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STATISTICAL EVALUATION OF DATA ON THE POLLUTION OF THE PRUT RIVER WITH AMMONIUM NITROGEN

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Abstract. This paper analyzes the pollution of the Prut River with ammonium nitrogen (NH_4^+) during the period 2019–2021, focusing on exceedances of the maximum allowable concentration (MAC) of 0.2 mg/L. The analyzed data comes from measurements taken in various localities along the river. The results indicate constant pollution with significant exceedances of the MAC, the highest measured concentration being 3.85 mg/L. Descriptive analysis reveals an asymmetric distribution, with extreme values raising the average to 0.8456 mg/L. The 2019–2021 period was chosen because this interval recorded significant MAC exceedances. Urban localities, such as Leova and Lipcani, show the highest concentrations, and are correlated with intense human activities. The conclusions emphasize the need for urgent action to reduce pollution and protect aquatic ecosystems and public health.

Keywords: *aquatic ecosystem, ammonium nitrogen pollution, maximum allowable concentration, Prut River, statistical analysis.*

Abstract. Această lucrare analizează poluarea râului Prut cu azot provenit din amoniu (NH_4^+) în perioada 2019–2021, punând accent pe depășirile concentrației maxime admisibile (CMA) de 0,2 mg/L. Datele analizate provin din măsurători efectuate în diverse localități de-a lungul râului. Rezultatele arată o poluare constantă, cu depășiri semnificative ale CMA, cea mai mare concentrație măsurată fiind de 3,85 mg/L. Analiza descriptivă evidențiază o distribuție asimetrică, cu valori extreme care ridică media la 0,8456 mg/L. Perioada 2019–2021 a fost selectată din considerentul că în acest interval s-au înregistrat depășiri semnificative ale CMA. Localitățile urbane, precum Leova și Lipcani, prezintă cele mai mari concentrații, fiind corelate cu activitățile umane intense. Concluziile subliniază necesitatea unor măsuri urgente pentru reducerea poluării și protejarea ecosistemelor acvatice și a sănătății publice.

Cuvinte cheie: *ecosistem acvatic, poluare cu azot de amoniu, concentrație maximă admisibilă, râul Prut, analiza statistică.*

1. Introduction

Water quality is a key indicator of the overall state of the environment and a key determinant of human health, biodiversity and ecosystem sustainability. Water pollution, caused by anthropogenic activities, is a global challenge affecting freshwater resources that are essential for life. Chemical, microbiological and organic pollutants can alter the natural balance of aquatic ecosystems, endangering both flora and fauna and human uses of water resources [1,2].

High concentrations of pollutants, such as ammonium nitrogen (NH_4^+), pose a significant threat to the health of aquatic ecosystems and the quality of drinking water. Ammonium nitrogen typically originates from agricultural and industrial activities, negatively impacting aquatic biodiversity and contributing to water eutrophication. This study focuses on analyzing ammonium nitrogen concentrations in the Prut River during the period 2019–2021, which exceeded the maximum allowable concentrations (MAC). According to environmental regulations for the protection of aquatic life, the maximum allowable concentration (MAC) for ammonium nitrogen in freshwater is 0.2 mg/L. Measured concentrations exceeding acceptable limits can negatively affect the aquatic ecosystem [3-5].

Furthermore, prolonged exposure to contaminated water with ammonium nitrogen can have serious consequences for human health, including an increased risk of gastrointestinal disorders, methemoglobinemia ("blue baby syndrome") on infants, and other metabolic disturbances. Consumption of water with high concentrations of ammonium nitrogen can worsen the health condition of individuals with pre-existing sensitivities, such as kidney or liver health disorders. Therefore, detailed monitoring of water quality is significant for protecting public health and ecosystems [1,6].

Computational solutions and statistical methods are essential for evaluating water quality and understanding the spatio-temporal distribution of pollutants in river systems. Techniques such as histograms and box plots enable visual representation of data distribution, highlighting concentration variability and potential anomalies over time. Frequency analysis for concentration intervals further allows for the categorization of pollution levels, offering a clear overview of how often specific thresholds are exceeded. These methods provide critical insights into the behavior of ammonium nitrogen concentrations, enabling researchers to identify pollution trends, assess the severity of exceedances, and support decision-making processes for water resource management. By employing computational tools to process and analyze environmental data, it becomes possible to derive actionable insights that contribute to safeguarding aquatic ecosystems and ensuring compliance with environmental regulations [7−9].

2. Problem formulation

2.1. Water quality in the Prut River

Prut River, as an important source of freshwater in the Republic of Moldova, plays an important role in supplying with drinking water, irrigation, and maintaining aquatic biodiversity. The water quality of this river has been constantly monitored in recent years, showing significant variability in physicochemical and biological indicators. According to data published by the Agency of Environment of the Republic of Moldova and reports from the European Union on the management of the Danube River basin, the Prut River has experienced episodes of pollution with nutrients, including nitrogen and phosphorus, which contribute to eutrophication and affect the ecological balance of aquatic ecosystems [10,11].

According to the International Commission for the Protection of the Danube River (ICPDR, 2021) water quality in transboundary rivers in the region, including the Prut River, is significantly influenced by agricultural and urban activities. Between 2019 and 2023, values for key water quality indicators, such as dissolved oxygen concentrations, total nitrogen, and phosphorus, showed occasional exceedances of the limits set by European environmental standards (Water Framework Directive, 2000/60/EC). Furthermore, these deviations were primarily attributed to nutrients runoff from anthropogenic activities, which have a direct impact on aquatic life [7,12,13].

For an efficient and detailed analysis of data on ammonia nitrogen pollution in the Prut River, the use of computational techniques plays an important role. These techniques allow the processing of large volumes of data, identification of trends, and visualization of the spatiotemporal distribution of pollutant concentrations. Advanced statistical tools, combined with computational methods such as modeling and numerical simulation, provide an in-depth understanding of pollution phenomena.

Moreover, the use of specialized software for statistical analysis and data visualization, such as R or Python, enables the generation of precise and reproducible results. This issue contributes to the formulation of evidence-based solutions, essential for reducing pollution and protecting aquatic ecosystems [7,8,11,14].

2.2. Ammonium nitrogen pollution

Ammonium nitrogen (NH_4^+) is one of the most important pollutants that affect water quality in rivers, and has diverse origins: runoff from agricultural land, industrial discharges, and insufficiently treated wastewater. The monitoring of the Prut River during the period 2019–2021 highlighted frequent exceedances of the maximum allowable concentration (MAC) of 0.2 mg/L set for surface waters intended for the protection of aquatic life [10].

High ammonium nitrogen concentrations can cause significant negative effects, such as to reduce dissolved oxygen level, harm sensitive species and increase fish mortality. Studies have shown that NH_4^{++} concentrations reached values of up to 0.8 mg/L in some parts of the river during the analyzed period, indicating chronic pollution [4,5,15].

Beyond its impact on aquatic ecosystems, elevated ammonium nitrogen levels can affect the usability of water resources for human consumption, recreation, and agriculture. Excessive NH_4^+ concentrations require additional treatment to meet drinking water standards, increasing costs and operational challenges for local water utilities. Moreover, such pollution can degrade the aesthetic and recreational value of river ecosystems, further emphasizing the need for proactive measures to address this issue [4,5,15].

The persistence of high ammonium nitrogen levels in the Prut River underscores the need for integrated water resource management strategies that address pollution sources holistically. Collaboration between governmental bodies, local communities, and industries is critical to implementing effective solutions. Measures such as reducing fertilizer runoff, upgrading wastewater treatment facilities, and enhancing river monitoring networks can significantly mitigate ammonium nitrogen pollution and safeguard the river's ecological integrity. Despite existing regulations and regular monitoring, ammonium nitrogen pollution of the Prut River remains a persistent problem. A detailed statistical assessment of NH_4^+ concentrations in 2019-2021 is needed in order to identify trends, the main sources of pollution and its effects on the ecosystem. This analysis will provide a basis for proposing viable solutions to reduce pollution and improve water quality in the Prut River.

The lack of comprehensive and integrated approaches to address pollution sources further exacerbates the problem. In many cases, monitoring programs focus on isolated measurements rather than continuous assessments, limiting the ability to detect real-time pollution dynamics. Moreover, insufficient coordination between local authorities and industries hampers the enforcement of environmental regulations, allowing polluting activities to persist without significant penalties or remediation efforts.

Addressing the ammonium nitrogen problem in the Prut River requires not only a detailed statistical evaluation but also a multi-sectoral approach. Collaborative efforts between scientists, policymakers, and local communities are essential to developing targeted interventions. Such efforts should include public awareness campaigns, stricter enforcement of pollution limits, and investments in modernizing wastewater treatment systems to prevent further degradation of water quality. Additionally, expanding monitoring networks to include more frequent sampling and advanced analytical techniques can provide deeper insights into pollution patterns. Without immediate and sustained action, the ecological and economic impacts of ammonium nitrogen pollution will continue to worsen.

3. Solving the problem

In order to solve the formulated problem, were studied the data on ammonium nitrogen concentrations in the Prut River, Table 1.

Table 1

Exceedances of the MAC for ammonium nitrogen in the Prut River (2019-2021)

Nr	Locality	Date	The registered value (mg/L)
1.	Village Valea Mare	15.05.2019	0.5
2.	Town Leova	19.06.2019	3.85
3.	Town Ungheni	13.11.2019	0.62
4.	Village Valea Mare	13.11.2019	1.07
5.	Village Giurgiulesti	20.11.2019	0.55
6.	Village Valea Mare	12.02.2020	0.629
7.	Town Lipcani	03.05.2020	0.53
8.	Town Lipcani	05.06.2020	2.445
9.	Village Valea Mare	10.06.2020	0.434
10.	Town Lipcani	10.07.2020	0.439
11.	Town Ungheni	15.07.2020	0.818
12.	Village Valea Mare	15.07.2020	0.870
13.	Town Cahul	19.08.2020	1.123
14.	Town Leova	19.08.2020	0.685
15.	Village Giurgiulesti	19.08.2020	0.706
16.	Village Giurgiulesti	09.09.2020	0.418
17.	Town Lipcani	13.10.2020	0.413
18.	Village Valea Mare	14.10.2020	0.402
19.	Village Giurgiulesti	21.10.2020	0.584
20.	Town Lipcani	03.03.2021	0.937
21.	Village Valea Mare	10.03.2021	0.51
22.	Village Giurgiulesti	17.03.2021	0.488
23.	Village Pererita	23.03.2021	1.013
24.	Town Lipcani	06.04.2021	0.442
25.	Village Braniste	06.04.2021	0.417
26.	Town Lipcani	05.05.2021	0.503

These values represent the concentrations of ammonium nitrogen measured at various sections of the river and within a specific time interval. From Table 1, significant variations in the measured concentrations can be observed, depending on the localities, including:

Maximum concentrations by locality:

The highest recorded value**:**

- town Leova (3.85 mg/L, 19.06.2019) **– an alarming level, nearly 20 times higher than the MAC of 0.2 mg/L.**

Other significant exceedances**:**

- town Lipcani (2.445 mg/L, 05.06.2020);
- village Valea Mare (1.07 mg/L, 13.11.2019);
- town Cahul (1.123 mg/L, 19.08.2020).

Exceedances of the MAC by locality:

- village Valea Mare: Most of the measured concentrations exceed the MAC, with a maximum value of 1.07 mg/L;
- town Lipcani: presents two significant exceedances, including one of 2.445 mg/L;
- town Leova: records the highest value during the analyzed period;
- village Pererita: A single measurement, but significant, with an exceedance of 1.013 mg/L;
- village Giurgiulești: the values are more moderate, but the frequency of exceedances suggests consistent pollution.

General observations:

- geographic distribution of pollution: Localities near large cities (Leova, Cahul, Ungheni) tend to record higher values, likely due to more intense human activities**;**
- rural localities (Valea Mare, Giurgiulești, Pererita): frequent exceedances, but at lower values than in cities, may be associated with agricultural pollution sources**;**
- severity of pollution: MAC exceedances are variable, and some extreme values (over 3 mg/L) indicate episodes of acute pollution**.**

To obtain an overview of the data distribution presented in Table 1, a descriptive analysis was performed. The following results were obtained:

Table 2

Results of the descriptive analysis

Parameter	Value	Interpretation
Average	0.8456 mg/L	On average, the ammonium nitrogen concentration exceeds the maximum allowable concentration (MAC).
Median	0.629 mg/L	The median being lower than the average suggests a skewed distribution, influenced by a few high values.
Standard deviation	0.7865 mg/L	The high variance indicates a large dispersion of the data, with the presence of extreme values.
Minimum value	0.402 mg/L	The lowest measured value is above the MAC limit of 0.2 mg/L, indicating constant pollution.
Maximum value	3.85 mg/L	A severe exceedance of the MAC, suggesting episodes of acute pollution.

The data shows significant exceedances of the MAC (0.2 mg/L). For example, values of 2.445 mg/L and 3.85 mg/L are considered extreme and can be visualized as outliers. In order to show the frequency with which concentrations occur in different intervals, a histogram was used, Figure 1.

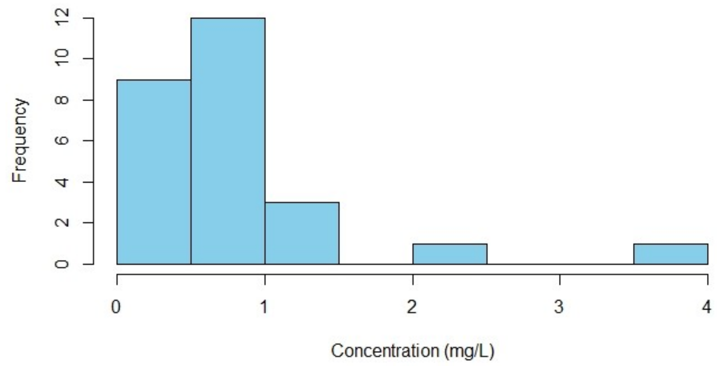

Figure 1. Histogram of Ammonium Nitrogen Concentrations in the Prut River.

From Figure 1, it can be noticed that most of the values are between 0.4 mg/L and 1.0 mg/L, but there are less frequent bars that exceed 2.0 mg/L and 3.0 mg/L. These highlight potential excessive pollution.

Figure 2 presents a boxplot graph, which summarizes the data distribution and highlights extreme values (outliers).

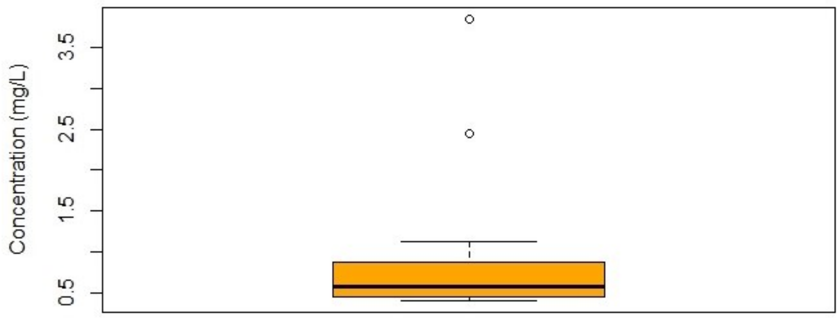

Figure 2. Boxplot of Ammonium Nitrogen Concentrations in the Prut River.

The thick line inside the rectangle represents the median (0.629 mg/L). The box represents the 25th and 75th percentiles (Q1 and Q3). The lines (whiskers) indicate values that fall within the normal range, while the points outside them are outliers. Significant outliers, such as 2.445 mg/L and 3.85 mg/L, are clearly outside the main distribution.

The evolution of the pollutant concentration during the observation period is presented in Figure 3. Each point represents a concentration value, and the line connects the observations to illustrate the variation. A dotted red line is included at 0.2 mg/L, representing the MAC. All values that exceed the MAC are above the MAC line.

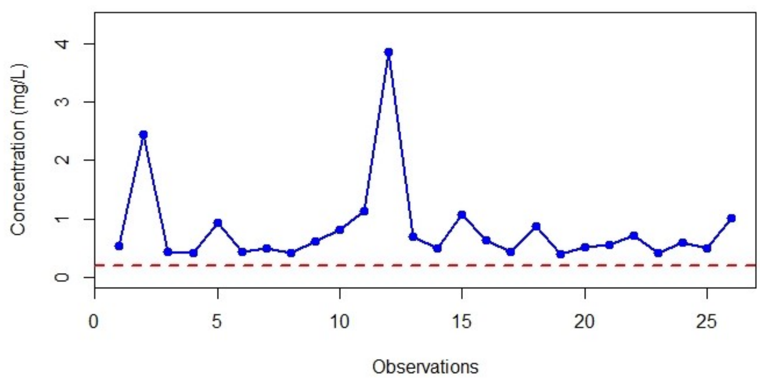

Figure 3. Ammonium Nitrogen concentration over time.

The results of the analysis in order to highlight how frequently the permissible limits of 0.2 mg/L are exceeded are presented in Table 3.

Table 3

Frequencies for concentration intervals

Concentration interval (mg/L)	Absolute frequency	Relative frequency (%)
0.0 – 0.5	13	50.0
0.5 – 1.0	9	34.6
1.0 – 1.5	2	7.7
1.5 – 2.0	0	0.0
2.0 – 2.5	1	3.8
2.5 – 3.0	0	0.0
3.0 – 4.0	1	3.8

From Table 3, the following can be observed:

- the majority of values (50%) are within the 0.0 – 0.5 mg/L range, indicating that at certain times, the ammonia nitrogen concentration was close to low values;

- 34.6% of the values are between 0.5 – 1.0 mg/L, and this range represents a significant exceedance of the MAC;

- concentrations greater than 2.0 mg/L are rare (7.6% in total), but they indicate severe pollution episodes.

There are 26 observations, and all exceed the MAC limit (0.2 mg/L). Therefore, the situation in the river indicates constant pollution.

4. Conclusions

The analysis of ammonium nitrogen concentrations in the Prut River for the period 2019–2021 highlights constant and significant pollution, all measured values exceeding the maximum allowable concentration of 0.2 mg/L. These exceedances are more pronounced in urban areas, such as Leova, where the maximum concentration reached 3.85 mg/L, nearly 20 times above the acceptable limit.

The analyzed data suggest a clear association between anthropogenic activities, such as intensive agriculture and the lack of proper wastewater treatment, and the high pollution levels. Rural localities, such as Valea Mare and Giurgiulești, frequently record exceedances of the MAC, but at more moderate levels, indicating more diffuse sources of pollution.

The distribution of concentrations is characterized by extreme values, reflected in the high standard deviation (0.7865 mg/L) and the presence of outliers. These aspects underline the need for strict monitoring policies and pollution reduction measures.

The use of statistical tools such as histograms, box plots, and frequency analysis provided valuable insights into the variability and trends in ammonium nitrogen concentrations. These methods revealed the magnitude and persistence of pollution, as well as its spatial and temporal distribution, supporting the hypothesis that both point and diffuse pollution sources significantly contribute to water quality degradation. Such analytical approaches are essential for effectively communicating the urgency of the issue to stakeholders and policymakers.

Implementing sustainable practices to mitigate pollution requires a multi-faceted approach, involving improved wastewater treatment infrastructure, promotion of environmentally friendly agricultural practices, and robust enforcement of environmental regulations. Awareness campaigns targeting local communities and industries are crucial for fostering cooperation and accountability in reducing pollutant discharge into aquatic systems.

Future research should focus on extending the monitoring period and incorporating additional chemical and biological indicators to provide a more comprehensive assessment of water quality. The integration of advanced computational models, coupled with real-time monitoring systems, can further enhance the ability to predict and manage pollution events, ultimately contributing to the long-term protection of the Prut River ecosystem.

5. Recommendations

1. **Implementation of strict pollution reduction measures.** To improve wastewater treatment and to promote sustainable agricultural practices in the affected regions.
2. **Extensive and continuous monitoring.** To establish an automated monitoring system in order to identify quickly the episodes of severe pollution.
3. **Education and awareness of the local population.** To inform communities about the impact of human activities on water quality and health.
4. **Cross-border cooperation.** Since the Prut River is a transboundary river, cooperation with neighboring countries in order to implement integrated environmental protection solutions.

These conclusions and recommendations aim to protect the ecosystems of the Prut River and to reduce the risks of public health.

Conflicts of Interest: The authors declare no conflict of interest.

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