INTRODUCTION

One of the most extensive environmental problems of economically developed countries is the pollution of waterbodies by wastewater (Odnorih et al. 2020, Belokon et al. 2018), diverted from industrial, agricultural and municipal enterprises (EU Water Framework Directive 2000, Zelnovach et al. 2022, Popovych et al. 2020). In a series of post-Soviet countries, in particular, in Ukraine, in order to prevent the level of waterbodies pollution above the safe level, regulations for discharges of pollutants are developed and approved. These regulations represent the mass of a substance permitted to be discharged into waterbodies per unit of time (Water Code of Ukraine 2004, Methodic Recommendations 2021).

Since the volume of wastewater is determined by the technological parameters of the enterprises-water users (Bobylev et al. 2014, Matukhno et al. 2019), the calculation of discharge regulations...
is reduced to the determination of the permissible composition of wastewater. The disadvantage of the existing approach to the solution of this problem is the failure to take into account the probabilistic nature of the content of substances in wastewater after purification at treatment plants. In the methodological literature, the instability of wastewater composition is specified only by the requirement to consider the arithmetic average values as the actual concentrations of substances in wastewater (Methodic Recommendations 2021). However, in general, the calculation has a deterministic character: permissible concentrations of substances in wastewater are calculated, which do not lead to the violation of water quality standards in the control points (CP) of the waterbody. Thus, it is relevant to improve the methodology for calculating the permissible composition of wastewater discharged into waterbody by taking into account the probabilistic nature of waste water composition and, consequently, the probabilistic nature of wastewater pollution in the zone of influence of the discharge. The solution of this problem will make it possible to increase the level of ecological safety of wastewater discharges into waterbody. The most perspective direction in this plan is considered to be the use of the mechanism of ecological risk assessment (Proskurnin 2013, Lisichenko et al. 2011). According to the classical definition, risk is a measure of uncertainty which can be estimated by the probability method (Lisichenko et al. 2011). At the same time, in practice, various criteria for the quantitative assessment of this uncertainty are used. In most cases, environmental risk is understood as either the probability of occurrence of negative changes in the environment, or the mathematical expectation of the amount of the damage as a result of such changes (Rybalova et al. 2018, Rybalova et al. 2022). Since in the tasks of rationing of water disposal, only the possible fact of exceeding the maximum permissible concentration (MPC) in waterbody water is considered without analyzing its consequences for the ecosystem and man, it is advisable to use the first definition of environmental risk – to consider the risk as the probability of violation of the established standards of waterbody quality due to the discharge of wastewater.

The purpose of this article was to develop a mechanism for calculating the permissible concentrations of substances in wastewater using an assessment of the environmental risk caused by wastewater discharge into the waterbody. The paper considers the simplest case: one discharge of waste water into a waterway in the absence of self-purification of water.

**STATEMENT OF THE PROBLEM**

The problem of ecological standardization of wastewater composition considering its probabilistic nature can be formally stated as follows. Let \( C_w \) – the desired permissible concentration of a pollutant in the wastewater after treatment, which eventually must be specified in the documents on special water use. In order to simplify mathematical calculations in this article consider not the concentration itself, but its multiple of exceeding MPC:

\[
X = \frac{C_w}{C_{lim}}
\]

where: \( C_{lim} \) – MPC of a substance.

Let \( x \) to be a random variable representing the multiple of exceeding MPC of a substance in wastewater at an random point in time:

\[
x = X + \varepsilon
\]

where: \( \varepsilon \) – is a random value with zero mathematical expectation.

Then the required value \( X \) in the simplest case is defined as the maximum possible value ensuring, in consideration of (2), observance of the following condition (Proskurnin 2013):

\[
P(\gamma(x) \leq 1) \geq 1 - \alpha
\]

where: \( P \) – designation of probability, \( \gamma(x) \) – multiplicity of MPC exceedance in wastewater watercourse CP below wastewater discharge (according to the Ukrainian legislation, 500 m below the outlet (Methodic Recommendations 2021)), \( \alpha \) – is the accepted maximum permissible risk.

In case of using complex indicators of water quality of waterbody condition (3) is replaced by the following:

\[
P(Y(\{x_j\}) \leq Y_{cr}) \geq 1 - \alpha
\]

where: \( Y \) – a complex index of water quality, defined by a set of values of concentrations of substances \( \{x_j\} \); \( Y_{cr} \) – critical value of complex index of quality.

In the second case, the solution of the problem will be ambiguous. Therefore, the necessary
conditions for determining the allowable concentrations must be supplemented by the requirement of the minimum cost of wastewater treatment, ensuring their acceptable composition.

The problem solution procedure when using a simple indicator of water quality (in the form of concentration of a pollutant)

Random character of $x$-value at a given mode of operation of wastewater treatment plants is a consequence of a large number of random natural and technical factors. This circumstance, according to the central limiting theorem (Jose et al. 2018), allows assuming that the value of $x$ is distributed with high probability under the normal law. The first parameter of distribution – mathematical expectation – is obvious: $X = \langle x \rangle$ (Hereinafter, angle brackets indicate mathematical expectation of a random value). The way to estimate the second parameter of the distribution – the standard deviation $\sigma_x$ – depends on the availability of information about the operation of wastewater treatment plant in different modes. If such information is available, the parameter $\sigma_x$ is taken on the basis of retrospective data processing. In the absence of retrospective information, an assumption about the constancy of the coefficient of variation of $x$-value can be made:

$$v = \frac{\sigma_x}{\langle x \rangle} = \text{const}$$  (5)

In this case, the coefficient of variation can be determined by measuring the output concentrations in any mode of the wastewater treatment plant, and then for an arbitrary value of $X$, the standard deviation will be:

$$\sigma_x = X \cdot v$$  (6)

Thus, the density of the frequency distribution of exceeding of MPC in wastewater is the following:

$$f_x = \frac{1}{\sqrt{2\pi \cdot \sigma_x}} \cdot \exp \left( -\frac{(x - \langle x \rangle)^2}{2\sigma_x^2} \right) = \frac{1}{\sqrt{2\pi \cdot X \cdot v}} \cdot \exp \left( -\frac{(x - \langle x \rangle)^2}{2X^2v^2} \right)$$  (7)

Concentration of a substance in CP (in the form of a multiple of exceeding of MPC) is calculated from the balance equation in the absence of self-purification:

$$y(x) = \frac{C_{\text{fan}}Q_{\text{fan}} + q \cdot x}{Q \cdot C_{\text{lin}}} = \frac{C_{\text{fan}}Q_{\text{fan}}}{Q \cdot C_{\text{lin}}} + \frac{q}{Q \cdot C_{\text{lin}}} \cdot x = A + B \cdot x$$  (8)

where: $C_{\text{fan}}$ – substance concentration in background alignment (BA) above wastewater discharge; $Q_{\text{fan}}$ – flow rate of wastewater in BA; $Q = Q_{\text{fan}} + q$ – water flow rate in CP; $C_{\text{lin}}$ – MPC of the substance; $A = C_{\text{fan}}Q_{\text{fan}}/(QC_{\text{lin}})$; $B = q/(QC_{\text{lin}})$.

Distribution density of $y$-value is determined based on the rule (Jose et al. 2018), according to which if a random variable $\eta$ depends linearly on a random variable $\mu$:

$$\eta = A + B\mu$$  (9)

then the distribution densities of both quantities are related by the following relationship:

$$f_\eta = \frac{1}{B} \cdot f_\mu \left( \frac{\eta - A}{B} \right)$$  (10)

Thus, the density of distribution of substance in CP is as follows:

$$f_y = \frac{1}{\sqrt{2\pi \cdot \sigma_y}} \cdot \exp \left( -\frac{(y - \langle y \rangle)^2}{2\sigma_y^2} \right) = \frac{1}{\sqrt{2\pi \cdot X \cdot v}} \cdot \exp \left( -\frac{(y - \langle y \rangle)^2}{2X^2v^2} \right)$$  (11)

In the traditional form, the distribution density of the quantity $y$ is as follows:

$$f_y = \frac{1}{\sqrt{2\pi \cdot \sigma_y}} \cdot \exp \left( -\frac{(y - \langle y \rangle)^2}{2\sigma_y^2} \right)$$  (12)

where: $\sigma_y = B \cdot X \cdot v$, $\langle y \rangle = A + B \cdot X$.

As according to the laws of probability theory (Jose et al. 2018):

$$P(y \leq 1) = \int_{-\infty}^{1} f_y \, dy$$  (13)

then, taking into account (1), the required concentration $C_w$ is found numerically from equation:

$$\frac{C_{\text{lin}}}{B\sqrt{2\pi \cdot C_w \cdot v}} \cdot \int_{-\infty}^{1} \exp \left( -\frac{(y - A - B \cdot C_w)^2}{2B^2C_w^2v^2} \right) \, dy = 1 - \alpha$$  (14)
This equation can also be written through the Laplace function:
\[
\frac{1}{2} + \Phi \left( \frac{1 - A - B \cdot C_w}{C_{\text{lay}}} \right) = \frac{1}{2} + \Phi \left( \frac{1 - (\bar{y})^2}{\sigma} \right) = 1 - \alpha
\]
(15)
where: \( F \) – is a Laplace function:
\[
\Phi(t) = \frac{1}{\sqrt{2\pi}} \cdot \int_{0}^{t} \exp \left(-\frac{t^2}{2}\right) dt
\]
(16)

**Problem solution procedure when using a complex indicator of water quality**

In ecological wastewater quality standardization, the sum of MPC exceedance multiplicity, which should not exceed 1, is considered as a complex indicator of water quality (Rybalova 2011, Vasenko et al. 2015). At the same time, substances are divided into groups on the basis of limiting signs of harmfulness (LSH): toxicological, sanitary-toxicological, fishery and others (Florica Brasoveanu et al. 2012, Dieter Prinz et al. 2015, Rybalova et al. 2017). Thus, the complex indicator is also a dimensionless value:
\[
Y(\{x_j\}) = \sum_{j=1}^{N_c} y_j \leq 1
\]
(17)
where: \( N_c \) – the amount of substances contained in wastewater under consideration and having the L-th LSH.

In order to simplify the presentation, only one LPV is considered further in the article, and the index \( L \) is omitted.

According to the laws of probability theory (Jose et al. 2018), the sum of random variables that have a normal distribution is also subordinated to the normal distribution law. In this case, mathematical expectations and dispersions of random variables are added. Therefore, the distribution of the complex index will be as follows:
\[
f_Y(\{x_j\}) = \frac{1}{\sqrt{2\pi \cdot \sigma^2}} \cdot \exp \left(-\frac{(Y - \bar{Y})^2}{2 \cdot \sigma^2}\right)
\]
(18)
where: \( \sigma^2 = \sum_{j=1}^{N_c} \sigma^2_j \), \( \bar{Y} = \sum_{j=1}^{N_c} \bar{y}_j \)
(19)

The final composition of wastewater is proposed to be determined by solving the optimization problem (Bajčetić Marko et al. 2016). The set of optimized variables will be the required permissible concentrations \( \{C_{W,j}\} \).

The following expression can be used as a target function:
\[
Z = \sum_{j=1}^{N_c} d_j \cdot (F_j - C_{W,j}) \rightarrow \min
\]
(20)
where: \( F_j \) – the actual concentration of pollutant \( j \) according to the data of field measurements, mg/dm³; \( d_j \) – the cost of purification of a unit volume of wastewater from substance \( j \), $/(m³·mg/dm³).

Limitations of the optimizing problem are dictated by the requirement not to exceed the value of acceptable environmental risk, the principle of non-deterioration of the existing water quality of waterbody, as well as the technical capabilities of the water treatment facilities:
\[
\left\{ \begin{array}{l}
\frac{1}{2} + \Phi \left( 1 - \frac{\left(\frac{C_{W,j}}{\sigma_j}\right)}{\sigma_j} \right) \leq 1 - \alpha, \ j = 1 + N; \\
C_{W,j} \geq P_{W,j}; \\
C_{W,j} \leq F_j;
\end{array} \right\
\]
(21)
where: \( P_{W,j} \) is the minimum concentration determined by the technological capabilities of the wastewater treatment plant.

**Calculation example of permissible concentrations of substances**

The demonstration example presented in the article is based on the developed and approved standards for wastewater discharge from the drinking water treatment system of Kharkov (Ukraine). The discharge is carried out into the Siverskyi Donets River (the right tributary of the Don River; according to the classification of the Water Code of Ukraine [Report on the research 2016], this waterbody refers to the large rivers) through the small Teteleha River. In the example, the substances with toxicological sign of harmfulness are considered: nitrites, ammonium nitrogen, phosphates, iron.

The low-water flow of the Teteleha River is practically equal to zero. This allows the calculation of permissible concentrations to consider the discharge of wastewater directly into the Siverskyi Donets River, where BA and CP are installed (Report on the research 2016), (Fig. 1).
Normative discharge of wastewater and low-water discharge of river water in the BA of the river Siverskyi Donets are equal to 0.12 m³/s and 3.74 m³/s, respectively. Table 1 shows the data on the background pollution of the river. Seversky Donets is higher than the discharge of wastewater, as well as the values of the MPC of substances. Table 1 shows the data on the background pollution of the Siverskyi Donets River above the wastewater outlet, as well as the values of MPC substances.

Table 2 shows the data of 2019 on the content of the mentioned substances in wastewater (as a multiple of exceeding MPC) after their treatment at water treatment facilities, as well as technical and economic parameters of the treatment (Zaitseva et al. 2021).

On the basis of the data in Table 2, the optimizing problem was solved using the “Solution Search” function in the Excel software system. Moreover, for comparison, on the basis of the same initial data, the problem of finding permissible concentrations without taking into account environmental risk (i.e., without taking into account the probabilistic nature of the composition of wastewater) was solved. In this case, the first condition in the restriction system (4) is replaced by the condition (Proskurnin 2010):

$$Y(\{C_{W,j}\}) = 1$$

The result of the solution is given in Table 3. As we can see, taking into account the environmental risk leads to lower permissible concentrations of substances in the wastewater. Figure 2 shows graphs of the density distribution of the complex index $Y$ at the found permissible average concentrations of substances in the wastewater.

As it can be seen from the graph, the calculation of the permissible composition of the wastewater, including environmental risk, ensures compliance with the required quality of river water according to the composite indicator, i.e. condition $Y \leq 1$, with a probability of 95%. When calculating without taking into account the allowable risk, the probability of meeting this condition is only 50%.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Nitrates</th>
<th>Ammonium nitrogen</th>
<th>Phosphates</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration, mg/dm³</td>
<td>0.033</td>
<td>0.2</td>
<td>1.05</td>
<td>0.078</td>
</tr>
<tr>
<td>MPC, mg/dm³</td>
<td>3.3</td>
<td>2</td>
<td>3.5</td>
<td>0.3</td>
</tr>
<tr>
<td>The frequency of exceeding the MPC</td>
<td>0.01</td>
<td>0.1</td>
<td>0.3</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Table 2. Composition of wastewater (as a multiple of exceeding MPC) over 2019, discharged into the Siverskyi Donets River, as well as technical and economic parameters of treatment

<table>
<thead>
<tr>
<th>Month of the year</th>
<th>Nitrites</th>
<th>Ammonium nitrogen</th>
<th>Phosphates</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.833</td>
<td>1.143</td>
<td>3.591</td>
<td>2.677</td>
</tr>
<tr>
<td>2</td>
<td>3.833</td>
<td>2.851</td>
<td>4.224</td>
<td>2.736</td>
</tr>
<tr>
<td>3</td>
<td>3.982</td>
<td>3.769</td>
<td>3.424</td>
<td>5.324</td>
</tr>
<tr>
<td>4</td>
<td>3.833</td>
<td>2.013</td>
<td>1.714</td>
<td>3.672</td>
</tr>
<tr>
<td>5</td>
<td>4.017</td>
<td>2.301</td>
<td>1.948</td>
<td>3.646</td>
</tr>
<tr>
<td>6</td>
<td>3.833</td>
<td>1.935</td>
<td>1.730</td>
<td>2.381</td>
</tr>
<tr>
<td>7</td>
<td>3.833</td>
<td>2.322</td>
<td>2.384</td>
<td>3.237</td>
</tr>
<tr>
<td>8</td>
<td>9.108</td>
<td>2.511</td>
<td>2.954</td>
<td>3.866</td>
</tr>
<tr>
<td>9</td>
<td>3.833</td>
<td>2.408</td>
<td>4.039</td>
<td>4.703</td>
</tr>
<tr>
<td>10</td>
<td>3.833</td>
<td>2.357</td>
<td>3.175</td>
<td>2.529</td>
</tr>
<tr>
<td>11</td>
<td>3.833</td>
<td>2.308</td>
<td>2.350</td>
<td>2.552</td>
</tr>
<tr>
<td>12</td>
<td>3.833</td>
<td>4.081</td>
<td>2.067</td>
<td>3.477</td>
</tr>
<tr>
<td>Average, &lt;F&gt;</td>
<td>4.302</td>
<td>2.502</td>
<td>2.802</td>
<td>3.402</td>
</tr>
<tr>
<td>Standard deviation, s</td>
<td>1.515</td>
<td>0.784</td>
<td>0.889</td>
<td>0.916</td>
</tr>
<tr>
<td>Coefficient of variation, s</td>
<td>0.352</td>
<td>0.313</td>
<td>0.317</td>
<td>0.269</td>
</tr>
<tr>
<td>Minimum possible concentration after treatment, P, mg/dm³</td>
<td>0.03</td>
<td>0.5</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Notional cost of treatment, d, $/(m³·mg/dm³)</td>
<td>1</td>
<td>2.5</td>
<td>1.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 3. Permissible concentrations of substances in the wastewater

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Considering environmental risk</th>
<th>Excluding environmental risk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrites</td>
<td>Ammonium nitrogen</td>
</tr>
<tr>
<td>Permissible concentration, mg/dm³</td>
<td>0.030</td>
<td>3.498</td>
</tr>
<tr>
<td>Permissible frequency of exceeding MPC</td>
<td>0.009</td>
<td>1.749</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The mechanism proposed in the article for calculating the permissible concentrations of pollutants in wastewater ensures that the permissible value of the ecological risk caused by wastewater infiltrating into the waterbody, with a certain probability, which increases the level of environmental safety of the wastewater discharge. Thus it is necessary to notice that at consideration of probabilistic character of concentration of the substance in wastewater at discharge from water treatment facilities, the following legislative problem arises (Yurchenko et al. 2013).

The permissible concentration of a substance indicated in the documents for special water use has two functions:
1) it determines the amount of tax for discharge of wastewater;
2) it is included when controlling compliance with the approved norms of wastewater discharge.

It seems reasonable to leave only the first function according to the concentration calculated by the proposed methods, and to make the conclusion about compliance with the established water disposal regime taking into account possible fluctuations in concentration.

The direction for further research in this area is to consider the stochastic dependence of concentrations of substances at the discharge from the water treatment system, as well as to solve a similar problem for the river basin area.

REFERENCES


