

# Journal of Geology, Geography and Geoecology

Journal home page: [geology-dnu-dp.ua](http://geology-dnu-dp.ua)

ISSN 2617-2909 (print)  
ISSN 2617-2119 (online)

Journ. Geol. Geograph.  
Geology,  
29(1), 166–175.  
doi: [10.15421/112015](https://doi.org/10.15421/112015)

V. A. Ovcharuk, M. E. Daus, N. S. Kichuk, M. I. Myroshnychenko, Y. V. Daus

Journ. Geol. Geograph. Geoecology, 29 (1), 166–175.

## The analysis of time series of river water mineralization in the Dnipro basin with the use of theoretical laws of random variables distribution

Valeriia A. Ovcharuk<sup>1</sup>, Mariia E. Daus<sup>2</sup>, Natalia S. Kichuk<sup>1</sup>, Mariia I. Myroshnychenko<sup>1</sup>, Daus Yurii V.<sup>2</sup>

<sup>1</sup> Odessa State Environmental University, Odessa, Ukraine, [valeriya.ovcharuk@gmail.com](mailto:valeriya.ovcharuk@gmail.com)

<sup>2</sup> Odessa National Maritime University, Odessa, Ukraine

Received: 18.09.2019

Received in revised form: 25.09.2019

Accepted: 16.02.2020

**Abstract.** The analysis of current scientific work on the use of statistical methods in hydrochemical research has shown that this approach is sufficiently substantial, both in Ukraine and abroad. The purpose of this work is to determine the main statistical parameters and to research the possibility of applying theoretical laws of distribution to the time series of water

mineralization. This research presents the results of the application of standard statistical methods of hydrometeorological information processing for data on water mineralization at 28 gauges of the Dnipro basin (within Ukraine) for the period from 1990 to 2015. The dynamics of the obtained statistical parameters (long-term annual average, coefficients of variation, asymmetry and autocorrelation) within the Dnipro basin in Ukraine has been analyzed. The average annual values of mineralization vary substantially within the studied part of the Dnipro basin - in the northern part the maximum value of the annual average mineralization is 447 mg/l, as it moves to the south, the mineralization increases and in the sub-basin of the Middle Dnipro it reaches a maximum of 971 mg/l; the highest values are observed in the south (sub-basin of the Lower Dnipro), where they can reach extremely high values for particular small rivers (the Solon River - Novopavlivka village, 3356 mg / l). The long-term variability of mineralization in the rivers of the studied area is insignificant, and the autocorrelation coefficients of the mineralization series are quite high, in most cases they are significant and tend to decrease from the sub-basin of the Prypyat' river in the north to the sub-basin of the Lower Dnipro river in the south. Within the framework of the presented research, the possibility of using theoretical distribution curves known in hydrology to describe the series of river mineralization, using the example of the Dnipro basin, has also been analyzed. Using Pearson's fitting criterion, the Pearson type III distributions and the three-parameter distributions by S.M.Krytsky and M.F.Menkel have been verified on their correspondence with the empirical series of mineralization. As a result, it was found that in 85% of cases the Pearson type III distribution can be used, and the three-parameter by S.M.Krytsky and M.F.Menkel can be used in 60% of cases.

**Keywords:** mineralization, statistical parameters, distribution laws.

## Аналіз часових рядів мінералізації води річок у басейні Дніпра з використанням теоретичних законів розподілу випадкових величин

Овчарук В.А.<sup>1</sup>, Даус М. Є.<sup>2</sup>, Кічук Н.С.<sup>1</sup>, Мирошніченко М.І.<sup>1</sup>, Даус Ю.В.<sup>2</sup>

<sup>1</sup>Одеський державний екологічний університет, Одеса, Україна, [valeriya.ovcharuk@gmail.com](mailto:valeriya.ovcharuk@gmail.com)

<sup>2</sup>Одеський національний морський університет, Одеса, Україна

**Анотація.** Аналіз сучасних наукових робіт щодо використання статистичних методів у гідрохімічних дослідженнях показав, що такий підхід достатньо обґрунтований, як в Україні, так і за кордоном. Мета даної роботи – визначити основні статистичні параметри та дослідити можливість застосування теоретичних законів розподілу до часових рядів мінералізації. В представленому дослідженні наведені результати застосування стандартних статистичних методів обробки гідрометеорологічної інформації для даних спостережень за мінералізацією води на 28 постах басейну Дніпра (у межах України) за період з 1990 по 2015 роки. Проаналізовано динаміку отриманих статистичних параметрів (середніх багаторічних значень, коефіцієнтів варіації, асиметрії та автокореляції) в межах басейну Дніпра на території України. Середні річні значення мінералізації суттєво змінюються в межах досліджуваної частини басейну Дніпра - у північній частині максимальне значення середньобаторічної мінералізації дорівнює 447 мг/л, із просуванням на південь мінералізація збільшується, і вже у суббасейні Середнього Дніпра її максимум досягає 971 мг/л; найбільші значення спостерігаються на півдні (суббасейн Нижнього Дніпра), де можуть досягати екстремально високих значень для окремих малих річок (р. Солоня – с. Новопавлівка, 3356 мг/л). Багаторічна мінливість мінералізації в річках досліджуваної території незначна, а коефіцієнти автокореляції рядів мінералізації доволі високі, у

більшості випадків вони є значущими та мають тенденцію до зменшення від суббасейну Прип'яті на півночі до суббасейну Нижнього Дніпра - на півдні. В рамках представленої дослідження також проаналізовано можливість застосування відомих у гідрології теоретичних кривих розподілу для опису рядів мінералізації річок, на прикладі басейну Дніпра. З використанням критерію згоди Пірсона, перевірено розподіли Пірсона III типу та трипараметричний С.М. Крицького і М.Ф. Менкеля на їх відповідність емпіричним рядам мінералізації. В результаті виявлено, що у 85 % випадків можна використовувати розподіл Пірсона III типу, а трипараметричний С.М. Крицького і М.Ф. Менкеля – у 60 % випадків.

*Ключові слова:* мінералізація, статистичні параметри, закони розподілу

**Introduction.** Hydrochemical indicators of river water and, in particular, mineralization, are formed under the influence of natural and anthropogenic factors, due to the complex processes that occur during the daily, seasonal, annual and secular periods. The influence of each factor on the formation of mineralization cannot be taken into account unambiguously, so this process can be considered stochastic or probabilistic. In this case, taking into consideration that the samples of hydrochemical characteristics are random variables, there is a basis for the use of mathematical statistics in the study of the processes of formation of hydrochemical parameters of rivers.

This approach is used in Ukraine by scientists of the Ukrainian Hydrometeorological Research Institute (Kovalchuk et al., 2008; Osadchiy and Kovalchuk, 2013), in particular, to divide the magnitude of hydrochemical concentrations into natural and anthropogenic components based on theoretical distribution laws. In the foreign literature such an example can be found in the work of Chinese scientists (Yang and Jian-Ying, 2017), who investigated the possibility of using empirical distribution curves to analyze the concentration of chemicals in the water runoff of the river in different phases of water and for values of probability. The use of multidimensional statistical analysis by the scientists of different countries is also noteworthy, for example, for the geochemical assessment of groundwater quality in Côte d'Ivoire (Guler et al., 2002), or the use of the principal component method for the study of the territory salinity in Spain (Morell et al., 1996). Among the recent works the studies by scientists from India on the hydrochemical composition of groundwater in different parts of the country (Reghunath et al., 2002; Umarani et al., 2019) using cluster and factor analysis are also worth noting.

**The purpose of this work** is to determine the main statistical parameters and to research the possibility of applying theoretical laws of distribution to the time series of water mineralization of rivers in the Dnieper basin (within Ukraine).

**Output data.** The research was carried out on the basis of data from the State Surface Water Survey, carried out by the State agencies for water resources management of the Civil Protection Department of the Ministry of

Emergency Situations of Ukraine. For determination of statistical regularities and distribution laws, the data of mineralization observations at 28 gauges of the Dnieper basin (Fig. 1) for the period from 1990 to 2015 has been selected (1990-2015, Shchorichni dani). The boundary of the study area of the Dnieper basin coincides with the state border between Ukraine and Belarus and Ukraine and Russia.

**Research methods.** When performing hydrological calculations, one of the main tasks is to determine the probabilistic properties of a random variable on the basis of distribution laws. Each random distribution law is a mathematical function that fully describes a random variable from a probabilistic point of view. In practice, it is not necessary to consider the law of distribution as a mathematical expression, it is sufficient to indicate individual numerical characteristics that reflect its main features (1997, Rukovodstvo).

Specific statistical methods have been developed to estimate statistical parameters on a sample basis. The method of statistical moments is the most universal, it is not related to any theoretical law of distribution. In hydrological calculations methods of determining statistical parameters based on certain distribution laws are also used. These methods include the highest-likelihood method, the calculation formulas of which are derived from a three-parameter gamma distribution, and a graph-analytic method that uses theoretical distribution laws (most often Pearson III and log-normal).

The number of statistical parameters used in a theoretical distribution law should not be large. The world experience shows that in calculating runoff, the most optimal in terms of practical application are those theoretical laws of distribution, which require two or three statistical parameters for description – such as mathematical expectation, dispersion and the coefficient of variation dependent on it, distribution asymmetry characteristics.

In modern hydrometeorology, as a rule, the three most common methods of determining statistical parameters are used – method of moments, method of greatest plausibility and graph-analytical method. The calculations are performed on the basis of hydrological series (Hopchenko et al., 2014; Shkolnyi et al., 1999),

but in this research it is proposed to use time series of mineralization as the initial data.

**Results and their analysis.** The authors have obtained statistical characteristics for the series of measured mineralization values for the long-term period from 1990 to 2015 with the help of the software “StokStat 1.2 - Statistics for hydrology” ([http://www.geodigital.ru/soft\\_hydr](http://www.geodigital.ru/soft_hydr)), such as: the average value of the series of total mineralization and relative average squared deviation of arithmetical mean value  $\sigma$ ; coefficient of variation  $C_v$ ; the  $C_s$  asymmetry coefficient of  $C_s/C_v$  ratio, as well as the autocorrelation coefficient (Table 1).

The analysis of Table 1 shows that the length of the series of river water mineralization in the subbasin of the Prypyat' varies from 132 (the Ubort' –Perga village) to 185 values (the Styr – Lutsk). Average values of ions over a multi-year period range from 368 mg/l (the Stokhid – urban settlement Liubeshiv) to 442 mg/l (the Styr – Lutsk), accurate to the average value calculating from 1.08% to 1.60%; maximum deviations are noted in the gauge of the Ubort'–Perga village with the value = 339 mg/l at  $\sigma = 3.17\%$ , as well as at the gauge the Uzh – Korosten city, where

= 232 mg/l at  $\sigma = 2.05\%$ . In most gauges, the value of  $C_v$  is 0.14-0.19, and in the gauges of the Uzh – Korosten city and the Ubort'–Perga village it is 0.26 and 0.36 respectively. The  $C_s$  value varies from 0.57 to 1.15, the  $C_s/C_v$  ratio ranges from 4.0 to 4.4.

For the Desna subbasin, the length of the series ranges from 97 (the Seim – Mutin village) to 204 values (the Desna – Chernihiv). Average values of ion sums within for a multi-year period range from 300 mg/l (the Snov – Shchors village) to 447 mg/l (the Seim –Mutin village), with the accuracy of calculating of the average value of  $\sigma$  from 1.06% to 2.11%. The  $C_v$  value makes 0.15-0.23. The value of  $C_s$  varies from 0.37 to 0.30, the ratio varies from 2.4 to 1.6.

The diagrams in the Fig.2 represent a more evident characteristic of the distribution of statistical parameters of mineralization within the basins. Thus, in the Prypyat' basin (Fig. 2a), the average value of mineralization tends to decrease towards the west, where the upper river is, to the southeast, towards the Uzh basin. Naturally, the dynamics of the coefficients of variation have the opposite direction - the highest values are characteristics of the basins of the Ubort' and the Uzh. The number of samples varies slightly by

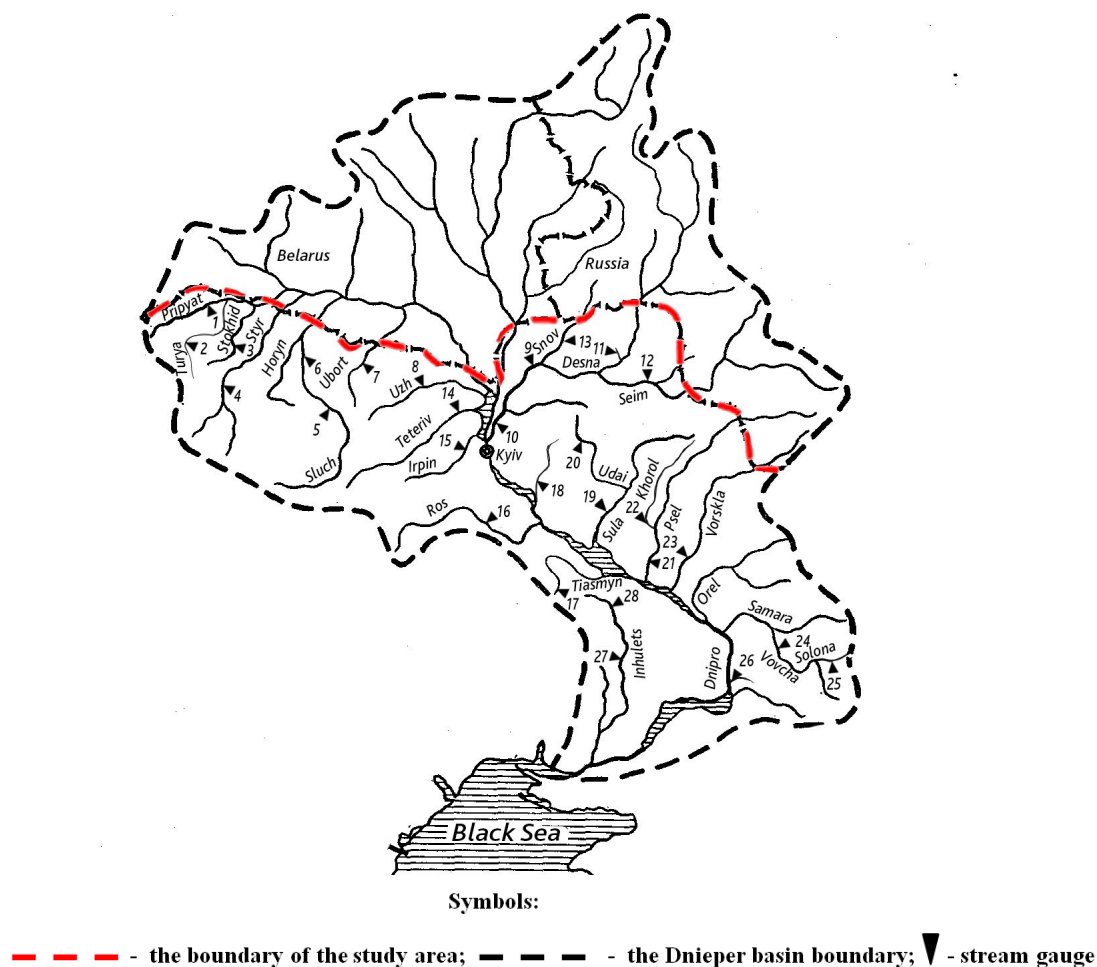


Fig. 1. Map-diagram of the observation gauge locations in the Dnipro basin (within Ukraine), mineralization data of which has been used in the research

**Table 1.** Statistical characteristics of the general mineralization series of water bodies in the Dnipro river basin for the period 1990-2015.

No of gauge on the map	River-gauge	Number of values $n$	Period average value $\bar{C}$ , mg/l	Coefficient of variation $C_v$	Asymmetry coefficient $C_s$	$C_s/C_v$	relative average squared-deviation of arithmetical mean value $\sigma = \frac{100\bar{N}_v}{\sqrt{n}}$	auto-correlation coefficient $r(1)$
Subbasin of the Prypyat' river								
1	The Prypyat'-Ritchysia village	169	405	0.19	0.71	3.7	1.48	0.36
2	The Turya – Kovel city	176	434	0.14	-0.57	-4.0	1.08	0.45
3	The Stokhid – urban settlement Liubeshiv	179	368	0.17	-0.06	-0.4	1.26	0.47
4	The Styr – Lutsk city	185	442	0.16	0.012	0.07	1.19	0.28
5	The Sluch - Novograd-Volynskiy city	140	407	0.15	-0.14	-0.9	1.28	0.51
6	The Sluch - Sarny	141	396	0.19	0.24	1.3	1.60	0.50
7	The Ubort'- Perga village	132	339	0.36	-0.04	-0.1	3.17	0.66
8	The Uzh – Korosten' city	166	232	0.26	1.15	4.4	2.05	0.19
<b>Average</b>		<b>161</b>	<b>378</b>	<b>0.20</b>	<b>0.16</b>	<b>0.51</b>	<b>1.64</b>	<b>0.43</b>
Subbasin of the Desna river								
9	The Desna – Chernigiv city	204	372	0.15	-0.37	-2.4	1.06	0.38
10	The Desna –Litky village	189	374	0.16	-0.23	-1.5	1.15	0.33
11	The Golovesnia – Pokoshechi village	120	398	0.23	-0.05	-0.2	2.11	0.46
12	The Seim –Mutyn village	97	447	0.19	0.00	0	1.93	0.08
13	The Snov –Shchors village	110	300	0.19	0.30	1.6	1.76	0.19
<b>Average</b>		<b>144</b>	<b>378</b>	<b>0.18</b>	<b>-0.07</b>	<b>-0.50</b>	<b>1.60</b>	<b>0.29</b>
Subbasin of the Middle Dnipro								
14	The Teteriv –Ivankiv village	92	373	0.18	1.21	7.1	1.85	0.26
15	The Irpin - Gostomel village (Mostyshche village)	171	476	0.13	-0.03	-0.2	0.99	0.21
16	The Ros' – Korsun'-Shevchenkivskiy city	92	531	0.13	-0.20	-1.5	1.35	0.24
17	The Tiasmyn –Velyka Yabkunivka village	105	699	0.20	0.14	0.7	1.91	0.29
18	The Trubizh – Pereryaslav-Khmelnyskiy city	179	610	0.12	-0.06	-0.5	0.90	0.09
19	The Sula – Lubny	177	807	0.19	0.72	3.8	1.43	0.31
20	The Udai – Pryluky city	87	831	0.18	-0.32	-1.8	1.91	0.01
21	The Psel – village Zapsillia	101	712	0.17	-0.03	-0.2	1.66	0.01
22	The Khorol – Myrgorod city	106	971	0.25	1.06	4.3	2.34	0.46
23	The Vorskla – Kobeliaky city	168	785	0.18	0.34	1.9	1.41	0.08
<b>Average</b>		<b>128</b>	<b>680</b>	<b>0.17</b>	<b>0.28</b>	<b>1.36</b>	<b>1.58</b>	<b>0.20</b>
Subbasin of the Lower Dnipro								
24	The Vovcha – urban settlement Vasylikivka	170	3305.0	0.15	-0.31	-2.04	1.17	0.33
25	The Solona – Novopavlivka village	159	3356.0	0.18	-0.19	-1.06	1.43	0.33
26	The Mokra Moskovka – Zaporizhia city	172	1377.0	0.26	0.79	3.04	1.98	0.28
27	The Ingulets –Sadove village	103	357	0.11	5.00	45.45	1.08	0.06
28	The Ingulets – Kryvyi Rih city	171	1524.8	0.35	0.96	2.74	2.68	0.43
<b>Average</b>		<b>155</b>	<b>1984</b>	<b>0.21</b>	<b>1.25</b>	<b>9.63</b>	<b>1.67</b>	<b>0.29</b>
<b>Average for sub-basins</b>		<b>145</b>	<b>772</b>	<b>0.19</b>	<b>0.36</b>	<b>2.26</b>	<b>1.61</b>	<b>0.29</b>
<b>Average for the Dnieper River</b>		<b>144</b>	<b>479</b>	<b>0.19</b>	<b>0.13</b>	<b>0.46</b>	<b>1.61</b>	<b>0.30</b>

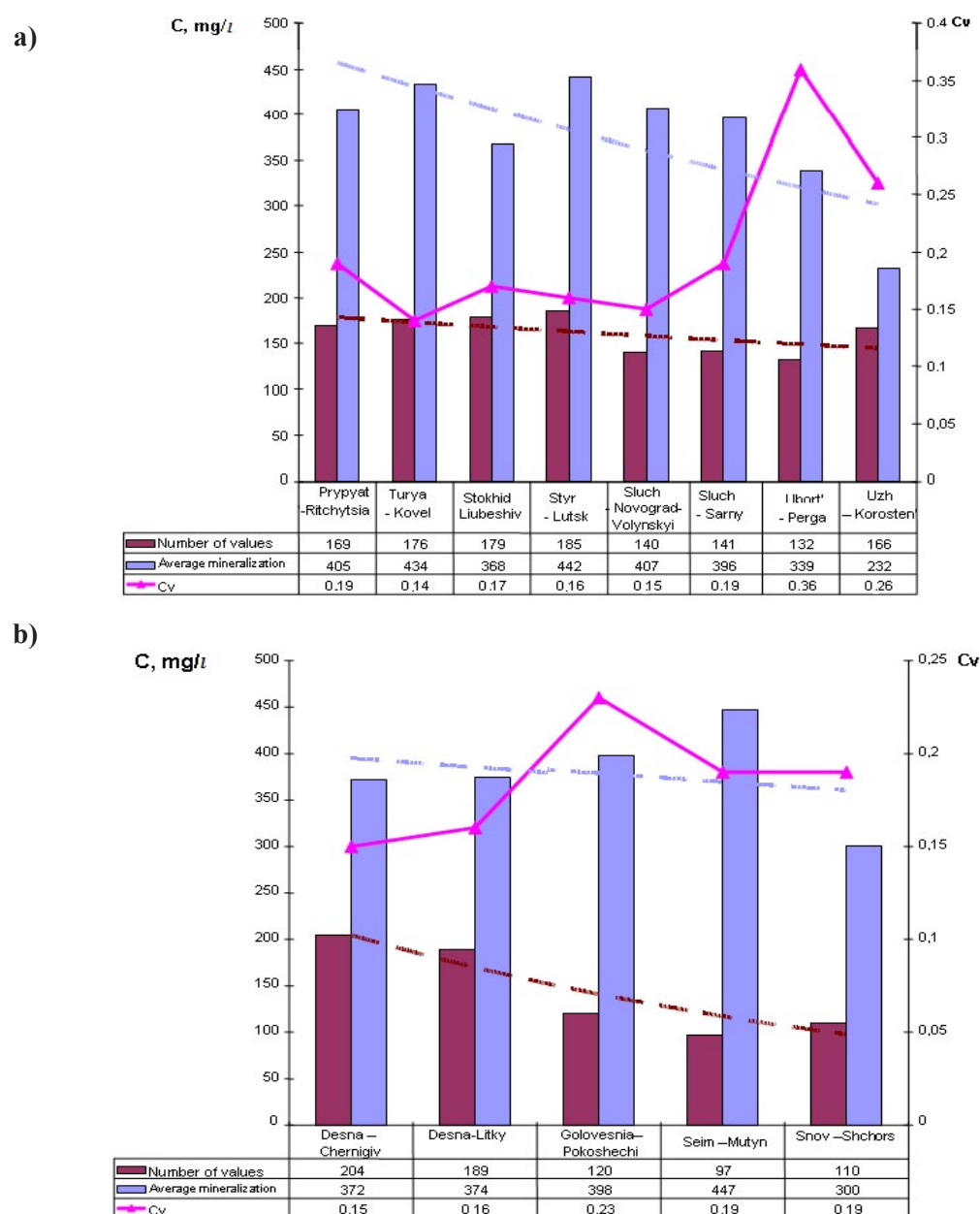


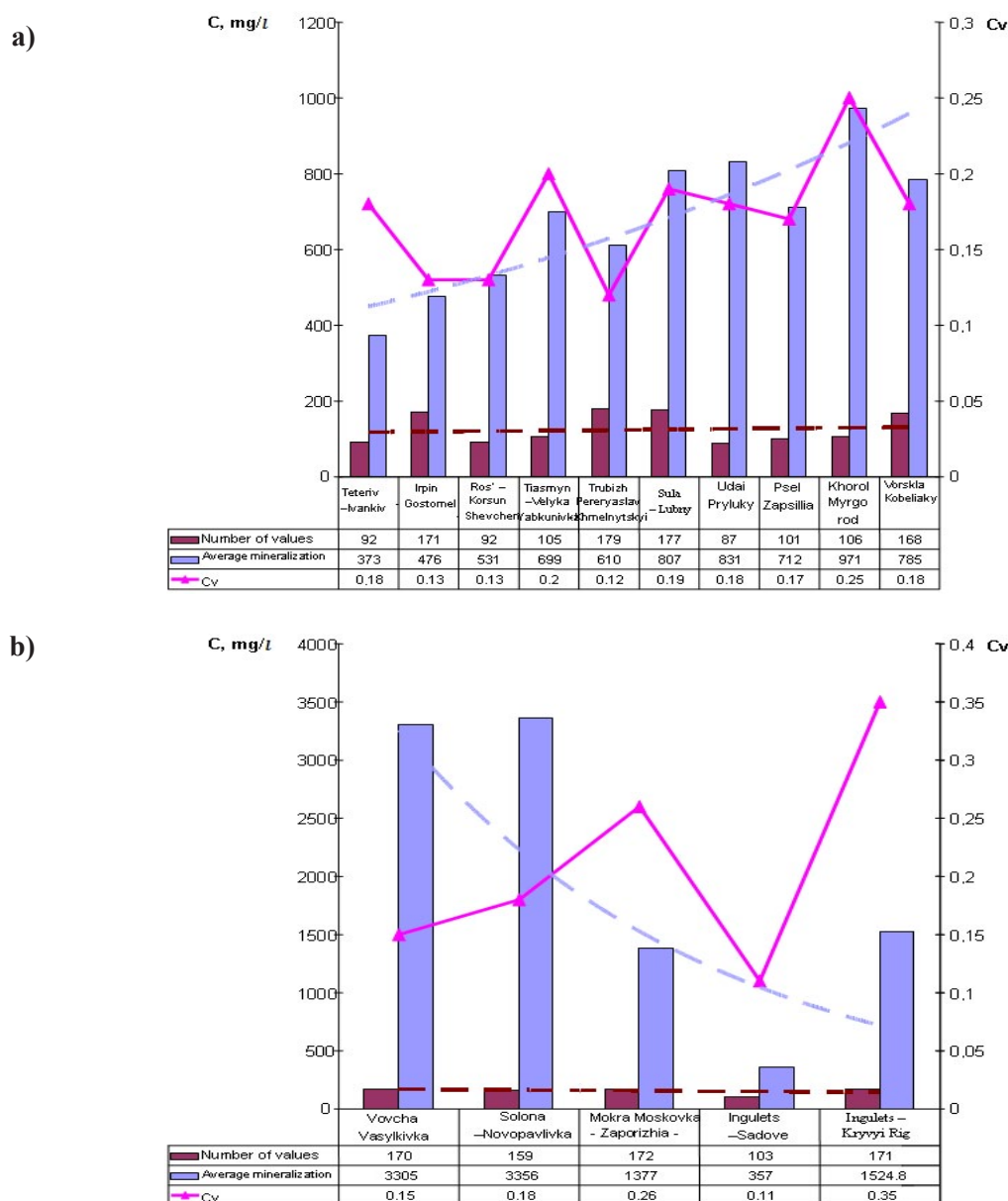
Fig. 2. Diagrams of statistical parameters of water mineralization in the Prypyat' (a) and the Desna (b) river basins.

the pool. In the Desna basin the situation is different - mineralization does not change substantially across the territory, with some deviations in the Seim river basin; the number of samples decreases remarkably from the Desna to the Seim, and the coefficient of variation increases (Fig. 2b).

In the subbasin of the Middle Dnieper the length of mineralization series changes from 87 (the Udai – Pryluky city) to 179 values (the Trubizh - Pereyaslav-Khmelnitskyi). The average values of the total sum of ions for the investigated period increase from the west to the south east from 373 mg/l (the Teteriv – urban settlement Ivankiv) up to 971 mg/l (the Khorol – Myrgorod), with the fluctuation of relative standard deviation  $\sigma$  from 0.9 % to 2.34% (Table 1, Fig. 3a).

At the gauge of the Irpin – urban settlement Hostomel, the Trubizh - Pereyaslav-Khmelnitskyi city and the Ros - Korsun-Shevchenkovskyi city the values  $C_v$  equal 0.12-0.13; at the gauges of the Teteriv – urban settlement Ivankiv, the Sula – Lubny city, the Udai – Pryluky city, the Psel - Zapsillia village and the Vorskla – Kobeliaky city, the values of  $C_v$  fluctuate between 0.17-0.19; the highest values of  $C_v$  are marked along the cross-sections of the Tiasmyn - Velyka Yablunivka village and the Khorol - Myrgorod city and make respectively 0.20 and 0.25 (Fig. 3a), so that there is a slight tendency to increase in the same direction as mineralization values. The values of asymmetry coefficients  $C_s$  vary at the most wide range - from -0.03 (the Irpin – urban settlement Hostomel





**Fig. 3.** Diagrams of statistical parameters of water mineralization in the subbasins of Middle (a) and Lower Dnipro (b).

and the Psel – Zapsillia village) to 1.21 (the Teteriv – urban settlement Ivankiv), and the  $C_s/C_v$  ratio varies accordingly from -0.2 to 7.1.

Considering the subbasin of the Lower Dnipro, it can be noted that the length of the series of mineralization observations here ranges from 159 (the Solona – Novopavlivka village) to 172 values (the Mokra Moskovka – Zaporizhia city), and only at the Ingulets point - Sadove village it makes 103 values. The average values of the sum of ions vary from 3356 mg/l (the Solona – Novopavlivka village) to 357 mg/l (the Ingulets – Sadove village) over the perennial period, with the accuracy of the average value  $\sigma$  1.08% - 2.68% (Table. 1, Fig. 3b), i.e. there was a decrease in mineralization from the northeast to the southwest.

The  $C_v$  values for the series of mineralization of the Lower Dnipro rivers vary from 0.11 - 0.35; the value of  $C_s$  ranges from -0.31 to 0.96, with the exception of the Ingulets – Sadove village, where the asymmetry coefficient is 5.00; the  $C_s/C_v$  ratio varies from -2.04 to 3.04, and for the Ingulets point - Sadove village reaches 45.45. Such a significant difference in all indicators for the Ingulets – Sadove village can be explained by the influence of the Dnipro waters, which flow down the river channel 75 km upstream (Khilchevskyi et al., 2012).

Table 1 also shows the average values of statistical characteristics for sub-basins and their averaged values for all basins. In this case, the average mineralization for a basin is equal to 772 mg/l, but this value will not be correct, because the small and

medium-sized rivers of the sub-basin of the Lower Dnipro have an average mineralization of 1984 mg/l, which is a feature of the small rivers of the Black Sea and Azov Sea region, but it does not correspond to the mineralization of the Dnipro itself in its lower flow. This situation can be explained by a small influence of the inflow of rivers of the Lower Dnipro on the runoff of the Dnipro River. Therefore, the average values of these rivers can be ignored in calculations, and the average mineralization of the Dnipro River can be calculated using its large tributaries in the upper and middle parts of the basin. Thus, the average mineralization for the Dnipro River (within Ukraine) can be accepted at the level of 479 mg/l, the average value of  $C_v$  is 0.19; the  $C_s / C_v$  ratio can be averaged as 0.5 and the autocorrelation coefficient is 0.30. The obtained values correspond well with the data on the mineralization of the main rivers of Ukraine presented in the paper (Khilchevskyi et al., 2018), where, according to the authors' calculations, the average mineralization of the Dnipro River is 488 mg/l, and the mineralization of the Black Sea and Azov region rivers is at the level of 2200 mg/l.

The analysis of the dynamics of variability and the autocorrelation coefficients throughout the Dnipro basin (within Ukraine) are also of interest. As well illustrated in the Fig.4, the variation of mineralization

The second stage of the research was checking of the series of general mineralization for compliance with the Pearson type III distributions and the three-parameter distributions by S.M.Krytsky and M.F.Menkel, the results of which are presented in the Table 2.

The analysis of the Table 2 shows that the series of mineralization during the study period at all the investigated gauge in the subbasin of the Prypyat' River, except for the gauge the Ubort' – Perga village, correspond to the the Pearson type III distributions and the three-parameter distributions by S.M.Krytsky and M.F.Menkel according to the fitting criterion  $\chi^2(\alpha, v)$  at  $\alpha = 0.05$  and  $v = 7$ . The series of mineralization of the Ubort' gauge – Perga village does not comply with any of the studied distribution laws. This can be explained by the fact that this series has the highest temporal variability and the highest autocorrelation coefficient, that is, the internal regulation of the series is not well described by the selected distribution laws.

In the subbasin of the Desna, the mineralization series at all the investigated gauges correspond to the Pearson type III distribution law and the three-parameter distribution by S.M.Krytsky and M.F.Menkel according to the fitting criterion  $\chi^2(\alpha, v)$  at  $\alpha = 0.05$  and  $v = 7$ , apart from the Golovesnia gauges – Pokoshychi village and the Snov – Shchors village, where the values  $\chi^2 > \chi^2(\alpha, v)$ , that is the series

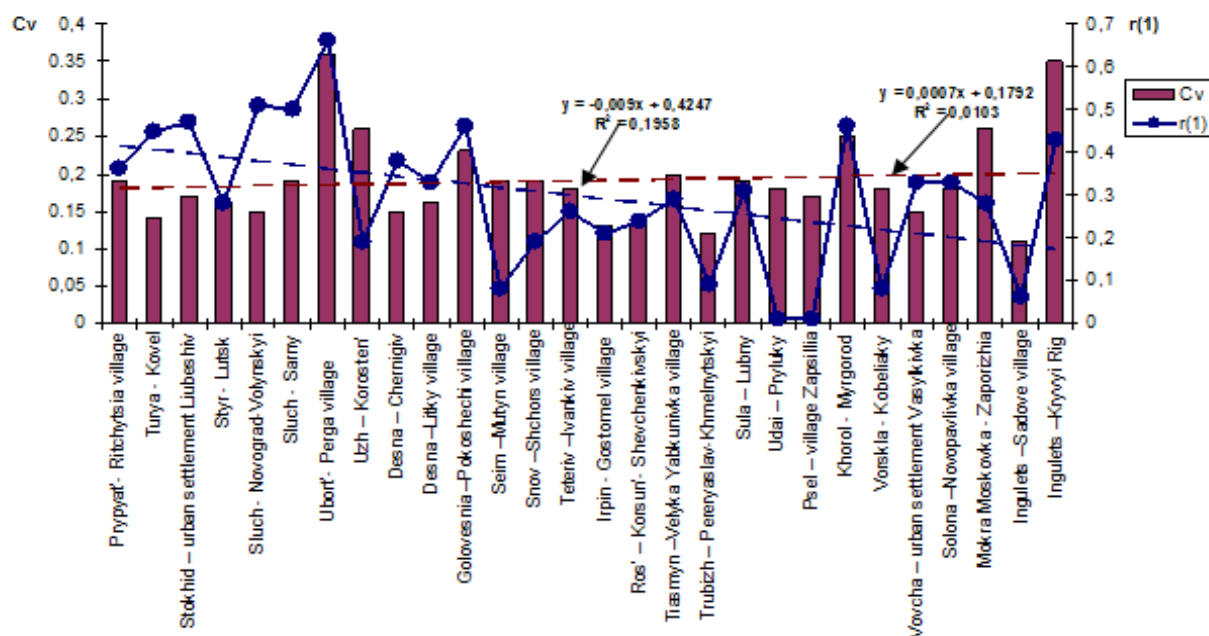


Fig. 4. Dynamics of variability and autocorrelation of river water mineralization series in the Dnipro basin.

within the considered territory is insignificant, the correlation coefficient of the trend line is not significant. On the other hand, the autocorrelation coefficients have a significant tendency to decrease from the subbasin of the Prypyat' to the Lower Dnipro.

of mineralization during the studied period do not correspond to the law of distribution by S.M.Krytsky and M.F.Menkel (Table 2).

In the subbasin of the Middle Dnipro, the series of mineralization during the studied period correspond

**Table 2.** Check of the series of general mineralization of water bodies in the Dnieper river basin for 1990-2015 for compliance with Pearson type III distribution law and three-parameter distributions by S.M.Krytsky and M.F. Menke

№ of gauge on the map	River- stream gauge	$\chi^2(\alpha, \nu)$	Pearson type III distribution		distribution by S.M.Krytsky and M.F.Menkel	
			$\chi^2$	compliance	$\chi^2$	compliance
Subbasin of the Prypyat’ river						
1	The Prypyat’ - Ritchysia village	12.6	12.5	compliant	12.5	compliant
2	The Turya – Kovel city	12.6	7.8	compliant	7.9	compliant
3	The Stokhid – urban settlement Liubeshiv	12.6	9.8	compliant	10.4	compliant
4	The Styr – Lutsk city	12.6	7.5	compliant	10.1	compliant
5	The Sluch - Novograd-Volynskyi city	12.6	12.3	compliant	10.1	compliant
6	The Sluch – Sarny	12.6	8.1	compliant	9.6	compliant
7	The Ubort’ - Perga village	12.6	17.7	not compliant	15.8	not compliant
8	The Uzh – Korosten’ city	12.6	7.1	compliant	11.5	compliant
Subbasin of the Dnieper river						
9	The Desna – Chernigiv city	12.6	7.1	compliant	7.4	compliant
10	The Desna –Litky village	12.6	7.4	compliant	11.1	compliant
11	The Golovesnia –Pokoshechi village	12.6	8.8	compliant	35.2	not compliant
12	The Seim –Mutyn village	12.6	8.7	compliant	12.4	compliant
13	The Snov –Shchors village	12.6	5.3	compliant	13.1	not compliant
Subbasin of the Middle Dnieper						
14	The Teteriv –Ivankiv village	12.6	13.2	not compliant	16.9	not compliant
15	The Irpin - Gostomel village (Mostyshche village)	12.6	5.90	compliant	11.7	compliant
16	The Ros’ – Korsun’-Shevchenkivskyi city	12.6	9.30	compliant	20.2	not compliant
17	The Tiasmyn –Velyka Yabkunivka village	12.6	7.48	compliant	15.5	not compliant
18	The Trubizh – Pereryaslav-Khmelnitskyi city	12.6	10.2	compliant	18.8	not compliant
19	The Sula – Lubny city	12.6	15.5	not compliant	14.4	not compliant
20	The Udai – Pryluky city	12.6	3.92	compliant	6.68	compliant
21	The Psel – village Zapsillia	12.6	2.86	compliant	12.96	not compliant
22	The Khorol – Myrghorod city	12.6	4.0	compliant	4.25	compliant
23	The Vorskla – Kobeliaky city	12.6	12.1	compliant	4.9	not compliant
Subbasin of the Lower Dnipro						
24	The Vovcha – urban settlement Vasylykivka	12.6	9.7	compliant	5.9	compliant
25	The Solona –Novopavlivka village	12.6	3.45	compliant	3.96	compliant
26	The Mokra Moskovka – Zaporizhia city	12.6	7.65	compliant	12.3	compliant
27	The Ingulets –Sadove village	12.6	8.9	compliant	20.7	not compliant
28	The Ingulets – Kryvyi Rih city	12.6	15.37	not compliant	15.49	not compliant

to the Pearson III type distribution law at all gauges except the Teteriv gauges – urban settlements Ivankiv and the Sula – Lubny city, and the three-parameter distribution by S.M.Krytsky and M.F.Menkel in three cross sections (the Irpin – urban settlement Gostomel (Mostyshche village), the Udai - Pryluky city and the Khorol – Myrghorod city) according to the fitting

criterion  $\chi^2(\alpha, \nu)$  at  $\alpha = 0.05$  and  $\nu = 7$  only within the cross section (Table 2).

To sum up: for the cross sections the Irpin – urban settlement Gostomel (Mostyshche village), the Udai - Pryluky city and the Khorol - Myrghorod city the series of mineralization correspond to both distribution laws, for other gauges it is possible to



use Pearson III type distribution law for calculations, which is determined by the condition  $\chi^2 < \chi^2(\alpha, \nu)$ , for the gauge of the Teteriv – urban settlement Ivankiv the series of mineralization do not correspond to any of the studied distribution laws (the Table 2).

In the subbasin of the Lower Dnipro, the series of mineralization at the three investigated gauges correspond to the Pearson type III distribution law and the three-parameter distribution by S.M.Krytsky and M.F.Minkel by the fitting criterion  $\chi^2(\alpha, \nu)$  at  $\alpha = 0.05$  and  $\nu = 7$ . At the gauge of the Ingulets River – Sadove village the series of mineralization correspond only to the Pearson III type distribution law, at the gauge of Ingulets – Kryvyi Rih the series do not correspond to any distribution law, which can be explained by significant anthropogenic loads and peak emissions of the mine waters of the Kryvyi Rih iron ore basin (the Table 2).

### Conclusions.

- As a result of a standard statistical processing (using the methods of moments and maximum likelihood), the statistical characteristics of the series of measured values of mineralization of water bodies of the Dnipro basin for the period from 1990 to 2015 have been determined.

- The average annual values of mineralization vary substantially within the studied part of the Dnipro basin within Ukraine. Thus, in the northern part (subbasins of the Prypyat' and the Desna) the average long-term mineralization fluctuates from 232 mg/l to 447 mg/l, and as it moves to the south, mineralization increases and in the subbasin of the Middle Dnipro it changes in the range from 373 mg/l to 971 mg/l; the highest values are observed in the south, in the subbasin of the Lower Dnipro, where they fluctuate from 357 mg/l (the Ingulets - Sadove village) to extremely high values of 3356 mg/l (the Solona - Novopavlivka village).

- The obtained data are consistent with the data (Khilchevskyi et al., 2018) on the spatial changes of the water mineralization of the rivers of Ukraine, in particular for the Dnipro basin, which indicates the statistical stability of the average long-term mineralization.

- The long-term variability of mineralization in the rivers of the studied territory is insignificant, the values of the coefficients of variation  $C_v$  vary in the Dnipro basin within Ukraine in the range from 0.11 to 0.3 and do not have a signified trend.

- The asymmetry of the mineralization series is sufficiently signified, and the corresponding coefficients vary over a wide range from -0.03 to 5.00.

- The autocorrelation in the mineralization series

is quite high and the coefficients  $r(1)$  are in most cases significant; in general within the basin there is a decrease of the autocorrelation coefficients from the north to the south.

- Within the framework of the presented research, the possibility of using theoretical distribution curves known in hydrology to describe river mineralization has been analyzed. In terms of the Dnieper basin, using the Pearson fitting criterion  $\chi^2$ , the type III Pearson distributions and the three-parameter by S.M. Krytsky and M.F.Menkel have been checked for their correspondence with the empirical series of mineralization. As a result, it was found that in 85% of cases the Pearson type III distribution can be used, whereas the three-parameter by S.M.Krytsky and M.F.Menkel in 60% of cases.

- The obtained results make it possible to use theoretical curves to determine the mineralization values of different probability of exceedance, but for the final conclusions it is necessary to continue the study using more source of initial information.

### References

- Guler, C., Thyne, G.D., McCray, J.E., Turner, A.K., 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeol J.* 10:455–474.
- Hopchenko, Ye.D., Loboda, N.S., Ovcharuk, V.A., 2014. *Hidrolohichni rozrakhunky* [Hydrological calculations]. TES, Odesa. (in Ukrainian).
- Khilchevskyi, V.K., Kravchynskyi, R.L., Chunarov, O.V., 2012. *Hidrokhimichniy rezhym ta yakist vody Inhultsia v umovakh tekhnohenezu* [Hydrochemical regime and water quality of Ingulets in the conditions of technogenesis]. Nika-Tsentr, Kyiv. (in Ukrainian).
- Khilchevskyi, V.K., Kurylo, S.M., Sherstyuk, N.P., 2018. Chemical composition of different types of natural waters in Ukraine. *Journal of Geology, Geography and Geoecology.* 27(1), 68-80. Retrieved from <https://doi.org/10.15421/111832>.
- Kovalchuk, L.A., Osadchaya, N.N., Osadchiy, V.I., 2008. *Naukovi pratsi Ukrainskoho naukovo-doslidnoho hidrometeorologichnoho instytutu: Zb. nauk. pr.: Veroyatnostno - statisticheskoe otsenivanie kachestva poverhnostnykh vod po kategoriyam* [Probabilistic - statistical assessment of surface water quality by categories]. 257, 162-175. (in Russian).
- Yang, L., Jian-Ying Z., 2017. *Journal of Coastal Research.* Application of a Load Duration Curve for Establishing TMDL Programs Upstream of Tiaoxi Within Taihu Watershed in China. June. 80, 80-85. DOI: 10.2112 / SI80-011.1
- Morell, I., Gimenez, E., Esteller, M.V., 1996. Application of principal components analysis to the study of

- salinization on the castellan plain, Spain. *Sci Total Environ.* 177:161–171.
- Osadchiy, V.I., Kovalchuk, L.A., 2013. *Dopovidi Natsionalnoi akademii nauk Ukrainy: Teoreticheskie osnovyi veroyatnostno-statisticheskogo razdeleniya velichiny pokazateley himicheskogo sostava vodnykh ob'ektov na prirodnyu i antropogennuyu sostavlyayuschie* [The theoretical basis of the probabilistic and statistical separation of the values of the chemical composition of water bodies into natural and anthropogenic components], 4, 97–103. (in Russian).
- Reghunath, R.T., Sreedharamurthy, R., Raghavan, B.R., 2002. The utility of multivariate statistical techniques in hydrochemical studies: an example from Karnataka, India. *Water Resour.* 36:2437–2442.
- Rukovodstvo po gidrologicheskoy praktike., 1997. *Sbor i obrabotka dannykh, analiz, prognozirovaniye i drugie primeneniya* / [Guide to hydrological practice. Data collection and processing, analysis, forecasting and other applications / 5th ed.; WMO 1994]. (in Russian).
- Shkolnyi, Ye. P., Loieva, I. D., Honcharova, L. D., 1999. *Obrobka ta analiz hidrometeorologichnoi informatsii* [Processing and analysis of hydrometeorological information]. Minosvity Ukrainy, Kyiv. (in Ukrainian).
- Shchorichni dani pro yakist poverkhnevykh vod sushi. [Annual data on surface water quality of land]. Vyp. 2: Basein Dnipra. Kyiv, 1990-2015.
- Umarani, P., Ramu, A., Kumar, V., 2019. Hydrochemical and statistical evaluation of groundwater quality in coastal aquifers in Tamil Nadu, India. *Environmental Earth Sciences.* 78:452. <https://doi.org/10.1007/s12665-019-8414-x>.