	risk of contamination
2	Bilochi – Shershentsi	5.69 (10.44–0.11)	risk-free zone
3	Yagorlyk – Artyrivka	3.02 (22.98–0.01)	risk of contamination in some years
4	Kuchurgan – Stepanivka	1.55 (7.38–0.77)	risk-free zone
5	Baraboy – Baraboy	1.93 (8.83–0.01)	risk-free zone
6	Kodyma – Balta	3.35 (20.26–0.04)	risk of contamination in some years
7	Alkalia – Shyroke	1.64 (6.36–0.04)	risk-free zone
8	Khajider – Serhiivka	9.65 (25.98–0.37)	risk of contamination in some years
9	Kaplan – Krutoyarivka	11.31 (25.64–0.77)	risk of contamination
10	Sarata – Miniailivka	3.73 (11.79–0.06)	risk of contamination in some years
11	Kogylnyk – Serpneve	4.64 (18.09–0.03)	risk of contamination in some years
12	Chaga – Petrivka	3.23 (10.68–0.02)	risk-free zone
13	Kyrgyzh – Kytai-Maloyaroslavets	7.11 (56.33–0.02)	risk of contamination in some years
14	Velykyi Yalpug – Tabaky	2.69 (17.17–0.09)	risk of contamination in some years
15	Malyi Kuyalnyk – Baranovo	0.61 (3.42–0.01)	risk-free zone
16	Velykyi Kuyalnyk – Ruska Slobodka	1.80 (36.29–0.01)	risk of contamination in some years
17	Tyligul – Berezivka	2.34 (25.12–0.10)	risk of contamination in some years



a

b

Fig. 1. Chronological course of the criterion of sensitivity to nitrate pollution at the observation point Okna — Labushne: *a* — daily observation data; *b* — data averaged over years

It was found that for the series kn the Gauss criterion varies from 1.23 to 1.29, which allows to accept a null statistical hypothesis about their subordination of the series to the normal distribution law.

The analysis of the patterns of the chronological course, carried out on the basis of regression analysis [27], showed that statistically significant trends (negative or positive) in the fluctuations of the total nitrogen content were not revealed (Fig. 2).

The distribution law of k_n as a random variable is presented in the form of an empirical probability curve (Fig. 3, 4). The probability of exceeding the threshold value k_n is in the range of 20–40 %.

The obtained result shows that the studied rivers in most cases (60–80 %) are not vulnerable to pollution by nitrogen compounds and there are prospects for the earliest possible achievement of their good ecological state by reducing the pollution of watershed surfaces with nitrogen compounds.

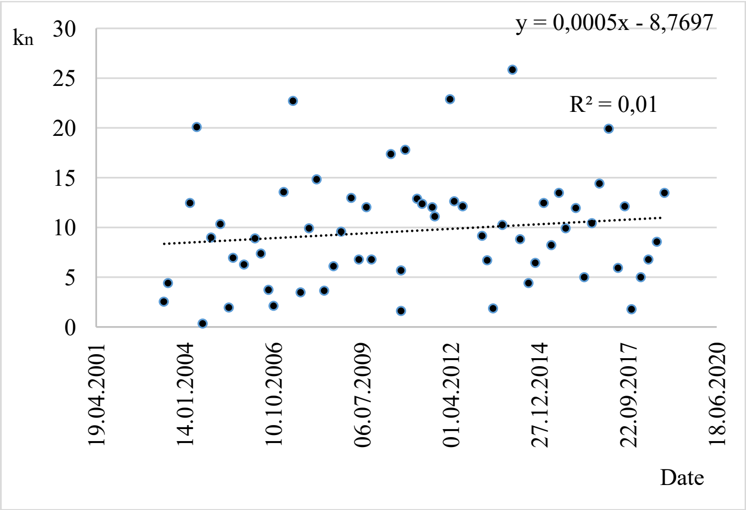


Fig. 2. Chronological course of the criterion of sensitivity to nitrate pollution at the observation point Khajider — Serhiivka and the corresponding regression equation (according to daily observations)

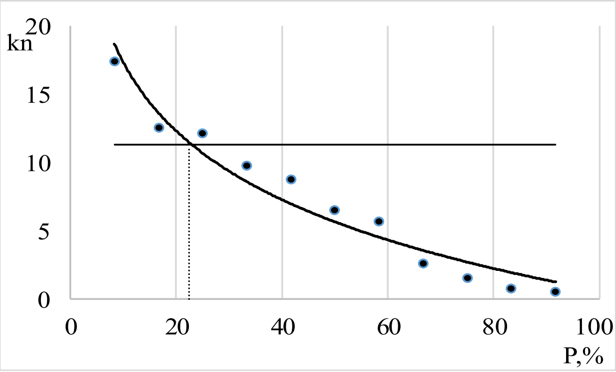


Fig. 3. The empirical distribution curve of the probability of exceeding the criterion sensitivity kn to pollution by nitrogen compounds at the observation site Kyrgyzh-Kytai – Maloyaroslavets

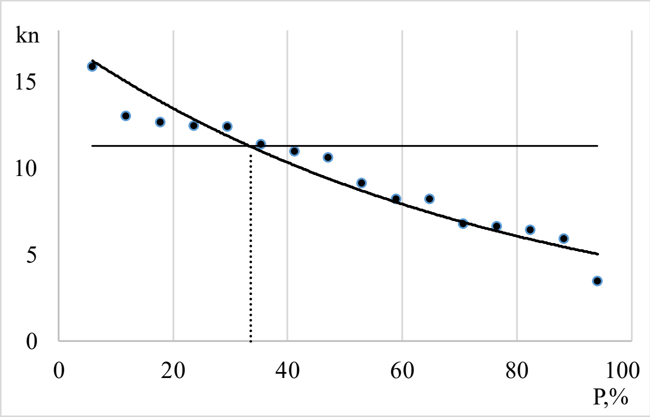


Fig. 4. The empirical distribution curve of the probability of exceeding the criterion sensitivity k_n to pollution by nitrogen compounds at the observation site Khajider – Serghiivka

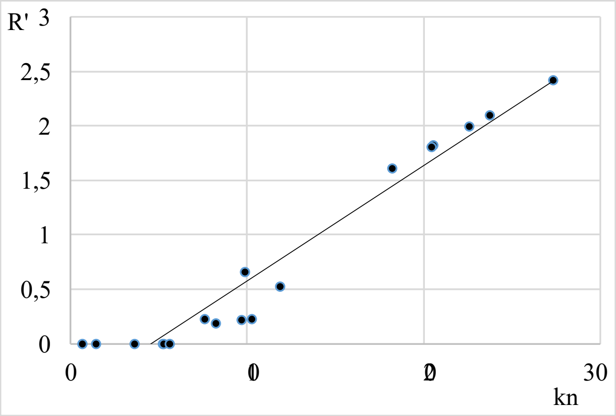


Fig. 5. The graph of the dependence $R`=f(k_n)$ in the observation point Okna – Labushne for the period 2000–2018

Taking into account the lack of hydrological and hydrochemical knowledge of the territory, for practical application, the obtained results were generalized in the form of a regional connection, which represents the dependence of the average long-term values of $R`$ on $k_n$ for individual catchments (Fig. 9). This type of dependence allows one to obtain the value of $R`$ for any river in the territory, even if only data from expeditionary observations of nitrogen compounds are available.

Regional dependence $R`=f(k_n)$ which is shown in Fig. 9 is approximated by a linear pairwise regression equation of the form

$$R`=0.0679\,k_n-0.197,\ r=0.95, \tag{7}$$

where $R`$ – indicator of the risk of pollution by nitrogen compounds

k_n – coefficient of sensitivity to pollution by nitrogen compounds

r – correlation coefficient.

5. 2. Assessment of the connecetions between risk indicators and indicators of sensitivity to pollution by nitrogen compounds

The indicator of the ecological risk of pollution by nitrogen compounds R` was determined by equation (6) for each year and for each observation point. The average annual value of the criterion of sensitivity to nitrogen kn was used as Ci, the threshold value kn=11.3 mg N/dm3 was used as CMPCi.

An analysis of the relationship graphs (Fig. 5–8) between the risk indicators R` and the sensitivity coefficients kn showed that the relationships between these values are described by linear regression equations with correlation coefficients r greater than 0.8, which indicates the statistical significance of the equations obtained. Table 4 shows the equations of linear pair regression R`=f(kn) and the correlation coefficients r.

Table 4

Form of linear pair regression equations $R`=f(k_n)$ and correlation coefficients (r) for rivers of southwestern Ukraine

No.	River – Post	Equation type	Correlation coefficient r
1	Okna – Labushne	y=0.106x–0.4864	0.97
2	Bilochi – Shershentsi	According to equation 6: if Ni= 0, then R`=0	
3	Yagorlyk – Artyrivka	y=0.0246x–0.0343	0.87
4	Kuchurgan – Stepanivka	According to equation 6: if Ni= 0, then R`=0	
5	Baraboy – Baraboy	According to equation 6: if Ni= 0, then R`=0	
6	Kodyma – Balta	y=0.0246x–0.0343	0.87
7	Alkalia – Shyroke	According to equation 6: if Ni= 0, then R`=0	
8	Khajider – Serhiivka	y=0.0907x–0.492	0.83
9	Kaplan – Krutoyarivka	y=0.0705x–0.268	0.91
10	Sarata – Miniailivka	y=0.0325x–0.0908	0.75
11	Kogylnyk – Serpneve	y=0.034x–0.108	0.86
12	Chaga – Petrivka	According to equation 6: if Ni= 0, then R`=0	
13	Kyrgyzh-Kytai – Maloyaroslavets	y=0.034x–0.0526	0.87
14	Velykyi Yalpug – Tabaky	y=0.0294x–0.0553	0.82
15	Malyi Kuyalnyk – Baranovo	According to equation 6: if Ni= 0, then R`=0	
16	Velykyi Kuyalnyk – Ruska Slobodka	According to equation 6: if Ni= 0, then R`=0	
17	Tyligul – Berezivka	y=0.0356x–0.0523	0.85

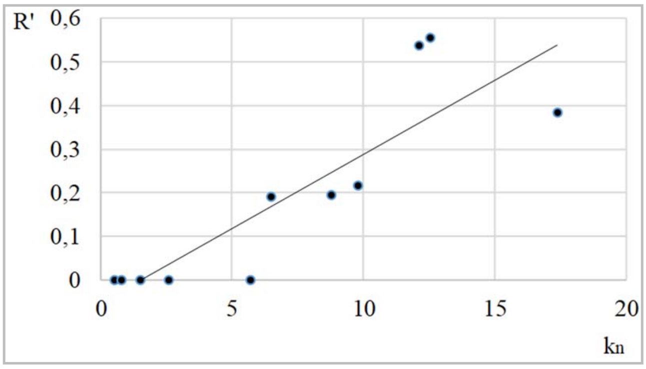


Fig. 6. Graph of dependence $R`=f(k_n)$ at observation point Kyrgyzh-Kytai – Maloyaroslavets for the period 2000–2018

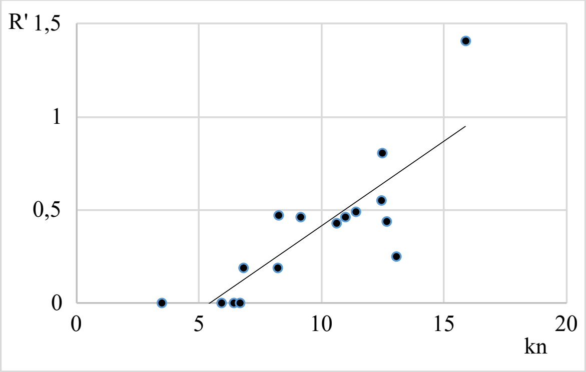


Fig. 7. Graph of dependence $R`=f(k_n)$ at observation point Khajider – Serhiivka for the period 2000–2018

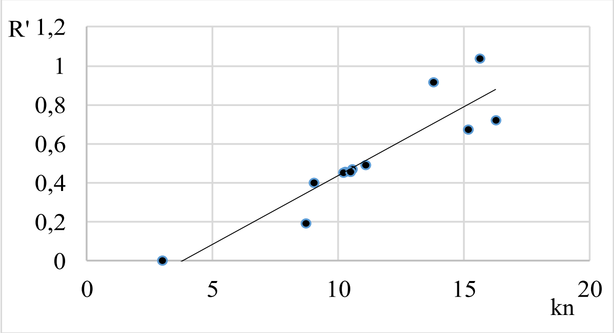


Fig. 8. Graph of dependence $R`=f(k_n)$ at observation point Kaplan – Krutoyarivka for the period 2000–2018

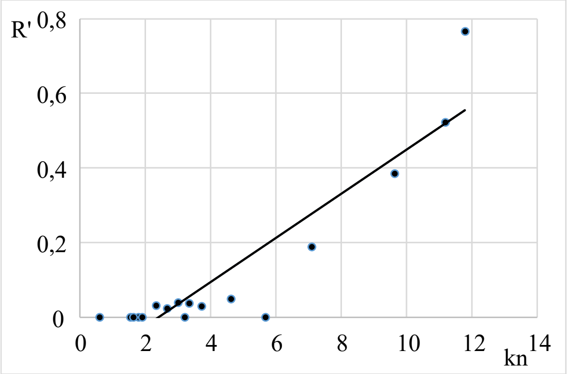


Fig. 9. The graph of the relationship of the average long-term values $R`=f(k_n)$ for the rivers of southwestern Ukraine

5. 3. Determination of the boundaries of zones of pollution by nitrogen compounds

The boundaries of the risk zones of contamination with nitrogen compounds were determined depending on the set value of k_n: 0.5 k_n; k_n; 3 k_n (threefold excess) 10 k_n (tenfold excess) and risk indicators calculated according to (7) (Table 5).

Table 5

Allocation of zones of contamination with nitrogen compounds based on sensitivity and risk indicators

Range of k_n values	$R`$ value range	Qualitative characteristics of the level of damage	Qualitative characteristics of the risk zone
k_n<0.5·11.3	$R`$<=0.19	acceptable	Initial contamination
5.65 ≤ k_n<11.3	0.19<$R`$<=0.58	permissible	Zone insensitive to contamination
11.3 ≤ k_n ≤ 3·11.3. three times the threshold value	0.58<$R`$<=2.10	significant	Contamination sensitive zone
k_n>10·11.3. ten times the threshold value	$R`$>2.10	high	Zone of catastrophic pollution or quality loss

The zone sensitive to pollution by nitrogen compounds corresponds to quantitative risk assessments $R`$>0.58. Based on the analysis of observational data, it was revealed that the greatest excess of the threshold value of 11.3 in the study area was 3. The value 3·11.3=33.9 was taken as the upper threshold of the zone sensitive to pollution. Exceeding the upper threshold means moving into a zone of high pollution.

5. 4. Development of a scale of qualitative and quantitative risk assessment based on the use of the statistical distribution law of the risk indicator

The probability of the risk coefficient R` falling into the above risk zones is determined by the regional probability curve (the probability of exceeding a given value). This regional curve is the result of averaging the empirical distribution curves of $R`$ in each investigated section (Fig. 10). According to data from southwestern Ukraine, it is most likely to fall into the zone of acceptable and acceptable risk (Table 6).

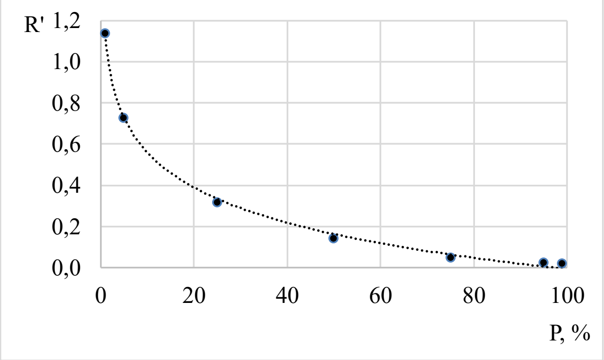


Fig. 10. Regional empirical distribution curve of the probability of exceeding the risk values R` of pollution by nitrogen compounds

Table 6

The value of the probability of the risk of pollution by nitrogen compounds (based on the data of small and medium rivers of southwestern Ukraine)

Risk zone rank	Qualitative characteristics of the risk zone	Probability of falling into a given risk zone, %
I	Acceptable risk zone (initial pollution) R`<0.19	55.00
II	Permissible risk zone (zone insensitive to pollution) 0.19<=R`<0.58	35.00
III	Zone of unacceptable risk zone (zone sensitive to pollution) 0.58<=R`<=2.10	9.08
IV	Catastrophic risk zone (quality loss zone) R`>=2.1	0.02

The qualitative characteristic of the possible level of loss (acceptable, say, significant, high) during pollution reflects various situations in the change in the quality of the aquatic environment. The qualitative characteristic of the risk zone is a guideline for making management decisions.

6. Discussion of the research results of the development of a method for assessing the risk of surface water pollution by nitrogen compounds

The most common in the practice of assessing environmental risks is the use of threshold values (criteria) for quantitative risk indicators. For example, the prospect of achieving environmental goals (good environmental status) is assessed on the basis of quantitative indicators of anthropogenic loads, for which threshold values have been established [28]. Depending on the indicators of anthropogenic pressures, 3 categories of the consequences of anthropogenic impact were identified: "without risk" of achieving environmental goals; "Possibly at risk"; "At risk." The basis for this kind of calculations is the assumption that the cumulative anthropogenic impact leads to a change in the quality of water in the river, which affects its physicochemical indicators. Among the physicochemical indicators proposed for use, the content of ammonium in water is taken into account. However, to assess the risk of water pollution by nitrogen compounds, this information only data on ammonium is insufficient [29]. Determination of the risks of failure to achieve environmental goals based on calculations of anthropogenic loads is only the first step in studying the ecological status of a water body, which provides only previous ideas about the consequences of water pollution from anthropogenic sources.

The basis for the expert qualitative and quantitative assessment of environmental risks should be a rank scale, which is created based on the results of spatio-temporal generalizations of the output data. Expert assessments of environmental risks are often subjective, since the ranking scale of risk gradations is created quite arbitrarily. The ranking scale of risk indicators should reflect different situations in terms of changes in the quality of the natural environment (semantic differentiation) depending on the degree of pollution. For the practical application of quantitative assessments of environmental risk, many authors have carried out their agreement with the indicator of the ecological state of the investigated component of the environment. For example, in [30, 31], a comparison (in tabular form) of the integral indicator of the quality state of atmospheric air (I_{air}) with the values of the air pollution index (API) is carried out. In works [32, 33], the agreement was carried out according to the considered integral indicator of the state of soils and the indicator of anthropogenic load on soils. In works [34, 35], a relationship was established between the values of risk indicators and indices of water and air pollution (WPI). The rank scale is used as the basis for expert qualitative and quantitative assessment of environmental risks, since it allows the information consumer to determine the degree of possible danger to the natural environment.

The authors of the presented work used an approach to assessing environmental risks implemented within the framework of the EU international project "Inventory, assessment and mitigation of the impact of anthropogenic sources of pollution in the Lower Danube region of Ukraine, Romania, the Republic of Moldova, 2007–2013" (MIS ETC CODE 995) [36]. The results of this work are aimed at obtaining more accurate quantitative estimates of pollution risks, which are characterized by a lower degree of uncertainty.

The developed method for calculating the quantitative assessment of the risk of surface water pollution by nitrogen compounds is based on the use of a probabilistic model. This means that the risk is calculated as the sum of the products of losses from various types of pollution by their probability in (5). The traditional assessment of damage in the calculations of environmental risk is defined as the excess of the concentration of the pollutant over its threshold value (the maximum permissible concentration of MPC). As it is known, the MPC can differ both for the substances included in the amount, and for different countries, where the corresponding MPC values are assigned. In addition, in the presence of correlations between the concentrations of the investigated substances, this fact is also taken into account by using the information of the correlation matrices. Taking into account the biogeo-toxicity of nitrogen [37], it is recommended to use the total content of inorganic nitrogen forms (N_{inorg}) in water as an indicator of the vulnerability of a territory to pollution by nitrogen compounds $\left(NH_4^+ + NO_2^- + NO_3^-\right)$ [38].

To calculate the risk, it was proposed to use the maximum permissible concentration of individual nitrogen compounds, and the threshold value (sensitivity coefficient k_n=11.3 mgN/dm^3) for the sum of nitrogen concentrations. This indicator is the property of the implementation of the provisions of the nitrate directive in different countries, including Ukraine [39]. A close linear relationship between the values of R` and k_n was established for individual rivers by year (Fig. 5–9) and for mean long-term values (Fig. 9). This circumstance made it possible to create a rank scale, which is formed according to the results of spatio-temporal generalizations of the output data. The ranking scale of the risks of contamination with nitrogen compounds is based on the existence of close relationships between the sensitivity coefficient k_n and risk assessments R`. The regional risk probability curve made it possible to determine the probabilities of falling into each of the zones.

The algorithm for the practical application of the method can be presented as follows:

1. According to actual or predicted data, the total content of nitrogen compounds in water is established according to the equation (1) $k_n = NH_4^+ + NO_2 + NO_3$.

2. According to the Table 5, depending on the value of k_n, the range of possible values of risks, the qualitative characteristics of damage and the qualitative characteristics of the risk zone are determined.

3. According to the Table 6 the probability of getting into the risk zone is established. It should be noted that the territory of southwestern Ukraine, given as an example, is insufficiently studied from the point of view of its coverage with the data of hydrological and hydrochemical observations. This circumstance required the use of spatio-temporal generalizations in the form of regional dependencies. In the presence of a significant amount of initial information, the research algorithm will enter the following form:

1. According to actual or predicted data, the total content of nitrogen compounds in water is established according to the equation (1) $k_n = NH_4^+ + NO_2 + NO_3$.

2. The quantitative indicator of risk $R`$ is determined according to the formula (6).

3. The connection $R`=f(k_n)$ is established in a given section according to the observation data.

4. Allocation of zones of contamination with nitrogen compounds based on k_n values depending on the task.

5. Determination of risk zones in accordance with the boundaries of contamination zones k_n.

6. Plotting the statistical distribution curve of the quantitative risk indicator $R`$.

7. Establishment of the distribution of the probability of falling into a given interval (risk zone) according to the selected law.

It is important to note that the coefficient of sensitivity to nitrogen pollution can serve as an indicator of the level of eutrophication [40]. The limitation of the proposed method is that the use of the criterion $k_n>11.3$ mg N/dm^3 is advisable only for rivers with the Strahler coefficient≤5. In rivers with this coefficient>5, the content of nitrogen in the water is masked by bioconsumption. In this case, the risk indicators should be calculated according to the eutrophication indices, for example, the ones given in [41].

The disadvantages of this study include the fact that phosphorus and silicon are also factors of biogenic pollution (in addition to nitrogen compounds). It should be noted that within the territory considered in the example, their concentrations are insignificant. When considering other catchments, the excess of the concentrations of phosphorus and silicon compounds over the MPC (maximum permissible concentration) should be included in the calculation of the quantitative risk indicator.

The applied aspect of using the obtained scientific result is the possibility of improving approaches to assessing water quality due to pollution with nitrogen compounds. This constitutes the preconditions for making managerial decisions to ensure man-made and environmental safety.

Perhaps the development of the study consists in determining the risks of pollution of surface waters with nitrogen compounds by seasons and months in order to determine the influence of genetic factors in the drainage formation.

7. Conclusions

1. According to the data on the total concentration of nitrogen for small and medium-sized rivers of southwestern Ukraine, it was found that the excess of the sensitivity index k_n over the threshold value is observed only on individual rivers. In the risk zone, reservoirs with a small area and a high percentage of plowing have been identified. Such rivers are characterized by violation of the boundaries of water protection zones and coastal protection zones. Agricultural land can be close to the very edge of the water. River water is used for irrigation and household needs. The maximum value of the sensitivity index k_n is 56.33, the minimum is 0.01. The empirical probability of exceeding the threshold value k_n varies from 20 to 40 %. This testifies to the episodic nature of the pollution of rivers in the study area with nitrogen compounds, where an acceptable and permissible level of damage prevails. Thus, the territory under consideration belongs to those where there is a prospect of achieving a good ecological state of water bodies by strengthening control over the quality of discharged waters and the degree of pollution of the surface of catchments with fertilizers and animal waste.

2. The search for individual and regional relationships between quantitative risk indicators $R`$ and coefficients of sensitivity to pollution with nitrogen compounds is the basic part of the method for qualitative and quantitative assessment of the level of risks. In the example under consideration, the existence of a close correlation (with correlation coefficients $r>0.8$) was established according to the data of individual rivers and the considered territory as a whole. A statistically significant correlation is provided by the fact that both the sensitivity indicator and the risk indicator use observational data on the content of nitrogen compounds in water. However, unlike the sensitivity indicator, the risk indicator takes into account the empirical probability of a hazardous event occurring (exceeding the threshold value of nitrogen concentration in water). In the case when $k_n>11.3$ mg N/dm^3 (for surface waters), then a decision is made to classify the catchment area as a vulnerable zone. The zones of high vulnerability are the most dangerous for water bodies.

3. The resulting dependence of the form $R`=f(k_n)$ allows performing semantic and quantitative reconciliation of data on the total content of nitrogen compounds in water and the value of the risk indicator. The boundaries of the risk zones are assigned as multiples of the sensitivity coefficient, and the limit values R` corresponding to each zone are calculated using the obtained regional equation.

4. The probabilistic characteristics of the risk of pollution by nitrogen compounds are determined based on the use of statistical distribution laws. In the given example, the averaged empirical curve of security (probability of exceeding a given value) of risk indicators is used. The limit values of the identified risk zones are used to calculate the probability of getting into each of the zones. The response to the detected risk should be manifested in a set of measures to prevent and mitigate the consequences. If the investigated water body falls into the zone of acceptable and acceptable risk, then the function of its management may be limited by carrying out control measures. An analysis of the indicators of aquatic flora should play a significant role during the latter.

5. The proposed method for determining the risk of pollution by nitrogen compounds based on the criterion of sensitivity (vulnerability) of water bodies to pollution by nitrogen compounds can be used in various countries with the involvement of observation data both for individual water bodies of water bodies, and on the basis of existing spatio-temporal generalizations.

References

1. Gao, Y., Yu, G., Luo, C., Zhou, P. (2012). Groundwater Nitrogen Pollution and Assessment of Its Health Risks: A Case Study of a Typical Village in Rural-Urban Continuum, China. PLoS ONE, 7 (4), e33982. doi: https://doi.org/10.1371/journal.pone.0033982
2. Wegahita, N. K., Ma, L., Liu, J., Huang, T., Luo, Q., Qian, J. (2020). Spatial Assessment of Groundwater Quality and Health Risk of Nitrogen Pollution for Shallow Groundwater Aquifer around Fuyang City, China. Water, 12 (12), 3341. doi: https://doi.org/10.3390/w12123341
3. Kakade, A., Salama, E.-S., Han, H., Zheng, Y., Kulshrestha, S., Jalalah, M. et. al. (2021). World eutrophic pollution of lake and river: Biotreatment potential and future perspectives. Environmental Technology & Innovation, 23, 101604. doi: https://doi.org/10.1016/j.eti.2021.101604
4. Zaprovadzhennia yevropeiskykh ekolohichnykh standartiv do haluzi tvarynnytstva Ukrainy (2018). Analitychnyi dokument. Praha-Kyiv. Available at: https://issuu.com/ecoact/docs/policy-paper-ukrainian_007
5. Osadcha, N. M., Ukhan, O. O., Chekhniy, V. M., Holubtsov, O. H. (2019). Otsinka emisiyi biohennykh elementiv ta orhanichnykh rechovyn u poverkhnevi vody baseinu r. Siverskyi Donets vid dyfuznykh dzherel. Problemy hidrolohiyi, hidrokhimiyi, hidroekolohiyi. Kyiv: Nika-Tsentr, 199–200.
6. Osadcha, N. M., Osadchyi, V. I., Ukhan, O. O., Klebanov, D. O., Luzovitska, Yu. A., Biletska, S. V. (2019). Antropohenne navantazhennia biohennymy elementamy na poverkhnevi vody baseiniv nyzhnoho Dunaiu, Dnistra ta Prutu. Hidrolohiya, hidrokhimiya i hidroekolohiya, 3, 77–78. Available at: http://nbuv.gov.ua/UJRN/glghge_2019_3_36
7. Implementation of the Nitrate Pollution Prevention Regulations 2015 in England. Method for designating Nitrate Vulnerable Zones for surface freshwaters. Available at: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/573530/surface-water-nvz-methodology-2017-2020.pdf
8. Kadiri, M., Zhang, H., Angeloudis, A., Piggott, M. D. (2021). Evaluating the eutrophication risk of an artificial tidal lagoon. Ocean & Coastal Management, 203, 105490. doi: https://doi.org/10.1016/j.ocecoaman.2020.105490
9. Ravindranath, I. G., Thirukumaran, V. (2021). Spatial mapping for Groundwater Vulnerability to Pollution Risk Assessment Using DRASTIC Model in Ponnaiyar River Basin, South India. Journal of Geology, Geography and Geoecology, 30 (2), 355–364. doi: https://doi.org/10.15421/112132
10. Triassi, M., Nardone, A., Giovinetti, M. C., De Rosa, E., Canzanella, S., Sarnacchiaro, P., Montuori, P. (2019). Ecological risk and estimates of organophosphate pesticides loads into the Central Mediterranean Sea from Volturno River, the river of the “Land of Fires” area, southern Italy. Science of The Total Environment, 678, 741–754. doi: https://doi.org/10.1016/j.scitotenv.2019.04.202
11. Ding, T.-T., Du, S.-L., Huang, Z.-Y., Wang, Z.-J., Zhang, J., Zhang, Y.-H. et. al. (2021). Water quality criteria and ecological risk assessment for ammonia in the Shaying River Basin, China. Ecotoxicology and Environmental Safety, 215, 112141. doi: https://doi.org/10.1016/j.ecoenv.2021.112141
12. Rao, K., Tang, T., Zhang, X., Wang, M., Liu, J., Wu, B. et. al. (2021). Spatial-temporal dynamics, ecological risk assessment, source identification and interactions with internal nutrients release of heavy metals in surface sediments from a large Chinese shallow lake. Chemosphere, 282, 131041. doi: https://doi.org/10.1016/j.chemosphere.2021.131041
13. Muller, G. (1969). Index of Geoaccumulation in Sediments of the Rhine River. GeoJournal, 2, 108–118.
14. Walling, D. E., Webb, B. W. (1985). Estimating the discharge of contaminants to coastal waters by rivers: Some cautionary comments. Marine Pollution Bulletin, 16 (12), 488–492. doi: https://doi.org/10.1016/0025-326x(85)90382-0
15. Akahashi, M., Nakatani, N., Majima, T., Hara, S., Shirota, H. (2016). Environmental risk assessment on coastal ecosystem owing to the stranded oil. OCEANS 2016 - Shanghai. doi: https://doi.org/10.1109/oceansap.2016.7485621
16. Belskaya, E. N., Brazgovka, O. V., Sugak, E. V. (2014). Method of calculation the environmental risks. Modern problems of science and education, 6. Available at: https://science-education.ru/ru/article/view?id=15755
17. Vodnyi Kodeks Ukrainy. Verkhovna Rada Ukrainy. Available at: https://zakon.rada.gov.ua/laws/show/213/95-%D0%B2%D1%80#Text
18. Shvebs, H. I., Ihoshyn, M. I. (2003). Kataloh richok i vodoim Ukrainy. Odessa: Astroprynt, 392.
19. Loboda, N. S., Gryb, O. M. (2017). Hydroecological Problems of the Kuyalnyk Liman and Ways of Their Solution. Hydrobiological Journal, 53 (6), 87–95. doi: https://doi.org/10.1615/hydrobj.v53.i6.90
20. Daus, M. Ye., Pintiyska, O. S., Polishchuk, O. O., Tvardievych, N. Yu. (2014). Otsinka yakosti vody malykh richok Pivnichno-Zakhidnoho Prychornomoria. Vestnik Gidrometcentra Chernogo i Azovskogo morey, 1 (16), 77–83.
21. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32000L0060
22. Consolidated text: Council Directive of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC). Available at: https://eur-lex.europa.eu/eli/dir/1991/676/2008-12-11
23. Shurda, K. E. (2020). Basic risk assessment methods. Annali d’Italia, 2 (11), 50–53.
24. Shurda, K. (2020). Methods of qualitative and quantitative risk analysis. Balanced Nature Using, 4, 64–72. doi: https://doi.org/10.33730/2310-4678.4.2020.226622
25. Metodychni rekomendatsiyi shchodo otsinky ymovirnosti ryzykovykh podiy vnaslidok zabrudnennia vodnykh obiektiv ta gruntiv ukrainskoi chastyny Nyzhnodunaiskoho rehionu (2016). Odessa: FOP Shylov M.V.
26. Ventcel', E. S. (1999). Teoriya veroyatnostey. Moscow: Vysshaya shkola.

27. Shkolnyi, Ye. P., Loieva, I. D., Honcharova, L. D. (1999). Obrobka ta analiz hidrometeorolohichnoi informatsiyi. Kyiv: Minosvity Ukrainy. Available at: http://eprints.library.odeku.edu.ua/id/eprint/451/1/Shkolnyiy_Obrobka_ta_analiz_GMI_1999.pdf
28. Common implementation strategy for the water framework directive (2000/60/EC). Guidance Document No 3. Analysis of Pressures and Impacts (2003). European Communities. Available at: https://circabc.europa.eu/sd/a/7e01a7e0-9ccb-4f3d-8cec-aeef-1335c2f7/Guidance%20No%203%20-%20pressures%20and%20impacts%20-%20IMPRESS%20(WG%202.1).pdf
29. Loboda, N. S., KatynskaI. V. (2020). Determination of main anthropogenic impacts and environmental risks for the Kryvyi Torets river basin (based on the EU Support Program for Ukrainian water policy). Ukrainian Hydrometeorological Journal, 25, 81–92. doi: https://doi.org/10.31481/uhmj.25.2020.08
30. Vasenko, O. H., Rybalova, O. V., Artemiev, S. R. (2015). Intehralni ta kompleksni otsinky stanu navkolyshnoho pryrodnoho seredovyshcha. Kharkiv: NUHZU. Available at: http://repositsc.nuczu.edu.ua/bitstream/123456789/6524/1/%D0%9E%D0%A0%D0%98%D0%93%20%D1%87%D0%B0%D1%81%D1%82%D1%8C%201%20%D0%B8%D1%81%D0%BF%D1%80%D0%B0%D0%B2%D0%BB%D0%B5%D0%BD%D0%BE%20%D0%B0%D0%B2%D1%82%D0%BE%D1%80%D0%BE%D0%BC.pdf
31. Rybalova, O. V., Korobkina, K. M., Horban, A. V. (2021). Yakisnyi stan atmosfernoho povitria v Ukraini. The 5th International scientific and practical conference “Science and education: problems, prospects and innovations”. Kyoto, 829–838. Available at: http://repositsc.nuczu.edu.ua/bitstream/123456789/12563/1/%D0%AF%D0%BA%D1%96%D1%81%D0%BD%D0%B8%D0%B9%20%D1%81%D1%82%D0%B0%D0%BD%20%D0%B0%D1%82%D0%BC%D0%BE%D1%81%D1%84%D0%B5%D1%80%D0%BD%D0%BE%D0%B3%D0%BE%20%D0%BF%D0%BE%D0%B2%D1%96%D1%82%D1%80%D1%8F%20%D0%B2%20%D0%A3%D0%BA%D1%80%D0%B0%D1%97%D0%BD%D1%96.pdf
32. Rybalova, O. V., Bielan, S. V. (2013). Ekolohichnyi ryzyk pohirshennia stanu gruntiv i zemelnykh resursiv Ukrainy. Ekologiya i promyshlennost', 3, 15–22. Available at: http://nbuv.gov.ua/UJRN/ekolprom_2013_3_5
33. Serbov, M., Hryb, O., Pylypiuk, V. (2021). Assessment of the ecological risk of pollution of soil and bottom sediments in the Ukrainian Danube region. Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu, 2, 137–144. doi: https://doi.org/10.33271/nvngu/2021-2/137
34. Loboda, N. S., Kulachok, K. V. (2019). Metodychni pidkhody do otsinky ekolohichnykh ryzykiv na bazi vykorystannia kompleksnykh pokaznykiv yakosti vody. Zbirnyk naukovykh prats. VII All-Ukrainian Congress of Ecologists with International Participation. Vinnytsia. 75. Available at: http://eprints.library.odeku.edu.ua/id/eprint/6160/1/LobodaNS_KulachokKV_Conf_7vze_2019.pdf
35. Daus, M. E., Daus, Y. V. (2021). Estimating environmental risk assessment for drinking and fisheries use (on the example of the Danube river – the city Vilkovo). Journal of Geology, Geography and Geoecology, 30 (1), 25–33. doi: https://doi.org/10.15421/112103
36. Burkynskyi, B. V., Rubel, O. Ye. (2016). Otsinka ryzykiv dlia zdorovia liudyny ta navkolyshnoho seredovyshcha vid dzherel zabrudnennia gruntu ta vod. Zvit “Inventaryzatsiya, otsinka ta zmenshennia vplyvu antropohennykh dzherel zabrudnennia v Nyzhnodunaiskomu rehioni Ukrainy, Rumunii, respubliky Moldova, 2007-2013” (MIS ETC CODE 995). NAN Ukrainy, Instytut problem rynku ta ekoloho-ekonomichnykh doslidzhen. Odessa, 84.
37. Osadchyy, V., Nabyvanets, B., Linnik, P., Osadcha, N., Nabyvanets, Y. (2016). Processes Determining Surface Water Chemistry. Springer, 265. doi: https://doi.org/10.1007/978-3-319-42159-9
38. Pro zatverdzhennia Metodyky vyznachennia zon, vrazlyvykh do (nakopychennia) nitrativ. Ministerstvo zakhystu dovkillia ta pryrodnykh resursiv Ukrainy. Nakaz No. 244 (z0776-21). vid 15.04.2021. Available at: https://zakon.rada.gov.ua/laws/card/z0776-21
39. Osadcha, N. M., Osadchyi, V. I., Osypov, V. V., Biletska, S. V., Kovalchuk, L. A., Artemenko, V. A. (2020). Methodology for the nitrate vulnerable zones designation in surface and ground water. Ukrainian Geographical Journal, 4 (112), 38–48. doi: https://doi.org/10.15407/ugz2020.04.038
40. Camargo, J. A., Alonso, Á. (2006). Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. Environment International, 32 (6), 831–849. doi: https://doi.org/10.1016/j.envint.2006.05.002
41. Billen, G., Garnier, J. (2007). River basin nutrient delivery to the coastal sea: Assessing its potential to sustain new production of non-siliceous algae. Marine Chemistry, 106 (1-2), 148–160. doi: https://doi.org/10.1016/j.marchem.2006.12.017