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RESEARCH ON WATER QUALITY IN THE DNIESTER RIVER 2019-2021

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Abstract: The article examines the water quality of the Dniester River for the period 2019-2021. Are analyzed the data concerning the degree of pollution of the Dniester River and its tributaries. Is discussed the negative impact of the detected pollutants on human health. The results of the statistical analysis using R language tools are presented. Is proposed the statistical model for approximation of the analyzed data.

Keywords: *river, water quality, pollutants, statistical analysis, prediction scenarios*

1. INTRODUCTION

Water has been since ancient times the most valuable resource without which there would be no life on earth. To make the most of this resource, certain quality standards must be respected. Water has the greatest impact on people's health of all environmental factors (Mogorean, Bernic and Ciobanu, 2017).

Water quality is a positive feature of it. It includes in itself all the essential elements by which the water in a given place differs from other waters (Zubcov, 212). The quality of life, i.e. human health, depends largely on the quality of water. When water is polluted, the chemical composition is found in most of the products we consume. Poor water quality is a problem, even if it's treated at sewage treatment plants (Railean, 2022).

The Dniester River, the largest and most important water artery, is a source of drinking water for more than 1/3 of the country's population of the Republic of Moldova, 99% of the population of Chisinau and Balti municipalities. (Water Magazine, 2012, Zubcov, 2012). The issue of safe drinking water has become a key issue for national public health security in recent years (Mogorean, Bernic and Ciobanu, 2017).

Various statistical data analysis techniques are successfully applied in order to analyze the water quality, including the determination of various parameters regarding the spatio-temporal evolution of pollutants. (Sentas, et al., 2016; Vassilis Z., et al., 2001; Yong-Hui Yang, et al., 2009).

2. PROBLEM FORMULATION

Moldova's water quality is getting worse. At least that's what the results of laboratory investigations of water quality in surface water sources show. For the Dniester River, the share of samples for sanitary-chemical parameters assigned to class I (very good) quality for 2019 was 7% compared to 23% in 2018. For bacteriological parameters the share of samples assigned to class IV (polluted) quality for the Dniester River increased from 4% - 2018, to 15% - 2019 and for class V (very polluted) from 16% - 2018, to 32% - 2019. The main causes of pollution are: untreated or partially treated wastewater from rural and urban settlements discharged into the tributaries of the Dniester River, untreated rainwater, inadequate sanitation of the territories of local settlements, non-compliance with the sanitary protection areas of water basins, placement of polluting targets in the sanitary protection area of water basins, etc (Railean, 2022).

As a result of anthropogenic activity, industrial development, climate change, increasing water consumption in all areas, surface water is continuously degrading. Class IV and V (polluted and heavily polluted) are assigned to water samples, which integrate the content of the following pollutants - ammonium, nitrites, nitrates, oxygen content, petroleum products and phenols (Şeico, Ilie and Cheptea, 2020).

During the monitoring of the water quality of the Dniester River according to hydrochemical parameters, a number of exceedances were detected, the most frequent were with CCO_{Cr} and total phosphorus, the cause of pollution being the human factor - the irrational use of fertilizers, which are then washed into the river, the dumping of waste and the bad habit of the population to wash their vehicles in the river (Environment Agency, 2022).

Based on the above, the problem of the article was formulated, which consists in researching the water quality of the Dniester River, which will be carried out on the basis of statistical analysis of data on exceptional situations of water pollution for the period 2019-2021.

The Shapiro-Wilk test and the functions hist(), qqnorm(), qqline(), boxplot() from the R language will be used for the statistical data analysis.

The purpose of applying the Shapiro-Wilk test is to check whether the analyzed data are normally distributed.

The statistic test is calculated according to the formula:

$$(1)\ W = \frac{b^2}{SS}$$

where:

- $b = \sum_{i=1}^{m} a_i (x_{n+1-i} - x_i)$;

- $x_1, x_2, \dots, x_n$ - the analyzed sample of values;

- a_i - the values (based on the value of n) from the Shapiro-Wilk tables;

- $SS = \sum_{i=1}^{n} (x_i - \overline{x})^2$;

- $\overline{x}$ - the average value of the sample.

In the R language, the mentioned calculations are performed by the function shapiro.test(x).

3. SOLUTIONS

In order to assess the water quality status of the Dniester River, were analyzed and estimated the data provided by the Environment Agency in their monthly bulletins on the environmental quality on the territory of the Republic of Moldova (Ministry of Environment, 2022) for the period 2019-2021.

The quality of the water in the Dniester River served as the object of study. 14 fixed observation points were analyzed (Naslavcea village, Olăneşti village, Soroca town (downstream), Palanca village, Cosăuți village, Vasilcău village, Vadul lui Vodă town, Sănătăuca village, Otaci town, Cremenciug village). In order to achieve the objectives of the study, were used statistical investigation methods represented by *statistical tests*.

Water quality was investigated for 18 chemical parameters: NO_2, Ammonium nitrogen, Mineral phosphorus, Petroleum products, Dissolved O_2, CCO_{Cr}, Total phosphorus, Magnesium ion, $Na^+ + K^+$, Hardness, Nitrate nitrogen, Nitrite nitrogen, Mineralization, Orthophosphates, Total iron, NH4+, Nitrite nitrogen, Suspended solids.

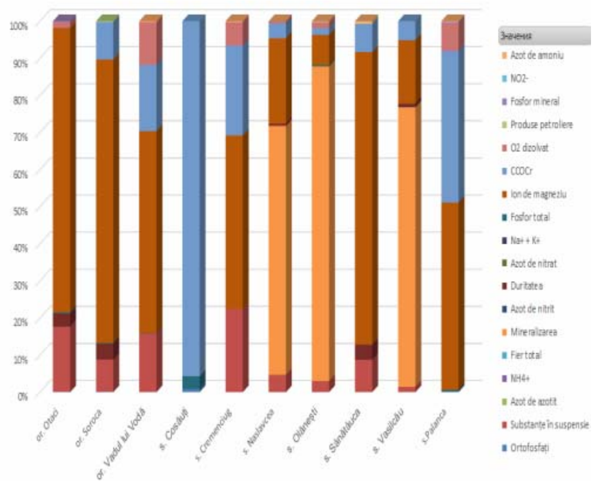

Fig. 1. The share of pollutants in the Dniester River by localities 2019-2021

The analysis resulted in the following diagram (Figure 1), which illustrates the share of pollutants in the Dniester River by localities in the period 2019-2021.

The presence of nitrogen salts in water is largely determined by the process of decomposition of organic substances as a result of the activity of micro-organisms. Another important indicator of water mineralisation is its hardness (Mogorean, Bernic and Ciobanu, 2017).

The presence of ammonia and nitrite in water is an indirect indicator of bacterial wastewater pollution. When humans are exposed to high doses, they can have severe toxic effects. High concentrations of nitrates cause acute health disorders due to the high affinity of these chemicals for hemoglobin in the blood. The interaction of nitrates with hemoglobin leads to the formation of methemoglobin, which loses its ability to transport oxygen to the tissues. Particularly sensitive to the toxic action of nitrates are infants, who are on artificial feed prepared with water containing excess of nitrates (Mogorean, Bernic and Ciobanu, 2017).

The highest degree of pollution of the Dniester River in 2019 was recorded on the following sections (Figure 2):

1. v.Palanca on 19.11.19:
   Ammonium nitrogen *(0,43 mg/l)*, Mineral phosphorus (*0,38 mg/l*) , Total phosphorus (*0,45 mg/l*), Magnesium ion (*92,4 mg/l*)..
2. v.Sănătăuca on 31.10.19:
   Petroleum products (*0,48 mg/l*),
   Magnesium ion (*177,5 mg/l*), Hardness (*9,2 Mmol/l*), Suspended solids (*19,6 mg/l*)
3. t.Soroca (downstream) on 30.10.19: Petroleum products (*0,52 mg/l*), Magnesium ion (*138,6 mg/l*), Hardness (*7,8 Mmol/l*), Suspended matter (*15,8 mg/l*).
4. t.Otaci on 05.11.19:
   Mineral phosphorus (*0,74 mg/l*), Total phosphorus (*0,78 mg/l*),Magnesium ion (*294,3 mg/l*), Hardness (*13,7 Mmol*/l).

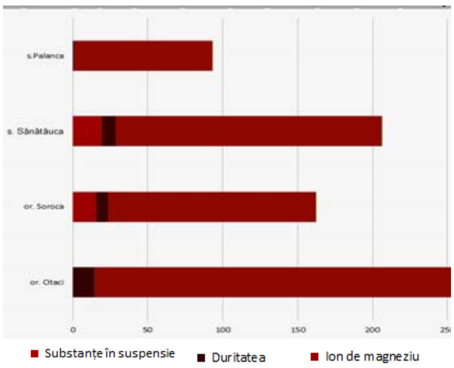

Fig. 2. Localiti es with maximum number of pollutants 2019

In 2020 (Figure 3), the most pollutants were recorded only in one section, in Olănești village on 28.01.20: Ammonium nitrogen (*0,59 mg/l*), Total phosphorus (*0,52 mg/l*), Nitrate nitrogen (*4,08 mg/l*).

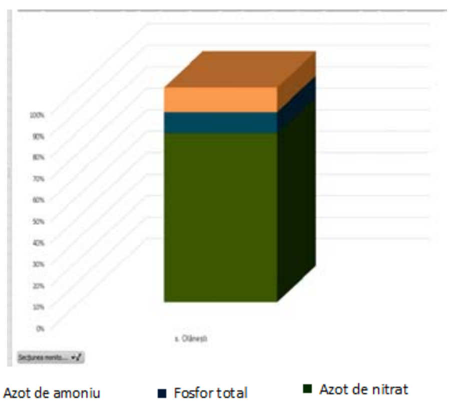

Fig. 3. The locality with the maximum number of pollutants 2020

In the figure 4 it is shown the localities with the highest number of pollutants in 2021:

1. v.Palanca on 17.08.21: Dissolved O_2 (*6,82 mgO_2/l*), Total Phosphorus (*0,40 mg/l*), Orthophosphates (*0,13 mgP/l*)
2. v.Olănești on 22.07.21: CCO_{Cr} (*15,93 mgO_2/l*), Total Phosphorus (*0,21 mg/l*), Mineralization (*998,1 mg/l*), Orthophosphates (*0,19 mgP/l*).

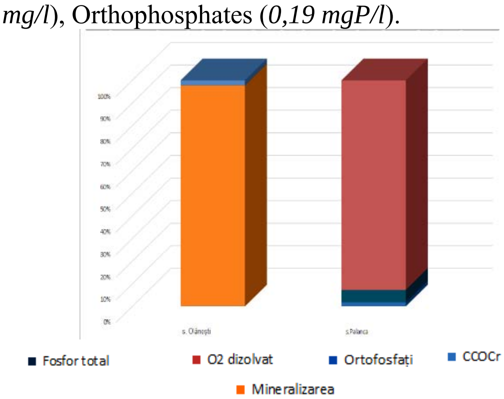

Fig. 4. Localities with maximum number of pollutants 2021

On 05.11.19 in the town Otaci were recorded maximum values of mineral phosphorus (*0,74 mg/l*), total phosphorus (*0,78 mg/l*), magnesium ion (*294,3 mg/l*) and hardness (*13,7 Mmol/l*). And on 22.07.21 in Olanesti village were recorded maximum values for Mineralization (*998,1 mg/l*) and Orthophosphates (*0,19 mgP/l*) (Figure 5).

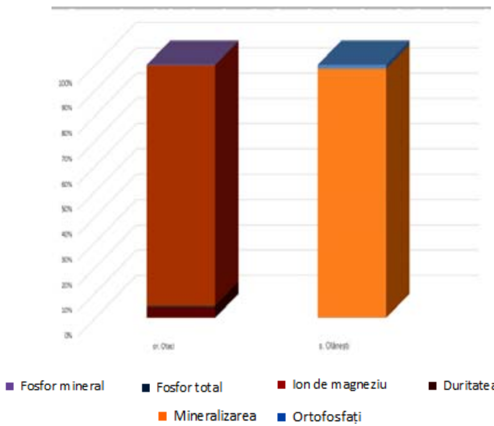

Fig. 5. Localities with maximum values of pollutants 2019-2021

The negative role of the tributaries of the Dniester River is represented in Figure 6, based on the analysis of data provided by the Environment Agency in the monthly bulletins on environmental quality in the Republic of Moldova (Zubcov E., 2012). 4 tributaries of the Dniester River were analyzed: Ichel river - Goian village, Greblești village, Răut river - Ustia village, Orhei town, Balți town, Floresti town, Bîc village - Gura Bîcului village, Chisinau municipality, Strășeni town, Botna district - Chircăiești village, Causeni town. Water quality was investigated for 19 chemical parameters

(Suspended solids, Dissolved O_2, CBO_5, CCO_{Cr}, Ammonium nitrogen, Nitrite nitrogen, Total phosphorus, Mineral phosphorus, Magnesium ion, $Na^+ + K^+$, Hardness, Petroleum products, Chloride ion, Nitrate nitrogen, Sulphate ion, Orthophosphates, Total iron, Nitrite nitrogen, Mineralization).

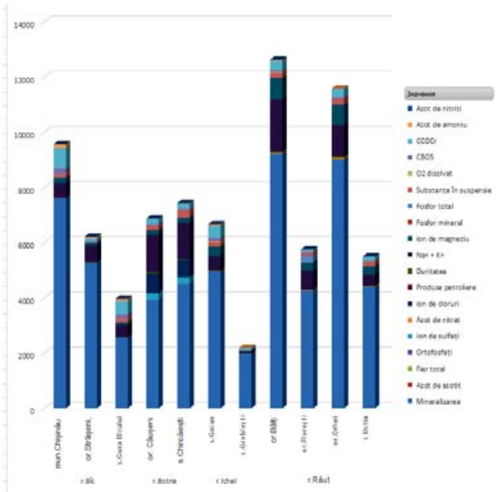

Fig. 6. The share of pollutants in the tributaries of the Dniester River by localities 2019-2021

On 05.08.2019 maximum values of the following pollutants were recorded (Figure 7):

1. r.Ichel, v.Goian: Suspended solids (*117,2 mg/l*), dissolved O_2 (*4,08 mgO₂/l*), CBO_5 (7,20 mgO₂/l), CCO_{Cr} *(20,32 mgO₂/l)*, ammonium nitrate (*8,94 mg/l*), nitrite nitrate (*0,35 mg/l*), Total phosphorus (*1,75 mg/l*), Mineral phosphorus (*1,47 mg/l*), Magnesium ion (*124,03 mg/l*), $Na^+ + K^+$ (*88,5 mg/l*), Hardness (*6,85 Mmol/l*).
2. r.Răut, t.Bălți: Suspended solids (98,4 *mg/l)*, dissolved O_2 (3,28 *mgO₂/l)*, CBO_5 (6,88 *mgO₂/l)*, CCO_{Cr} (20,32 *mgO₂/l)*, Ammonium nitrate (10,1 *mg/l)*, nitrite nitrate (3 *mg/l)*, Total phosphorus (0,31 *mg/l)*, Mineral phosphorus (0,11 *mg/l)*, Magnesium ion (104,58 *mg/l)*, $Na^+ + K^+$ (120 *mg/l)*, Hardness (6,5 *Mmoli/l)*, Petroleum products (0,17 *mg/l)*.

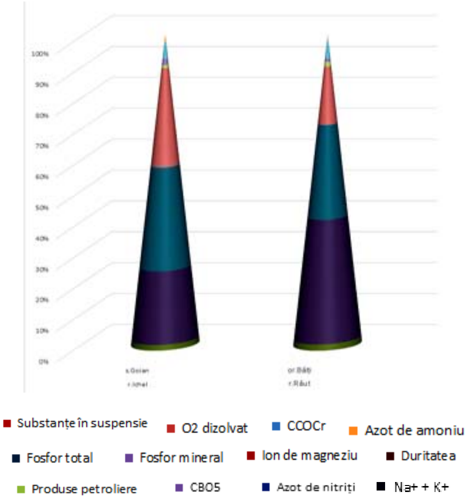

Fig. 7. Tributaries and localities with maximum number of pollutants

On 19.11.2019 in river Botna, town Causeni was detected a maximum volume of pollutants represented in Figure 8:

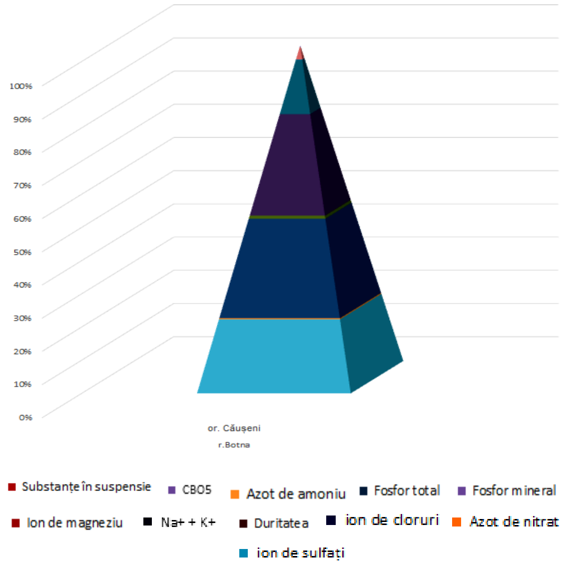

Fig. 8. Tributaries and localities with maximum number of pollutants

Suspended substances (40 *mg/l)*, CBO_5 (5,18 *mgO₂/l)*, Ammonium nitrate (1,2 *mg/l)*, Total phosphorus (0,63 *mg/l)*, Mineral phosphorus (0,39 *mg/l)*, Magnesium ion (178,8 *mg/l)*, $Na^+ + K^+$ (334 *mg/l)*, Hardness (9,75 *Mmoli/l)*, Chloride ion (327,4 *mg/l)*, nitrite nitrate (3,48 *mg/l)*, Sulphate ion (243,2 *mg/l)*.

Based on the analysis and evaluation of the results obtained for the period 2019-2021, the water quality of the Dniester River in all monitored sections corresponds to classes III, IV and V, which would mean moderate and highly polluted (Ministry of Environment, 2022).

The most frequent exceedances of the MAC were recorded for the following pollutants: O2, CCO_{cr}, total phosphorus, magnesium ion. Therefore, the values of the samples taken with exceedances of the MAC of the mentioned pollutants were subjected to statistical analysis.

The data were analyzed by the help of R language, using the tools: the Shapiro-Wilk test, the functions - qqnorm(), qqline(), hist(), boxplot(). The obtained results are shown in Figures 9-12.

For *dissolved oxygen* the results are shown in Figure 9. The results indicate that the data are not normally distributed. These results can also be seen from the graph Q-Q Plot. In the figure 9 it is shown that data in the range 6.5 mg/l - 7mg/l is the most common.

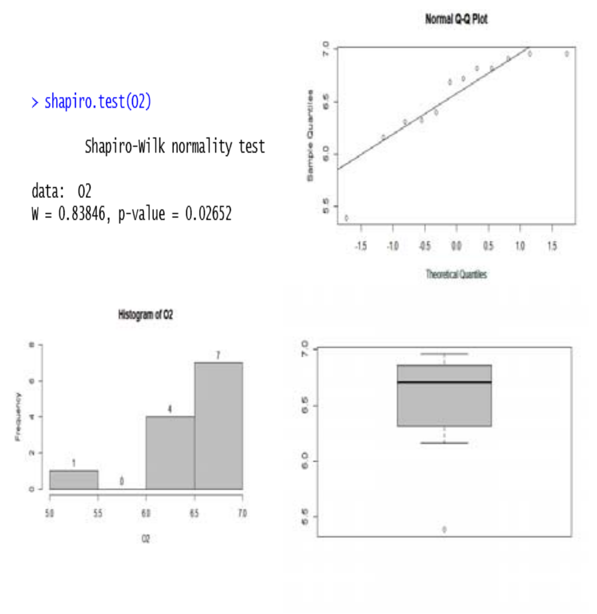

Fig. 9. Results of statistical analysis for dissolved oxygen

In the figure 10 it is shown the results of the statistical analysis for CCOcr. It can be seen that the dispersion of this pollutant is not normally distributed.

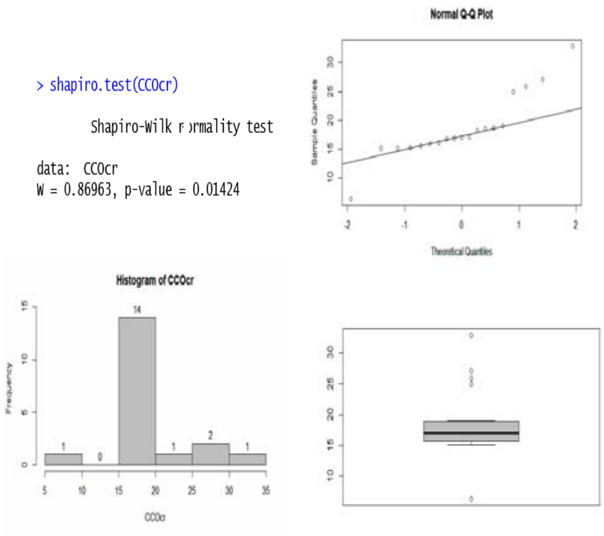

Fig.10. Statistical analysis results for CCOcr

Pollutants are most commonly found in the range 15 mg/l- 20 mg/l. Outliers are also observed, but their weight is insignificant in the statistical model.

The statistical results for *total phosphorus* content in the Dniester River are shown in Figure 11.

The statistical model follows the normal distribution. The highest frequency of occurrence of the pollutant is found in the range 0.2 mg/l to 0.3 mg/l.

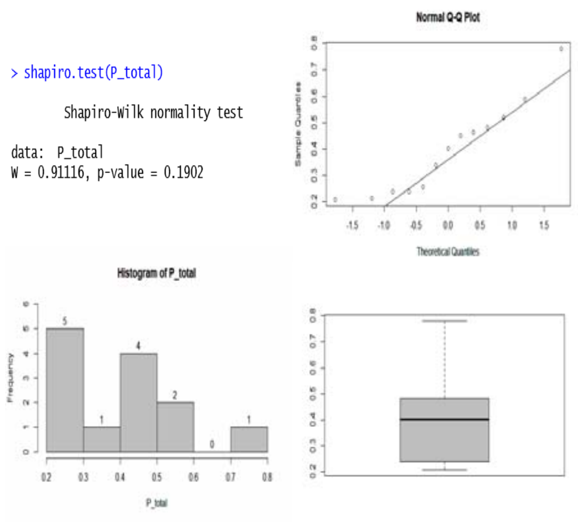

Fig. 11. Results of statistical analysis for *total phosphorus*

Figure 12 shows the statistical model for *magnesium ion*, which shows that the dispersion of the pollutant doesn't follow the normal distribution.

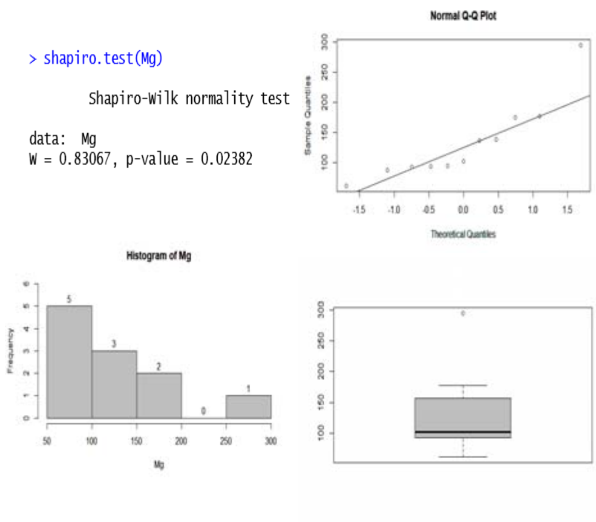

Fig. 12 Statistical analysis results for *magnesium ion*

The most common values are in the range: 50 mg/l- 100 mg/l. From this we can deduce that it is necessary to apply water cleaning measures for the values of the mentioned range.

Based on the results of the statistical analysis of the Dniester River pollution data for the years 2019 - 2021, the approximate distribution for some pollutants was determined. This means that we can develop prediction scenarios for the transport and dispersion of the analyzed pollutants. Based on the fact that the pollution data behave according to a distribution, it is possible to identify the source of pollution and develop prediction scenarios related to the behavior of the pollutant, including radical water pollution abatement and clean-up measures.

4. CONCLUSIONS

A study on the water quality of the Dniester river for the period of 2019-2021 was carried out. It was found a high degree of pollution with different pollutants. The most frequent exceedances of the maximum permissible concentration were recorded for O2, CCOcr, Total Phosphorus, Magnesium Ions. It was carried out the statistical data analysis of the pollutants with the most frequent exceedances of the maximum permissible concentration. The approximate distribution for the analyzed pollutants was detected. Only some statistical models were found to approximate the normal model. For each pollutant were determined the limits where the highest frequency of occurrence of the values is attested. The obtained results allow to develop the prediction scenarios regarding the transport and dispersion of pollutants.

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