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 (N\text{Nichtorg}), that is, $\{NH_4^+ + NO_3^- + NO_2^-\}$. 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 $kn$ 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.
sirable, 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

Nitrate is 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 concentration) [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 river [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/dm³, 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 km² [17]. The exceptions are the rivers Kodyma, Kogyl-nyk, Tyligul, which are medium. The rivers of the study area belong to four basins. The rivers Kuchurgan, Yagoryk, Okna, Bilochi belong to the Dniester basin. The Kodyma River is located in the Southern Bug basin. The rivers Kyrgyzh-Kytai and Velykii 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

| No. | River     | Drainage area, km² | River length, km | Average slope, % | Forestedness, % | Plowed, % |
|-----|-----------|--------------------|-----------------|------------------|----------------|-----------|
| 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   | Kurchuran | 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  | Kyrgyzh-Kytai | 3910    | 243             | 1.10             | 16             | 60        |
| 12  | Chaga     | 1270               | 120             | 1.10             | –              | –         |
| 13  | Velikyi Yalpug | 705     | 63              | 1.90             | –              | –         |
| 14  | Malyi Kuyalnik | 3280   | 142             | 1.10             | –              | –         |
| 15  | Velykii Kuyalnik | 1540   | 89              | 0.78             | 0.8            | –         |
| 16  | Velikyi Kuyalnik | 1860   | 150             | 0.70             | 4.87           | 61.3      |
| 17  | Tiligul   | 3550               | 173             | 0.90             | 8              | 60        |

The rivers of the Danube-Dniester interfluve (Alkalia, Khajider, Kaplan, Koglyhnk, Chaga, Sarata) originate on the territory of Moldova and flow into Lake Burnas, Lake Khajider, 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 Kuyalnik, Velykii Kuyalnik, Tiligul rivers flow in the Dniester-Southern Bug interfluve and flow into the Khadzhibeys, Kuyalnyk and Tiligul 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 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:

\[ k_s = \text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^- \]  (1)

where \( k_s \) – indicator of the sensitivity of the territory to pollution by nitrogen compounds;

\( \text{NH}_4^+ \) – concentration of ammonium nitrogen, mg N/dm³;

\( \text{NO}_2^- \) – concentration of nitrite nitrogen, mg N/dm³;

\( \text{NO}_3^- \) – concentration of nitrate nitrogen, mg N/dm³.

If \( k_s > 11.3 \) mg N/dm³, 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 probability of the event 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 \( \frac{C}{C_{\text{MPC}}} \).

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]:

\[ \frac{R}{C_{\text{MPC}}} \]

\[ R = \frac{C}{C_{\text{MPC}}} > 1 \]

where \( R \) – quantitative indicator of risk;

\( C \) – concentration level of the i-th pollutant;

\( C_{\text{MPC}} \) – maximum permissible concentration for the i-th pollutant. \( C_{\text{MPC}} \) 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

\[ R = \sum \frac{C_i}{C_{\text{MPC}}}_i \times N_i > 1 \]

where \( C_i \) – concentration of the i-th pollutant;

\( C_{\text{MPC}} \) – maximum permissible concentration of the i-th pollutant;

\( N_i \) – the number of samples with a chemical indicator when the MPC was exceeded;

\( N \) – 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 \( k_s \) value as the sum of the concentrations of nitrogen compounds up to the threshold value of 11.3 mg N/dm³, multiplied by the relative frequency of the event:

\[ R = \frac{N}{N_i} \]

where \( N_i \) – the number of cases when \( k_s > 11.3 \);

\( N \) – 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...
In the first quarter, autumn floods – in the second. Winter thaws or spring floods are formed in March) and the fourth quarter (October, November, December). Winter thaws or spring floods are 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 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 2

| No. | River – Post          | Observation period, years | Number of measurements | Number of excesses | Relative frequency of excess, % |
|-----|-----------------------|---------------------------|------------------------|-------------------|-------------------------------|
| 1   | Okna – Labushne       | 2000–2008, 2010–2018      | 59                     | 29                | 49                            |
| 2   | Bilochi – Shershentsi | 2000–2018                 | 66                     | 0                 | 0                             |
| 3   | Yagorylk – Artyrivka  | 2000–2018                 | 67                     | 4                 | 6                             |
| 4   | Kuchurhan – 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 – Miniaivliva  | 2007–2018                 | 38                     | 2                 | 5                             |
| 11  | Kogylnyk – Serpnieve  | 2007–2018                 | 48                     | 4                 | 9                             |
| 12  | Chaga – Petrivka      | 2007–2018                 | 46                     | 0                 | 0                             |
| 13  | Kyrgyzh – Kytai Maloyaraslavets | 2003–2018 | 55 | 11 | 20 |
| 14  | Velykyi Yalpug – Tabaky | 2003–2018 | 39 | 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                             |

### Table 3

| 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   | Yagorylk – Artyrivka  | 3.02 (22.98–0.01)                                       | risk of contamination in some years|
| 4   | Kuchurhan – Stepanivka| 1.55 (7.38–0.77)                                        | risk-free zone                     |
| 5   | Baraboy – Baraboy     | 1.93 (8.33–0.01)                                        | 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 – Miniaivliva  | 3.73 (11.79–0.06)                                       | risk of contamination in some years|
| 11  | Kogylnyk – Serpnieve  | 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 Maloyaraslavets | 7.11 (36.33–0.02) | 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|
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. 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

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)
5.2. Assessment of the connections 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 \( k_n \) was used as \( C_i \), the threshold value \( k_n = 11.3 \text{ mg N/dm}^3 \) was used as \( C_{MPCi} \).

An analysis of the relationship graphs (Fig. 5–8) between the risk indicators \( R' \) and the sensitivity coefficients \( k_n \) 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 \( R' = f(k_n) \) and the correlation coefficients \( r \).

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

\[
R' = 0.0679 k_n - 0.197, \quad r = 0.95, \quad (7)
\]

where \( R' \) – indicator of the risk of pollution by nitrogen compounds
\( k_n \) – coefficient of sensitivity to pollution by nitrogen compounds
\( r \) – correlation coefficient.

| 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 \( N_i = 0 \), then \( R' = 0 \) |                                 |
| 3   | Yagorlyk – Artyrivka          | \( y = 0.0246x - 0.0343 \) | 0.87                            |
| 4   | Kuchurgan – Stepantivka       | According to equation 6: if \( N_i = 0 \), then \( R' = 0 \) |                                 |
| 5   | Baraboy – Baraboy             | According to equation 6: if \( N_i = 0 \), then \( R' = 0 \) |                                 |
| 6   | Kodyma – Balta                | \( y = 0.0246x - 0.0343 \) | 0.87                            |
| 7   | Alkalia – Shyroke             | According to equation 6: if \( N_i = 0 \), then \( R' = 0 \) |                                 |
| 8   | Khajider – Serhiivka          | \( y = 0.0907x - 0.492 \) | 0.83                            |
| 9   | Kaplan – Krutyariivka         | \( y = 0.0705x - 0.268 \) | 0.91                            |
| 10  | Sarata – Minialievka          | \( y = 0.0325x - 0.0908 \) | 0.75                            |
| 11  | Kogylnyk – Serpneve           | \( y = 0.034x - 0.108 \) | 0.86                            |
| 12  | Chaga – Petrivka              | According to equation 6: if \( N_i = 0 \), then \( R' = 0 \) |                                 |
| 13  | Kyrgyzh-Kytai – Maloyaroslavets | \( y = 0.034x - 0.0526 \) | 0.87                            |
| 14  | Velykyi Kalug – Tabakiv       | \( y = 0.0294x - 0.0553 \) | 0.82                            |
| 15  | Malyi Kuyalnyky – Baranovo    | According to equation 6: if \( N_i = 0 \), then \( R' = 0 \) |                                 |
| 16  | Velykyi Kuyalnyky – Ruska Slobodka | According to equation 6: if \( N_i = 0 \), then \( R' = 0 \) |                                 |
| 17  | Tyligul – Berezivka           | \( y = 0.0356x - 0.0523 \) | 0.85                            |
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 $k_n$: $0.5 k_n$; $3 k_n$ (threefold excess) $10 k_n$ (tenfold excess) and risk indicators calculated according to (7) (Table 5).

| 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                     |
| $5.65 \leq k_n <11.3$ | $0.19<R'<0.58$   | permissible                                   | Zone insensitive to contamination         |
| $11.3 \leq k_n \leq 3·11.3$ | $0.58<R'<2.10$ | significant                                   | Contamination sensitive zone              |
| $k_n>10·11.3$         | $R'>2.10$        | 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).
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 qualitative 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 amount 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 \(I_{\text{air}}\) 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 \(N_{\text{aer}}\) in water as an indicator of the vulnerability of a territory to pollution by nitrogen compounds [\(\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-\)] [38].

To calculate the risk, it was proposed to use the maximum permissible concentration of individual nitrogen compounds, and the threshold value (sensitivity coefficient \(k_s=11.3 \text{mgN/dm}^3\)) 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 \(k_s\) 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 \(k_s\) 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) \(k_s=\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-\).
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) $k_n=\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$. 

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 $\leq 5$. 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., Kulshreshtha, 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. Запровадження європейських еколого-інженерних стандартів до хурулу тваринництва України (2018). Аналітичний документ. Прахій. Available at: https://issuu.com/ecoact/docs/policy-paper-ukrainian_007

5. Osadcha, N. M., Ukhlan, O. O., Chekhnyi, V. M., Holubtsov, O. H. (2019). Оцінка емісії біогенного елемента та орханічних речовин водойми в основі р. Сіверські Донці вид дифузних злющер. Проблеми гідрохімії, гідрохімії, гідроекології. Київ: Ніка-Тсентр, 199–200.

6. Osadcha, N. M., Osadchyi, V. I., Ukhlan, O. O., Klebanov, D. O., Luzovitska, Yu. A., Biletka, S. V. (2019). Антропогенна навантаження біогенними елементами на повірхневі водойми басейнів низького Дніпра, Дністра та Проти. Гідрохімія, гідрохімія і гідроекологія, 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/573360/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., Thirukumar, V. (2021). Spatial mapping for Groundwater Vulnerability to Pollution Risk Assessment Using DRASTIC Model in Ponnayar River Basin, South India. Journal of Geology, Geography and Geocology, 30 (2), 355–364. doi: https://doi.org/10.15421/112132

10. Triassi, M., Nardone, A., Giovineti, 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. Available at: 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 accidental oil spill in 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 Kuyalynky Liman and Ways of Their Solution. Hydrobiological Journal, 53 (6), 87–95. doi: https://doi.org/10.1615/hydrobj.v53.i6.90

20. Dauš, M. Řeč, Pintiyska, O. S., Ppilshchuk, O. O., Tvardievych, N. Yu. (2014). Оцінка впливу водних малих річок Прип'яті-Західної Прути на рослинний покрив. Вісник Гідрометцентр Чернігів i Азовського моря, 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), 30–53.

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. Методичні рекомендації шкоду отсюди ймовірності різкозавжджих падій внаслідок забруднення водних об'єктів та грунтів урбанізованої чавунності Ніжньодунайського регіону (2016). Одеська: FOP Shylov M.V.

26. Ventcel’, E. S. (1999). Теория вероятностей. Москва: Vyshshaya shkola.
27. Shkolnyi, Ye. P., Loieva, I. D., Honcharova, L. D. (1999). Obrobka ta analiz hidrometeorolohichnoi informatysi. 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/7e01a7e0-9ceb-4f3d-8ee-cael-1335c27/Guidance%20No%203%20-%20%20pressures%20and%20%20Impacts%20-%20IMPRESS%20(WG%202.1).pdf

29. Loboda, N. S., KatynskaІ. 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). Integralni ta kompleksni otsinky stanu navkovlyshnoho pryrodnoho seredovyschha. 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%20%D0%B2%D0%B5%D0%BD%D0%BE%20%D0%B0%D0%B2%D1%82%D0%BE%D1%80%20%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%BD%20%n%20%D0%B5%D0%BD%D0%BE%20%D0%B2%D1%82%D0%BE%20%D0%BF%D0%BE%20%D0%B2%20%D1%96%20%D0%A3%20%D0%BA%D1%97%D0%BD%20%D1%96.pdf

32. Rybalova, O. V., Bielan, S. V. (2013). Ekologichnyi ryzyk pohirshennia zemelnykh resursov 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 ekolohichnych ryzykiv na bazi vykorystannia kompleksnykh pokaznykiv yakosti vody. Zbirnyk naukovykh prats. VII All-Ukrainian Congress of Ecologists with International Participation. Vinnytsya. 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/10.15421/112013

36. Burkynskyi, B. V., Rubel, O. Ye. (2016). Otsinka ryzykiv dlia zdorovja liudyny ta navkolyshnoho seredovyschha vid dzherel zabrudnennia gruntiv ta vod. Zvit “Inventaryzatsiya, otsinka ta zmenshennia vplyvu antropohennykh dzherel zabrudnennia v Nyzhno-dunaiskomu rehioni Ukrainy, Rumunii, republiki Moldova, 2007-2013” (MIS ETC CODE 995). NAN Ukrainy, Instytut problem rynku ta ekoloho-ekonomichnykh doslidzhen. Odessa, 84.

37. Osadchyy, V., Nabynavets, B., Linnik, P., Osadcha, N., Nabynavets, Y. (2016). Processes Determining Surface Water Chemistry. Springer, 265. doi: https://doi.org/10.1007/978-3-319-42159-9

38. Pro zatverdzhennia Metodky vyznauchennia zon, vraazyvkykh do (nakopychennia) nitrativ. Ministerstvo zakhystu dovkillia ta pryrodnykh resursov 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., Ospyov, 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/ugj2020.04.038

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