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Adapting the Methods for Assessing a Water Quality when Normalizing the Pollutant Discharges in Ukraine to the Regulatory Requirements of the European Union

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ABSTRACT

The article presents general positions and features of a water quality assessment according to the norms of the European Union (EU), shows their difference from the national (Ukrainian) standards. It is proposed to improve the Ukrainian standards for assessing a water quality in accordance with the EU standards. On the example of the Danube and the Dniester rivers, a chronological variability of the water quality indicators is considered, the time trends of the indicators are approximated and the parameters of their distribution laws are determined. The following dependences are established: when approximating the distribution of the indicators it is better to use the lognormal law; an indicators time trend is reflected more accurately by the exponential dependence; a lognormal distribution of a trend-normalized indicator can be formally considered as one-parameter (one of the parameters – an average value of the logarithms of the normalized series – is zero). It is shown that for the previous period of time and in the future when normalizing the discharges of pollutants together with wastewater, a water quality assessment in the control points of the water bodies will meet the requirements of the EU standards on a frequency of exceeding the maximum permissible concentrations with the security which is equal to 5 or 10% depending on the purpose of the water body (5% – for fishery facilities, 10% – for drinking and recreational water use facilities).

Keywords: water quality, EU standards, variability of indicators, distribution law, normalizing the discharges.

INTRODUCTION

Assessing a river water quality and normalizing the discharges of pollutants together with wastewater into the surface water bodies is an urgent environmental problem (Odnorih et al., 2020). If a river water quality assessment is performed independently, calculating the maximum permissible discharges (*MPD*) of the pollutants (Instruction, 1994) involves assessing a water quality in the control point of the water body taking into account its background condition, i.e. outside the wastewater discharge impact zone.

The basis for assessing a water quality in accordance with the EU standards is Council Directive 75/440/EEC (June 1975) and Council Directive 76/160 / EEC (December 1975), which take into account an analysis of an exceeding frequency of the water quality standards: a water object meets the sanitary requirements if the number of standard exceedances for each indicator is not more than 10% of this indicator total values obtained in some previous period and used in assessing a water quality (according to the fisheries standards – 5%).

This condition should also be applied to a water quality in the control points when calculating the *MPD* of the pollutants. However, assessing a background value according to the existing methods (Instruction, 1994; GD 52.24.622–2001, 2001) does not allow to determine whether the EU requirement on an exceeding frequency of the standards will be met when calculating the *MPD* of pollutants. This is due to the fact that the upper (or lower, if the limit is limited below) limit of the 95% confidence interval of the number of hydrochemical parameters average values for the most unfavorable hydrological or hydrochemical conditions is taken as a background value of the indicator in a certain point of the water body (Instruction, 1994). The probabilistic characteristics of unfavorable water quality conditions are unknown. Therefore, a security problem of (an exceeding probability) the upper limit of the 95% confidence interval of the average values of the indicator remains open until the law of its distribution is determined.

The Ukraine's desire to join the EU obliges to bring its legislation (including the environmental legislation) in line with the European legislation.

MATERIALS AND METHODS

The purpose of the study is to develop proposals for adapting and improving the methods for assessing a water quality and normalizing the discharges of pollutants together with wastewater in Ukraine in accordance with the EU countries regulatory requirements.

An assessment of a water quality indicators variability was performed based on the results of monthly observations on the Danube (an observation point in Vilkove) and the Dniester (a point in Bilyaivka). The research is based on the primary statistical processing of the information array, as well as on a linear and nonlinear regression analysis. The published data, as well as the materials of own researches were used when doing the work.

RESULTS AND DISCUSSION

Assessing a water quality for drinking, recreational and fishery purposes is performed by a detailed analysis, which consists in comparing the water quality indicators values with their standards. When implementing this method, the answers to the following questions are very important: 1) what water quality indicators values should be used in the analysis? 2) should we use the average values of the water quality indicators during a certain period (for the worst season) or the results of urgent observations?

According to Council Directives 75/440/EEC and 76/160/EEC, a water quality complies with the sanitary standards if:

1) the indicators do not exceed the mandatory standards (correspond to the safe impact levels in Ukraine) in 95% of samples;
2) the indicators do not exceed the guide standards (meet the maximum permissible concentrations in Ukraine) in 90% of samples;
3) there are no deviations from the established standards by more than 50%, except for pH, dissolved oxygen and microbiological parameters in 5 and 10% of the samples that do not meet the standards;
4) there is no threat to the public health;
5) there are no deviations from the standards in the successively selected samples.

The requirement for the fishery water bodies Council Directive 78/659/EEC is stricter: it is necessary that 95% of samples do not exceed the mandatory and guide standards.

Later, the Water Directives were substantially supplemented and revised (Council Directive 98/83/EC, 1998; Directive 2000/60/EC, 2000; Directive (EU) 2020/2184, 2020), but the basic points of assessing a water quality have not changed.

As you can see, in the EU countries, along with the value of an individual indicator a frequency of exceeding standards (a total length of the time intervals of the contaminated water) for the study period (not more than 5 or 10% of the analyzed period), a ratio of an indicator value to its standard (no more than 1.5 times) and a maximum duration of the one-time water pollution time intervals (with observing four times a month – no more than one week, twice a month – no more than 2 weeks) are also normalized.

An analysis of the normative and methodological documents (State standard, 2007; State sanitary rules, 2010; Gritsenko et al., 2012; Yurasov et al., 2012; State standard, 2016), as well as the works of individual scientists (Fesenko, 2013; Osadchiy & Blazhko, 2017; Chugai & Safranov T., 2020; Lianzburg & Yevtushenko, 2021) showed that the mentioned approach to a water quality assessment in Ukraine is not implemented. That is, neither a frequency of exceeding the standard, nor a frequency of its excess, nor a one-time water pollution duration are not taken into account. Usually, in a detailed and comprehensive water quality assessment, the average values of the indicators for some past time period are compared with the standards. And the data of the urgent supervision are used only at the water quality operative control. In the existing Ukrainian norms, similarly to the European ones, only a tap water quality is assessed according to the microbiological indicators (State sanitary rules, 2010).

When assessing a water quality useing an average value of the indicator (C_{CP}) leads to the fact that when the C_{CP} coincides with the standard (permissible by the Ukrainian standards) the number of standard excesses (Fig. 1) is approximately equal to a half of these observations for the whole period (C_{CP} security is approximately 50%). A water quality assessment will be performed in accordance with the EU standards, if instead of C_{CP} the values of the indicators with the security, which meets the previously mentioned restrictions – 5 or 10% (C_5 or C_{10}), depending on the purpose of the water body are used (Yurasov & Kur'nova, 2017). In this case, if C_5 or C_{10} will not exceed the standard, the number of its excesses will meet the requirements of the European standards. Fig.1 shows the distribution of the Mn^{2+} concentration in the Danube waters (Vilkove). The Mn^{2+} sanitary and hygienic maximum permissible concentrations (*MPC*) is equal to 0.10 mg/dm^3. An average value of the Mn^{2+} concentration (a dotted line) is 0.049 mg/dm^3, which corresponds to the Ukrainian standards and means that the assimilation capacity of the Danube for Mn^{2+} is exhausted by half. The Mn^{2+}concentration with a 10% security (C_{10}) is equal to 0.10 mg/dm^3 and coincides with the *MPC*, the EU standards are met at the limit. According to them, the assimilation capacity for Mn^{2+} is completely exhausted.

It is possible to find the required values of the water quality indicators (C_5 or C_{10}) when establishing the laws of these indicators distribution.

To assess a water quality for the previous period, the parameters of the lognormal law of a quality indicators distribution and their values with a security of 5 and 10% (C_5 and C_{10}) were found. Some results of the calculations performed by the authors earlier are given in Table 1–2.

Searching the parameters of the laws of a water quality indicators distribution is performed in the following sequence:

1. for each indicator an average long-term value of a number of observations (C_{LTi}) was found;
2. the series normalized by the long-term averages (C_{ij}/C_{LTi}); the normalized series are logarithmic ($ln(C_{ij}/C_{LTi})$);
3. the parameters of the distribution laws were found (average values of the logarithmic series ($\check{C}_{HCi} = [ln(C_{ij}/C_{LTi}]_{CP}$) and their standard deviations ($\check{G}_{HCi} = \sigma[ln(C_{ij}/C_{LTi})]$)).

Calculating the value of the C_{Fi} indicator with F (0.05 or 0.10) security was performed by the formula:

$$C_{Fi} = \\ = C_{LTi} \cdot \text{LOGNORM.INV}(1 - F; \check{C}_{HCi}; \check{G}_{HCi}), \quad (1)$$

where: C_{LTi} is an *i* indicator average long-term value (Tables 1, 2); LOGNORM.INV () – an operator in the Excel spreadsheet editor (LOGNORM.INV Function, 2022); $\check{C}_{NCi}$ and $\check{G}_{HCi}$ are the parameters of an *i* indicator lognormal distribution (Tables 1, 2).

The indicator "dissolved O_2" is limited at the bottom (i.e. its value should not be less than the standard), so when calculating C_{Fi} by formula (1) instead of (1 – *F*) *F* was used. The *pH* indicator has a limited top and bottom range, so for it two values: for (1 – *F*) and *F* were found by formula (1).

Formula (1), as well as the data in Table 1–2 can be used to assess a water quality for the

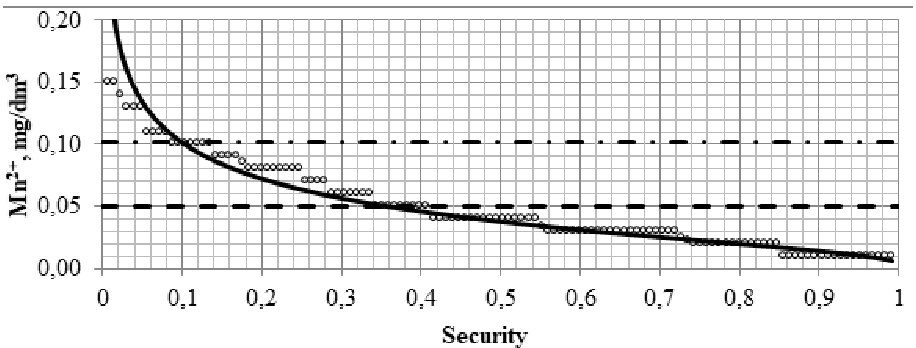

Fig. 1. A distribution of the Mn^{2+} concentration values in the Danube water – Vilkove: a marker circle is the observations results; a horizontal dotted line – an average value; a horizontal dotted line with points – 10% security value; a solid line – an approximation by the lognormal law

Table 1. Parameters of a long-term lognormal distribution of the normalized (according to C_{LT}) values of the Danube water quality indicators (Vilkove) and these indicators values with security of 5 and 10% (C_5 and C_{10})

No.	Indicator	C_{LTi}	$\check{C}_{HCi}$	$\check{G}_{HCi}$	C_{5i}	C_{10i}
1	HCO_3^-	178.8	–0.007268	0.1215	217	207
2	Na^++K^+	20.24	–0.03929	0.2856	31.1	28.1
3	Ca^{2+}	52.33	–0.009119	0.1369	64.9	61.8
4	Mg^{2+}	13.77	–0.01326	0.1617	17.7	16.7
5	SO_4^{2-}	36.92	–0.01223	0.1568	47.2	44.6
6	*pH*	8.043	–0.0001907	0.0196	7.79/8.30	7.84/8.25
7	*Si*	3.453	–0.04919	0.3268	5.63	5.00
8	NO_3^-	5.809	–0.05530	0.3405	9.62	8.50
9	NO_2^-	0.07086	–0.1734	0.6087	0.162	0.130
10	O_2 dissolved	9.300	–0.02015	0.2021	6.54	7.04
11	*Fe*	0.06537	–0.2933	0.7634	0.171	0.130
12	Mn^{2+}	0.04948	–0.2669	0.7697	0.134	0.102

previous period of time. The prediction according to these tables can be performed only for those water quality indicators that do not have a time trend.

When normalizing discharges of pollutants together with wastewater into any water body, there is a need to assess a background water quality of the study object. A hydrochemical background is estimated from the results of the observations outside the area of a wastewater discharge impact for the worst hydrological or hydrochemical conditions. The disadvantage of this approach is following:

1. a chronological variability of water quality indicators may have a positive or negative trend, and in this case, when assuming a constant background water quality in the future, the *MPD* of some pollutants may be overstated if these pollutants have a positive long-term trend (calculating their *MPD* will be performed with some reserve in case if these pollutants have a negative long-term trend);
2. it is impossible to determine whether the requirements of the EU standards will be met in calculating the pollutants *MPD*, as the availability of the water quality indicators background values found for the worst hydrological or hydrochemical conditions is unknown.

It is possible to eliminate these shortcomings when predicting the values of the water quality indicators with a given security (according to the EU standards of 5 or 10%), taking into account a water quality indicators long-term variability.

An analysis of the observations results showed that a long-term variability of most water quality indicators has a negative trend. And only for some indicators the trend is positive.

It can be assumed that a steady long-term trend of changing the water quality indicators values is a consequence of changing the conditions of forming a water quality in the water body

Table 2. Parameters of a long-term lognormal distribution of normalized (in shares of C_{LT}) values of the Dniester River water quality indicators (Bilyaivka) and these indicators values with security of 5 and 10% (C_5 and C_{10})

No.	Indicator	C_{LTi}	$\check{C}_{HCi}$	$\check{G}_{HCi}$	C_{5i}	C_{10i}
1	HCO_3^-	199.7	-0.007270	0.1204	242	231
2	Na^++K^+	28.17	-0.07504	0.4180	52.0	44.7
3	Ca^{2+}	56.65	-0.02150	0.2193	79.5	73.4
4	Mg^{2+}	21.15	-0.05222	0.3467	35.5	31.3
5	SO_4^{2-}	70.12	-0.02607	0.2260	99.1	91.3
6	*pH*	8.058	-0.0001543	0.01764	7.83/8.29	7.88/8.24
7	*Cu*	0.2605	-0.1527	0.6130	0.613	0.491
8	NO_3^-	7.272	-0.04162	0.3023	11.5	10.3
9	NO_2^-	0.05288	-0.2361	0.7261	0.137	0.106
10	O_2 dissolved	9.245	-0.03062	0.2504	5.94	6.50
11	*Fe*	0.4286	-0.1299	0.5343	0.901	0.743
12	Mn^{2+}	0.04279	-0.2533	0.6855	0.0877	0.0729

and its catchment area under the influence of the anthropogenic factors. A negative trend can be explained by the effective implementation of the environmental measures or the reductions of an economic activity in the basin of the water body.

A trend of the Danube and Dniester rivers water quality indicators (Fig. 2) was approximated by the exponential dependence:

$$C_{Tj} = a_0\, exp(b \cdot j), \quad (2)$$

where: C_{Tj} is a value of the trend function at time j;
a_0 is a value of a trend function at the initial time ($j = 0$);
b – a parameter of an exponential dependence; j – an ordinal time number (an ordinal month number).

When determining the parameters of the distribution laws, the trend was eliminated (Fig. 3) by dividing the value of (Cj) indicator at time j by the trend function value (C_{Tj}) at the same time:

$$C_{HTj} = C_j / C_{Tj} \quad (3)$$

where: C_{HTj} – values of the water quality indicators normalized along a trend line.

Table 3–4 shows the parameters of trend lines and the parameters of the distribution laws of the water quality indicators, where a_{0i} and a_{ki} are the values of a trend function at the beginning and the end of the observation period; b_i – a trend function parameter; $\check{C}_{HTi}$ and $\check{G}_{HTi}$ are parameters of the distribution laws of the quality indicators, normalized along a trend line.

For the Danube, a pronounced positive trend ($b_i > 5 \cdot 10^{-4}$) was observed for 7 indicators: $Na^+ + K^+$; Cl^-; NO_2^-; Fe; Mn^{2+}; Cr^{3+}; $\sum Cr$. An expressed negative trend ($b_i < -5 \cdot 10^{-4}$) – for 12 indicators: SO_4^{2-}; NH_4^+; $БСК_{20}$; NO_3^-; a permanganate oxidation; PO_4^{3-}; $\sum P$; a chemical oxygen demand; synthetic surfactants; Cu; petroleum products; Zn. A weak expressed trend ($-5 \cdot 10^{-4} < b_i < 5 \cdot 10^{-4}$) was observed for the rest indicators.

In the Dniester River, a significant negative trend was observed for most indicators. Only the Cu content has a pronounced positive trend. For 10 indicators the trend is weak: pH; Ca^{2+}; HCO_3^-; Al; an alkalinity; a mineralization; Fe; F^-; dissolved O_2; a biochemical oxygen consumption (full).

The parameters of the distribution laws ($\check{C}_{HT}$ i $\check{G}_{HT}$) of all quality indicators are determined for the normalized series along a trend line (Tables 3–4). In this case, the average value of the $\check{C}_{HT}$ logarithmic series becomes very small (for the waters of the Danube $|\check{C}_{HT}| < 2 \cdot 10^{-6}$, for the waters of the Dniester $|\check{C}_{HT}| < 2 \cdot 10^{-4}$), and when calculating the water quality indicators values with some security $\check{C}_{HT}$ can be assumed to be zero.

Table 5 shows the results of calculating C_5 and C_{l0} water quality indicators in the Danube with $\check{C}_{HT}$ obtained from the empirical data, and

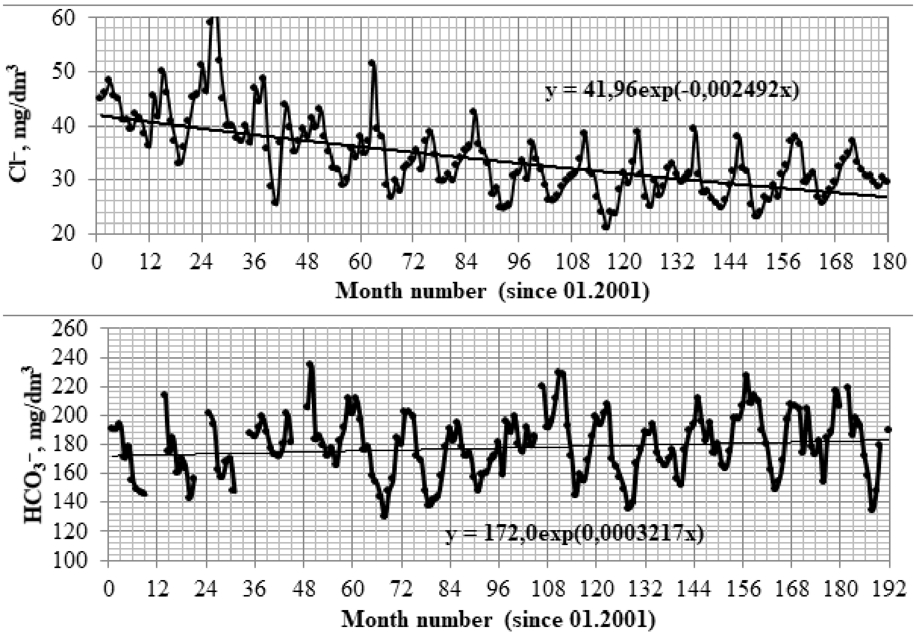

Fig. 2. A chronological variability of the Cl^- concentrations (the Dniester, Bilyaivka) and HCO_3^- concentrations (the Danube, Vilkove) according to the results of the observations.

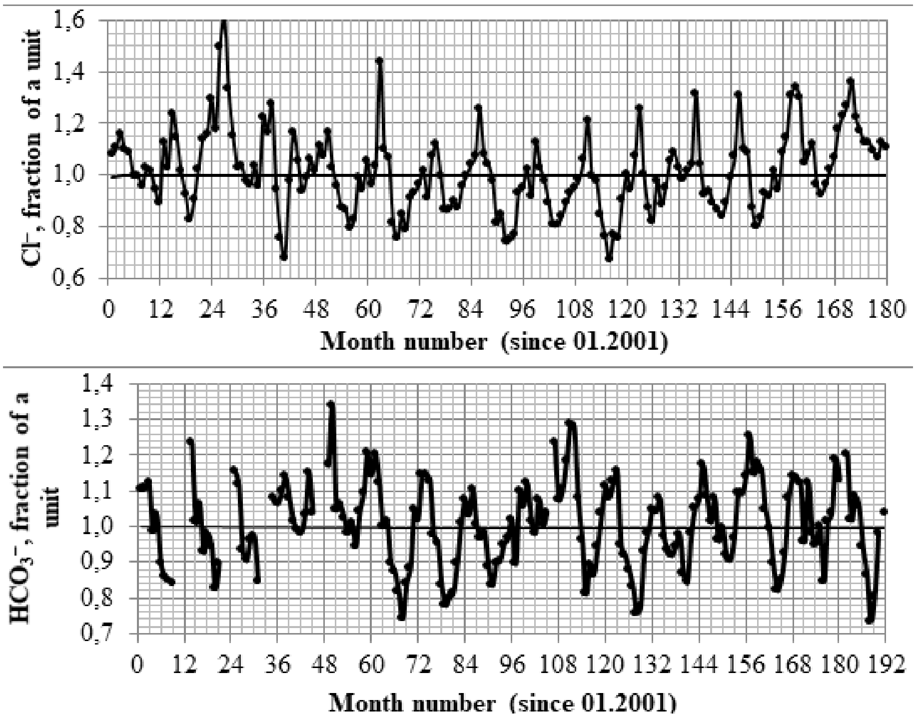

Fig. 3. A chronological variability of the Cl^- concentration (the Dniester River, Bilyaivka) and HCO_3^- concentration (the Danube River, Vilkove) with an eliminated trend

$\check{C}_{HT} = 0$. The table shows that the calculation results for all the indicators coincide to four significant figures. Similar results were obtained for the Dniester River.

The prediction of the value of the i water quality indicator with F security at time j (C_{Fij}) is performed by the formula:

$$C_{Fij} = a_{Ki} \cdot exp(j \cdot b_i) \cdot \text{LOGNORM.INV}(1–F; \check{C}_{HTi}; \check{G}_{HTi}) \tag{4}$$

where: a_{ki} is a value of a trend function of i indicator at the end of the observation period;
j – time (a serial number of the month), calculated from the end of the observation period;
b_i – a parameter of an i indicator trend line (Tables 3–4).

The parameter a_{ki} can be taken as equal to an average value of i indicator for the last 2–3 years of the observation period, if the number of

Table 3. Parameters of a long-term lognormal distribution of the normalized (according to a trend line) water quality indicators of the Danube – Vilkove (a fragment from (Yurasov & Kuryanova, 2021))

No.	Indicator	C_{HTCi}	Trend line			Distribution law parameters	
			a_{0i}	a_{Ki}	bi	$\check{C}_{HTi}$	$\check{G}_{HTi}$
1	HCO_3^-	1.007	172.0	182.9	3.217E-04	-2.111E-07	0.1197
2	Na^++K^+	1.027	17.71	21.19	9.325E-04	3.820E-07	0.2811
3	Ca^{2+}	1.009	51.17	52.60	1.436E-04	-3.673E-07	0.1363
4	Mg^{2+}	1.013	13.07	14.05	3.760E-04	1.027E-07	0.1607
5	SO_4^{2-}	1.012	38.97	34.47	-6.392E-04	-4.466E-07	0.1527
6	*pH*	1.000	8.029	8.054	1.647E-05	2.952E-07	0.01962
7	*Si*	1.051	3.347	3.247	-1.576E-04	-1.117E-07	0.3280
8	NO_3^-	1.056	6.405	4.922	-1.371E-03	2.533E-07	0.3364
9	NO_2^-	1.188	0.03945	0.08536	4.020E-03	3.357E-07	0.5723
10	O_2 dissolved	1.020	9.165	9.043	-6.980E-05	-4.604E-07	0.2018
11	*Fe*	1.342	0.04578	0.05198	6.608E-04	3.036E-07	0.7626
12	Mn^{2+}	1.290	0.02988	0.04430	2.052E-03	-4.032E-07	0.7616

Table 4. Parameters of a long-term lognormal distribution of the normalized (according to a trend line) Dniester River water quality indicators – Bilyaivka (a fragment from (Yurasov & Kuryanova, 2021))

No.	Indicator	C_{HTCi}	Trend line			Distribution law parameters	
			a_{0i}	a_{Ki}	bi	$\check{C}_{HTi}$	$\check{G}_{HTi}$
1	HCO_3^-	1.007	197.6	199.0	3.923E-05	-3.979E-09	0.1204
2	Na^++K^+	1.069	34.70	18.97	-3.356E-03	6.607E-05	0.3848
3	Ca^{2+}	1.022	56.86	54.07	-2.799E-04	1.705E-07	0.2188
4	Mg^{2+}	1.053	21.20	19.01	-6.064E-04	2.058E-07	0.3453
5	SO_4^{2-}	1.022	79.90	58.51	-1.731E-03	6.290E-05	0.2072
6	pH	1.000	8.121	7.992	-8.876E-05	-1.158E-07	0.0170
7	Cu	1.173	0.2120	0.2357	5.896E-04	1.038E-07	0.6123
8	NO_2^-	1.248	0.04874	0.03648	-1.609E-03	3.202E-05	0.7121
9	NO_3^-	1.031	9.140	5.339	-2.987E-03	4.930E-05	0.2592
10	O_2 dissolved	1.031	9.368	8.585	-4.852E-04	2.419E-07	0.2491
11	Fe	1.134	0.3784	0.3776	-1.157E-05	2.924E-07	0.5278
12	Mn^{2+}	1.120	0.06485	0.02807	-4.652E-03	-6.967E-05	0.4795

observations during this time was sufficient. The values of C_5 and C_{10} are calculated by formula (4) with $j = 24$.

At the required (predicting) time, a value of a trend line is determined and a value of the indicator with a given security is calculated relative to the obtained point (Fig. 4).

Earlier it was said that normalizing the series along a trend line allows the lognormal law $\check{C}_{HT}$ parameter to equate to zero, i.e. formally to make the law to be one-parameter. In this case, there is theoretically a connection between an average value of the normalized series (C_{HTC}) s and a parameter of its lognormal distribution $\check{G}_{HT}$.

$$\check{G}_{HT} = [2 \cdot ln\,(C_{HTC})]^{0,5}. \tag{5}$$

When normalizing the series by the average long-term value C_{LT} between the parameters of its lognormal distribution $\check{C}_{HC}$ and $\check{G}_{HC}$, there is also a connection:

$$\check{C}_{HC} = -0,5\check{G}_{HC}^{\,2}. \tag{6}$$

Formulas (5) and (6) are derived from the following considerations. If a random value has a lognormal distribution, then the mathematical expectation of this random value (a sample average value C_{CP}) is related to the parameters of a lognormal distribution $м$ and a known dependence σ (Leemis, 2020; Lognormal Distribution, 2022):

$$C_{CP} = exp\,(м + 0,5\sigma^2) \tag{7}$$

Table 5. Values of the water quality indicators with 5 and 10% security with different values of $\check{C}_{HT}$ parameter (the Danube – Vilkove) (a fragment from (Yurasov & Kuryanova, 2021))

No.	Indicator	$\check{C}_{HTi}$ empirical		$\check{C}_{HTi}$=0	
		C_{5i}	C_{10i}	C_{5i}	C_{10i}
1	HCO_3^-	224.5	214.9	224.5	214.9
2	K^++Na^+	34.41	31.06	34.41	31.06
3	Ca^{2+}	66.05	62.85	66.05	62.85
4	Mg^{2+}	18.47	17.42	18.47	17.42
5	SO_4^{2-}	43.63	41.28	43.63	41.28
6	pH	7.802/8.322	7.857/8.263	7.802/8.322	7.857/8.263
7	Si	5.548	4.925	5.548	4.925
8	NO_3^-	8.283	7.330	8.283	7.330
9	NO_2^-	0.2410	0.1957	0.2410	0.1957
10	O_2 dissolved	6.478	6.970	6.478	6.970
11	Fe	0.1851	0.1403	0.1851	0.1403
12	Mn^{2+}	0.1629	0.1235	0.1629	0.1235

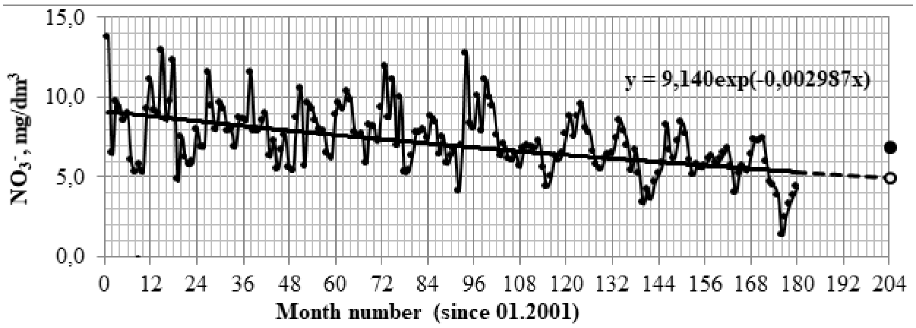

Fig. 4. A scheme of predicting a value of the indicator with some security

When normalizing a random value along a trend line, a parameter of its lognormal distribution $м = \check{C}_{HT}$ (an average value of the normalized series logarithms) is equal to 0:

$$C_{HTC} = exp\,(0 + 0{,}5\check{G}_{HT}^{\,2}) \tag{8}$$

Having obtained the logarithms of the right and left parts of formula (8) and having converted the obtained expression with respect to $\check{G}_{HT}$, we obtain formula (5). If you normalize the sample by C_{LT}, its average value will be equal to 1. Then formula (7) for the normalized sample with previously accepted symbols (formula (1)) will take the form:

$$1 = exp(\check{C}_{HC} + 0{,}5\check{G}_{HC}^{\,2}). \tag{9}$$

From formula (9) it is easy to obtain formula (6), and formula (5) is easy obtained from formula (8). Formulas (5) and (6) are confirmed by the empirical data (Figs. 5–6). Figure 5 is based on the logarithms of the empirical values of C_{HTC} and $\check{G}_{HT}$ parameters (Tables 3–4), a solid line shows an aligned dependence (5):

$$ln\,(\check{G}_{HT}) = 0{,}5ln(C_{HTC}) + 0{,}3466 \tag{10}$$

Figure 6 shows the logarithms of the empirical values of C_{HTC} and $\check{G}_{HT}$ parameters (Tables 1–2), as well as an aligned dependence (6):

$$ln\,(-\check{C}_{HC})=2ln(\check{G}_{HC}) - 0{,}6931. \tag{11}$$

Calculation the *i* conservative substance *MPD* without the total action effect is performed according to the formulas (Instruction, 1994):

$$MPD_i = q_{WW}\, C_{MPDi} \tag{12}$$

$$C_{MPDi} = min(C_{MPi};\, C_{FACTi}), \tag{13}$$

$$C_{MPCi} = n(C_{MPDi} - C_{BGi}) + C_{BGi}, \tag{14}$$

where: q_{WW} – a maximum hourly wastewater flow, m^3/h;
C_{MPDi} – a maximum allowable pollutant concentration for discharges, g/m^3;
C_{MPi} – a maximum substance estimated concentration in the wastewater for discharges, g/m^3;
C_{FACTi} – a substance concentration in the actual wastewater discharge, g/m^3; *n* is a multiplicity of a wastewater dilution in the control point;

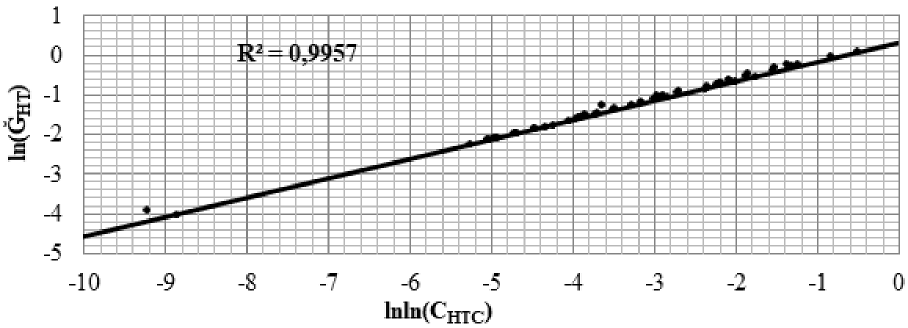

Fig. 5. A dependence between C_{HTC} and $\check{G}_{HT}$ parameters (a marker circle – empirical data; a solid line – a dependence (10))

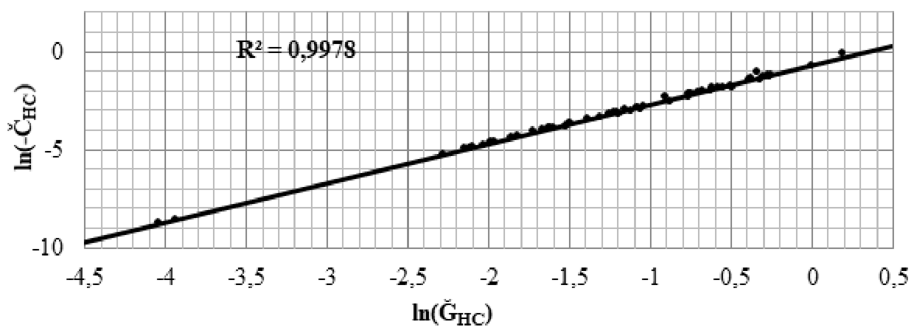

Fig. 6. A dependence between $Č_{HC}$ i $Ğ_{HC}$ parameters (a marker circle – empirical data; a solid line – a dependence (11))

C_{MPCi} – a substance content standard (*MPC*) in a water body, g/m³; C_{BGi} is a pollutant background content in a water body, g/m³.

The paper (Yurasov & Kuryanova, 2015) outlines shortcomings of the existing methods for estimating the *MPD* for pollutants with a summation effect and offers other formulas with verifying the final results for calculating:

$$\Psi_{MP} = n\,(\Psi_N - \Psi_{BG}) + \Psi_{BG}, \quad (15)$$

where: Ψ_{MP} is a limit value of Ψ indicator for m_{WW} substances in the wastewater;
Ψ_N is a normative value of Ψ indicator in the control point ($\Psi_N = 1$);

$$\Psi_{BG} = \sum(C_{BGi}/MPC_i)exp(k_{Hi}t) \quad (16)$$

where: Ψ_{BG} – a background value of Ψ indicator for m_{BG} substances.

Formula (15) allows us to find such Ψ_{MP} value for the substances with a summation effect in the wastewater, which in the control point will meet the condition: $\Psi_{EXT} = \Psi_N$ for any set of substances and any ratio of their concentration in the wastewater and in the flow: $C_{WWi} \geq C_{BGi} \geq 0$ i $C_{BGi} \geq C_{WWi} \geq 0$.

Limit values for the substance concentrations in the wastewater are calculated by the following formula:

$$C_{MPi} = k_{WWi}\,\Psi_{MP}\,MPC_i\,exp(-k_{Hi}\,t) \quad (17)$$

where: k_{WWi} – proportionality coefficients of the substances concentration in the fractions from *MPC* in the wastewater ($k_{WWi} = C_i / (MPC_i\,\Psi_{WW})$);
k_{Hi} is a coefficient of an *i* substance non-conservativeness (for a conservative substance it is equal to 0).

Coefficients k_{WWi} are selected based on the condition:

$$0 < k_{WWi} < 1 \text{ i } \sum k_{WWi} = 1. \quad (18)$$

A verification of the calculations is performed according to the formula:

$$C_{EXTi} = \{[C_{WWi} + C_{Ei}\,(n-1)]/n\}\ exp(k_{Hi}t) \quad (19)$$

where: C_{EXTi} is an extreme concentration of the substance in the control point in the calculated flow (if a substance concentration in the wastewater C_{WWi} is greater than a background concentration, then $C_{EXTi} = C_{MAXi}$, on the contrary $C_{EXTi} = C_{MINi}$).

The Danube and Dniester rivers are objects of fishery useing and centralized water supplying, so when regulating the pollutants discharges together with wastewater, it is necessary to use more "strict" standards – the fisheries standards.

CONCLUSIONS

For the previous period of time and in the future when normalizing discharging the pollutants together with the wastewater an assessment of a water quality in the control points of the water bodies will meet the requirements of the EU standards on a frequency of exceeding the MPC, if the calculations use the values of a water quality with 5 or 10% security depending on the purpose of the water body: 5% – for fishery facilities; 10% – for drinking and recreational facilities. Assessing and predicting the water quality indicators values with a given security is better to carry out useing the lognormal law, an approximation of a time trend of the indicators – exponential. Normalizing the time series of the water quality indicators along a trend line approximated by the exponential law eliminates a transformed series trend and changes the law of its distribution to one-parameter lognormal: an average value of the logarithms of the normalized series is zero. When approximating the trend by a linear dependence the corresponding patterns are not observed.

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