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Asessment of environmental risks of pollution with chemical substances according to the probability approach

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SUMMARY

Methodical approaches to quantitative assessments of environmental risks of water pollution in rivers based on hydrochemical data using probabilistic methods are considered in the work. Environmental risks were calculated as averages weighted by the probability of exceeding standards (maximum permissible concentrations, MPC) of the content of pollutants in surface waters. A method of building a qualitative and quantitative scale of environmental risks based on the use of statistical relationships between environmental risk indicators and water quality indices with their subsequent semantic matching is proposed. In order to assess the probability of the degree of pollution of the river by one or another type of pollutants, an analysis of the empirical frequency curve is carried out, according to which estimates of the risks of pollution in different gradations are provided. In the work, the quantitative indicator of water pollution by chemical substances was evaluated as one of the variants of the modified water pollution index (WPI), in which, in addition to the mandatory ones, certain groups of pollutants are used. The proposed approach was used to determine the environmental risk of pollution by heavy metals (Siversky Dinets basin) and biogenic substances (North-Western Black Sea region), nitrogen compounds (Dniester, Odesa region).

Introduction

The definition of environmental, climatic, economic and other types of risk most often includes a combination of the probability of the occurrence of the investigated negative phenomenon and potential negative consequences for human health, the environment, cultural heritage and economic activity. Risk management is focused on prevention and protection from a possible negative event. A significant role in the development of a risk management plan is played by establishing the repeatability of the investigated negative phenomenon, which determines the probability (authenticity) of its occurrence (low, medium, high). On the Ukrainian rivers, there are few cross-sections where observations of biological components that reflect the ecological state of the water body are organized. However, observational data on the concentrations of pollutants entering rivers as a result of anthropogenic activities include a sufficient amount of information for analysis. In this regard, the assessment of the ecological state and the occurrence of risks of its deterioration are often provided based on the data of observations of chemical and physico-chemical elements. The practical solution to the task of assessing the risk of contamination of surface waters by chemical substances discharged into watercourses consists in obtaining a statistical law of the distribution of environmental risks and establishing quantitative and semantic relationships with water quality indicators. Scales of qualitative and quantitative assessment of environmental risks built on this basis allow classification of risks in relation to water quality indices, establishing the probability of one or another degree of risk, identifying risk zones and a possible ecological situation and the probability of their occurrence.

Method and Theory

Quantitative assessments of environmental risk were provided on the basis of probability theory, based on the assumption that a series of risk values is considered as a sample from a random variable. The negative consequences of the discharge of pollutants into surface watercourses were estimated as exceeding the maximum permissible concentration (C_{MPCi}) and actual concentrations of pollutants (C_i). The environmental risk of pollution was defined as the probability-weighted average value of (C_i/C_{MPCi}) (*Burkynskyi et al., 2016*):

$$R' = \sum_{i=1}^{n} \frac{C_i}{C_{MPC_i}} \frac{N_i}{N} > 1\,, \tag{1}$$

where R' – is a quantitative risk indicator; C_i – concentration of the *i*-th pollutant; C_{MPCi} –is the maximum permissible concentration for the *i*-th pollutant (this indicator is assigned depending on the type of water user). N_i – the number of samples with a chemical index of C_i/C_{MPCi}, when the maximum permissible concentration (MPC) was exceeded; N – the total number of selected samples.

To determine the risks of pollution by nitrogen compounds, the ratio of the sensitivity coefficient k_H (*Osadcha et al., 2020*) to the threshold value of 11.3 mgN/dm^3 multiplied by the relative frequency of the event was used as a characteristic of the scale of pollution (*Loboda et al., 2021*):

$$R' = \sum_{i=1}^{n} \frac{k_{H}}{11{,}3} \frac{N_i}{N}, \tag{2}$$

where N_i - is the number of cases when k_H>11.3.

The ratio $N_i/N = p_i$ is a characteristic of the empirical probability of the appearance of such a negative consequence of discharges as contamination of surface waters with chemical substances.
In practice, the risk of disrupting the well-being of the aquatic ecosystem can also be estimated by determining the probit function according to the following equation:

$$P_{rob} = -2{,}3 + 2{,}2\, lg \sum \frac{C_i}{C_{EHi}}, \quad (3)$$

where P_{rob} - is the probit indicator, which is a quantile function associated with the standard normal distribution law (*Rybalova et al., 2019*); C_i – concentration of the i-th substance in the reservoir, mg/dm^3; C_{EHi} – ecological standard (MPC) for the i-th substance in the reservoir, mg/dm^3.

The indicator of the probit function P_{rob} is an intermediate value in the calculations. Special tables have been developed to directly determine the environmental risk indicator ER (*Rybalova et al., 2017*). Depending on the value of the established ER indicator, an assessment of the degree of environmental risk is provided, conclusions are provided about the water quality class, qualitative risk assessment and trophicity. In order to avoid the mandatory use in calculations of the normal distribution law, with which the probit method is closely related, it was proposed to investigate the empirical distribution laws of the environmental risk indicator R', calculated according to equation (1).

Examples

The study of statistical laws of the distribution of enironmental risks of pollution by chemical substances was carried out on the basis of the use of hydrochemical observation data on the Dniester River in the area of the Belyaevsky water intake, which provides the city of Odessa with drinking water (*Loboda et al., 2019*), on small and medium-sized rivers of the North-Western Black Sea region where a high level of pollution with nitrogen compounds due to agricultural activity was found (*Loboda et al., 2021*); on the rivers of the Siversky Dinets basin, where water discharges from mining and heavy industry took place for many decades; as well as on the rivers of industrially developed territories (on the example of the city of Kharkiv) (*Loboda et al., 2023*).

Research was based on the search for relationships between risk indicators R' and water quality indices (Figure 1). To determine water quality indicators, a common scheme was chosen, according to which the quality indicator is calculated as the arithmetic mean of a certain number of exceedances of MPC by concentrations of pollutants. For example, the water pollution index (WPI) is determined for 6 specified pollutants. The modified WPI is recommended to be calculated based on the following six indicators: dissolved oxygen (O_2), biological oxygen consumption for 5 days (BOC_5), which are mandatory, and the other four indicators, selected according to the greatest ratio to the MPC from the list of substances that are discharged into the water stream. The number of selected chemical substances can be expanded if necessary.

To assess the effects of a particular type of surface water pollution, it is proposed to use in the calculations groups of pollutants according to their origin or in accordance with their intended purpose, for example, a group of heavy metals or a group of biogenic substances, etc. It was found that the risk indicator R' increases with an increase in the water quality indicator I. The correspondence between the level of water pollution I and the ecological risk R' is established on the basis of the obtained regression equations $R'=f(I)$, after which the classifications of the two considered are semantically and quantitatively matched values (Table 1). The statistical law of the division of environmental risks as a random value is presented in the form of an empirical frequency curve. Reliability P – is the probability of exceeding a given value of a random variable. The empirical frequency curve is used as a basis for assessing the level of pollution of the river with chemical substances.

A comparison of risk indicators R' and ER, determined for the same groups of pollutants, showed the presence of a close relationship between them.

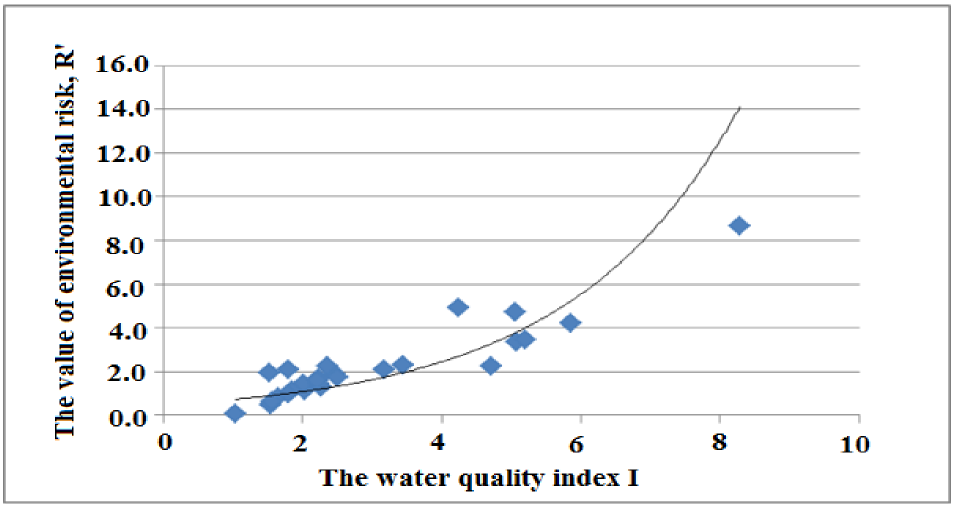

Figure 1 *Dependence of the environmental risk indicator (R') on the modified water quality index (I) for the Lopan River (group of heavy metals)*

Table 1 *Qualitative and quantitative scale of environmental pollution risks for the Lopan River (by biogenic elements)*

Water quality class	*Characteristics of the water quality class*	*Water quality index (WPI)*	*Environmental risk*	*Range of frequency*	*Empirical probability of hitting the range, %*	*Risk zone*	*Ecological situation*
I	*Very clean*	≤ 0,30	≤0,351	≤94	3,85	*No-risk zone*	*Favorable*
II	*Clean*	0,31 – 1,00	0,352-0,472	93,9-89,3	3,85	*No-risk zone*	*Favorable*
III	*Moderately polluted*	1,01 – 2,50	0,473-0,894	89,2-75,0	3,85	*Zone of acceptable risk*	*Satisfactory*
IV	*Contaminated*	2,51 – 4,00	0,895-1,68	74,9-53,9	15,4	*Permissible risk zone*	*Tense*
V	*Dirty*	4,01 – 6,00	1,69-3,94	53,8-21,2	57,7	*Critical risk zone*	*Critical*
VI	*Very dirty*	6,01 – 10,0	3,95-21,5	21,1-0,02	15,4	*Catastrophic risk zone*	*Catastrophic*
VII	*Extremely dirty*	> 10,0	>21,5	0,02	0	*The zone of irreversible loss of object quality*	*Extremely catastrophic*

Results

The qualitative and quantitative scale of environmental risks allows to establish (according to the data of past years) the most probable environmental situations in the main-stream river stations; to predict ecological situations that may arise with different degrees of surface water pollution. In the case when the obtained dependencies and the law of distribution can be generalized within the studied territory (for example, regional dependencies for the risks of pollution by biogenic substances in the territory of the North-Western Black Sea region), regional scales also provide the possibility of forecasts of the ecological state for rivers on which stationary hydrological-hydrochemical studies are not carried out.

Conclusions

The proposed approach to determining surface water pollution risk indicators based on hydrochemical observations showed that the construction of a qualitative and quantitative scale of these risks based on close stochastic relationships with water quality indicators allows for objective analysis and classification of the obtained risk indicators in order to predict possible ecological situations depending on the given level of pollution. The reliability of the obtained results is confirmed by the satisfactory agreement of the risk indicators obtained by different methods.

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