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STUDY OF THE DYNAMICS OF SOME WATER QUALITY PARAMETERS IN THE PRUT RIVER AREA DURING 2014-2023

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Abstract

The Prut River area represents an area of maximum importance, considering its international character and RAMSAR-type areas. In this study, we present the statistical analysis of the measurements carried out on the water quality parameters in the Prut River area, covering a period of 10 years. In this way, we were able to establish the trend of evolution of temperature, pH, turbidity, etc. and predictions can be made in this way. The methods used were ANOVA and especially multivariate analysis procedures. The conclusions that emerge are of great importance, especially for the evaluation of the protected area of Lake Beleu and the lower Prut floodplain area.

Key words: *ANOVA, multivariate methods, statistical methods, water quality parameters.*

INTRODUCTION

In recent years, considering climate change, the monitoring and protection of water bodies have become extremely important topics (Banescu et al., 2020). In this context, the European Union has issued several important directives aimed at mitigating the threats and pressures exerted by anthropogenic activities on rivers and other categories of surface waters (Burada et al., 2016).
In this framework, the study of pollution factors in Eastern Europe represents a topic of major importance. The present study provides an investigation conducted over a 10-year period, between 2014 and 2023, based on measurements of monitored parameters in the Republic of Moldova, focusing on the water quality of the Prut River (Cordeli et al., 2023). The applied study methods are commonly used in the scientific literature, with emphasis on assessing the evolution trends of parameters considered essential for objectively describing the level of pollution (Resz et al., 2023).
The aim of this study is to investigate the evolution of water quality parameters in the Prut River, in the Cahul-Oancea sector, using a 10-year dataset covering the period 2014-2023.

MATERIALS AND METHODS

The statistical analysis of the dataset was carried out following an algorithm frequently used in the literature: correlations between the sets of parameters were evaluated for each individual year, and then procedures based on Principal Component Analysis (PCA) were applied (Mocanu et al., 2021).
Principal Component Analysis (PCA) is a multivariate statistical method used to reduce data dimensionality and to identify patterns and correlations among variables.
In the final stage, the strongest correlations between the variables describing water quality - i.e., pH, alkalinity, and temperature, which shows a clear evolutionwere presented in the form of response surfaces (Popa et al., 2018).

The aim of this study is to highlight the evolution of water quality parameters in the Cahul area, Republic of Moldova. Correlations between the parameters were evaluated for each year of study. Table 1 presents the 12 physical parameters that were measured daily. Figure 1 shows the location of the monitoring point.



Figure 1. Map of Prut River

Table 1. Parameters monitored in the Cahul monitoring network

Parameter	Measure unit	Evaluation
Temperature	[°C]	Daily averaged
Transparency	[cm]	Daily averaged
Colour	[degrees HU - Hazen Units]	Daily averaged
Turbidity	[mg/dm3]	Daily averaged
pH	pH unit	Daily averaged
Ammonium	[mg/dm3]	Daily averaged
Nitrites	[mg/dm3]	Daily averaged
Nitrates	[mg/dm3]	Daily averaged
Oxidability	[mg/dm3]	Daily averaged
Chlorides	[mg/dm3]	Daily averaged
Suspended matter	[mg/dm3]	Daily averaged
Alkalinity	[mg/dm3]	Daily averaged

RESULTS AND DISCUSSIONS

In this section, we present the results of the statistical analysis and, respectively, the results of the numerical simulations.

Obviously, the first step was to investigate the correlations between the measured physical parameters for the dataset corresponding to the years 2014–2023.

Subsequently, the PCA method was applied to each annual experimental dataset. Thus, for the year 2014, the obtained diagram is presented in Figure 2.

For the year 2014, the most significant correlations were identified between temperature and transparency (correlation= −0.8348, p=0.001), temperature and turbidity (correlation =0.7733, p=0.001), temperature and chlorides (correlation= −0.8607, p= 0.001), temperature and alkalinity (correlation = −0.7445, p=0.001), and temperature and nitrates (correlation=−0.7806, p= 0.001).

For the dataset corresponding to the year 2015, the most significant correlations were identified between temperature and chlorides (correlation =−0.9068, p=0.001), transparency and suspended matter (correlation= −0.7051, p=0.001), turbidity and suspended matter (correlation= 0.9998, p=0.001), as well as between temperature and chlorides (correlation= −0.9068, p=0.001) and temperature and alkalinity (correlation = −0.8840, p=0.001) and is a significant difference is noted between the considered data (Table 2).

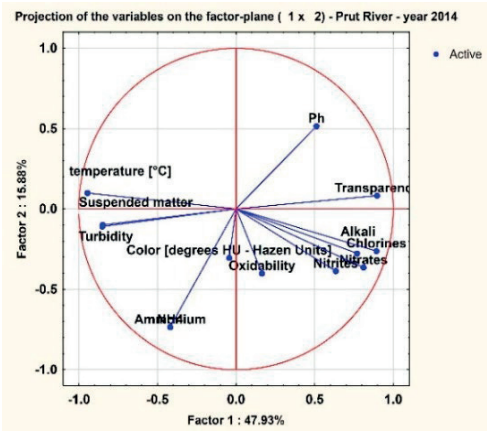


Figure 2. PCA diagram for 2014 database study case

Thus, in Figure 2 it can be observed that the first principal component, which explains the variance of the dataset, includes temperature, transparency, turbidity, pH, nitrites, nitrates, oxidability, chlorides, suspended matter, and alkalinity. In Figure 3, the PCA diagram for the dataset corresponding to the year 2015 is presented. The first principal component includes the following parameters: temperature [°C], colour [degrees HU – Hazen Units], pH, as well as nitrates, oxidability, chlorides, and alkalinity.

In Table 2 are presented the t-test results for average temperature. Many insignificant differences are observed.

Table 2. Results of t-test values for temperature

Group 1 vs. Group 2	Mean Group 1	Mean Group 2	t-value	*p*
t[°C] 2014 vs. t[°C] 2015	13.026	13.317	-0.37	0.706
t[°C] 2015 vs. t[°C] 2016	13.317	13.767	-0.56	0.576
t[°C] 2016 vs. t[°C] 2017	13.767	12.454	1.711	0.088
t[°C] 2017 vs. t[°C] 2018	12.454	12.952	-0.65	0.518
t[°C] 2018 vs. t[°C] 2019	12.952	12.219	0.967	0.334
t[°C] 2019 vs. t[°C] 2020	**12.219**	**13.429**	**-2.01**	**0.045**
t[°C] 2020 vs. t[°C] 2021	**13.429**	**12.227**	**2.231**	**0.026**
t[°C] 2021 vs. t[°C] 2022	12.227	13.086	-1.32	0.1850
t[°C] 2022 vs. t[°C] 2023	13.086	12.9128	0.237	0.813

In the same manner as Figure 2, were considered the PCA results for year 2015 (Figure 3), 2016 (Figure 4) and 2017 (Figure 5). Could be easily observed significand differences by comparing year 2105 (Figure 3), and year 2016 (Figure 4), especially for Factor 2. The PCA diagrams show the main groups operating during the studied period. Significant changes are observed from one year to another (Figure 5, Figure 6).

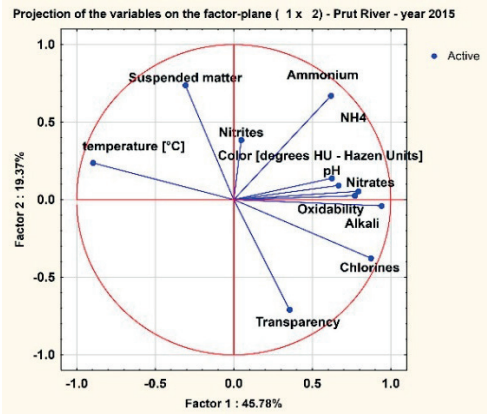


Figure 3. PCA diagram for 2015 database study case

For the dataset corresponding to the year 2018, the most significant correlations are those between pH and temperature (correlation = −0.7156, p = 0.001), as well as between temperature and suspended matter (correlation = 0.76056, p = 0.001) and temperature and alkalinity (correlation = −0.7856, p = 0.001).

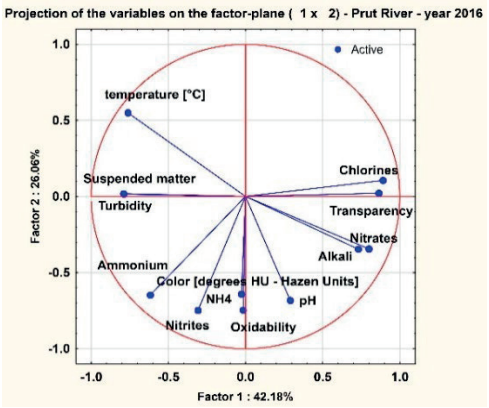


Figure 4. PCA diagram for 2016 database study case

Thus, PCA diagrams show the main group F1 operating during the studied period i.e. Suspended matter, Turbidity, Chorines, Nitrates (Figure 4). By comparing year 2016 and 2017, significant changes are observed from year to year (Figure 5, Figure 6). For example, Transparency became to F2 factor.

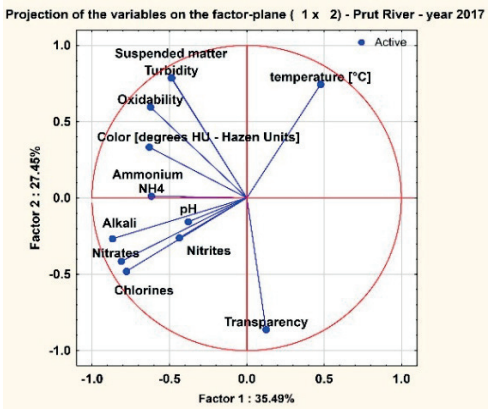


Figure 5. PCA diagram for 2017 database study case

For the dataset corresponding to the year 2018 (Figure 6) and 2019 (Figure 7), the following relationships can be identified: temperature and transparency (correlation = −0.7047, p = 0.001), temperature and turbidity (correlation = 0.7599, p = 0.001), temperature and chlorides (correlation = −0.7259, p = 0.001), and respectively temperature and alkalinity (correlation = −0.7260, p = 0.001). The same

relationships were also observed for the datasets corresponding to the years 2020–2023.

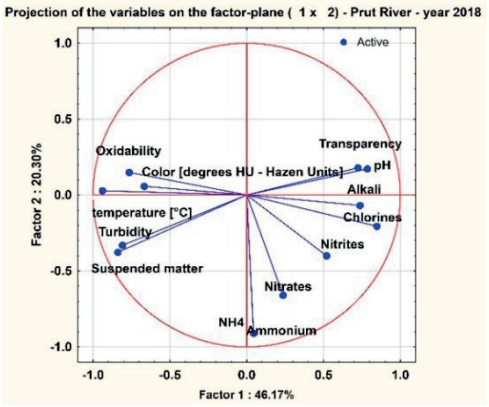


Figure 6. PCA diagram for 2018 database study case

In Table 3 are presented the t-test results for average pH values. Many significant differences are observed – the bold marked records.

Table 3. Results of t-test values for pH

Group 1 vs. Group 2	Mean Group 1	Mean Group 2	t-value	*p*
pH 2014 vs. pH 2015	**8.064**	**8.189**	**-11.59**	**0.000**
pH 2015 vs. pH 2016	**8.189**	**8.035**	**12.94**	**0.000**
pH 2016 vs. pH 2017	**8.035**	**8.068**	**-2.89**	**0.004**
pH 2017 vs. pH 2018	8.068	8.046	1.70	0.094
pH 2018 vs. pH 2019	**8.046**	**8.382**	**-13.89**	**0.000**
pH 2019 vs. pH 2020	**8.382**	**8.236**	**6.63**	**0.000**
pH 2020 vs. pH 2021	**8.236**	**8.323**	**-6.93**	**0.000**
pH 2021 vs. pH 2022	**8.323**	**8.608**	**-25.73**	**0.000**
pH 2022 vs. pH 2023	**8.608**	**8.327**	**16.79**	**0.000**

In Table 4 are presented the t-test results for average NO_2 values. Many insignificant differences are observed - the bold marked records.

For the dataset corresponding to the year 2020 (Figure 8) and 2021 (Figure 9), the following relationships can be identified: temperature and Ammonium (correlation = +0.787, p = 0.001), temperature and Oxidability (correlation = 0.7699, p = 0.001), temperature and chlorides (correlation = −0.079, p = 0.001), and respectively temperature and alkalinity (correlation = −0.8260, p = 0.001) - Figure 9.

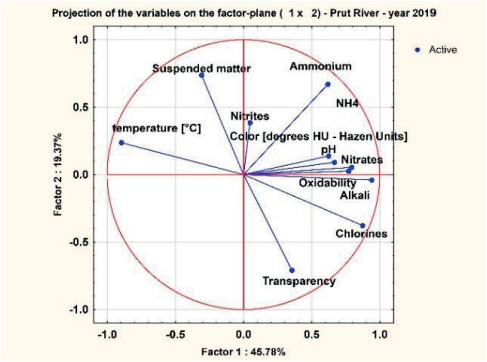


Figure 7. PCA diagram for 2019 database study case

Table 4. Results of t-test values for Nitrites

Group 1 vs. Group 2	Mean Group 1	Mean Group 2	t-value	*p*
NO_2 2014 vs. NO_2 2015	**0.019**	**0.027**	**-3.30**	**0.019**
NO_2 2015 vs. NO_2 2016	**0.027**	**0.033**	**-2.22**	**0.027**
NO_2 2016 vs. NO_2 2017	**0.033**	**0.022**	**5.326**	**0.033**
NO_2 2017 vs. NO_2 2018	**0.022**	**0.015**	**4.95**	**0.022**
NO_2 2018 vs. NO_2 2019	**0.015**	**0.025**	**-10.43**	**0.015**
NO_2 2019 vs. NO_2 2020	**0.025**	**0.018**	**17.04**	**0.025**
NO_2 2020 vs. NO_2 2021	0.012	0.031	-7.68	0.0118
NO_2 2021 vs. NO_2 2022	0.031	0.025	2.12	0.031
NO_2 2022 vs. NO_2 2023	0.019	0.027	-3.30	0.019

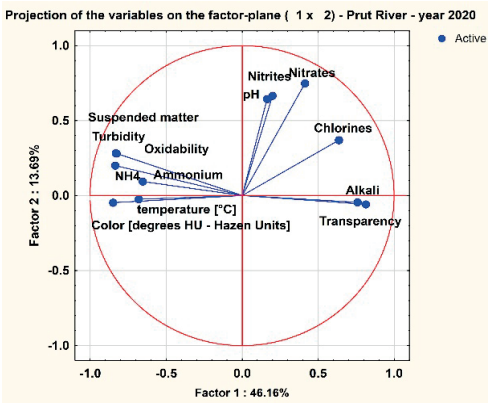


Figure 8. PCA diagram for 2020 database study case

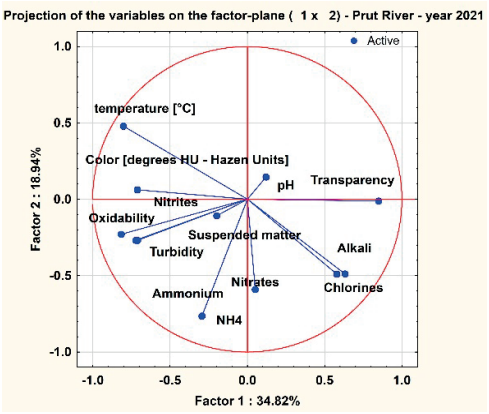


Figure 9. PCA diagram for 2021 database study case

In Table 5 are presented the t-test results for Nitrates average values. Many insignificant differences are observed – the bold marked records.

As is well known, in the case of nitrates, the concentration increases proportionally with agricultural and urban pollution; the concentration of chlorides increases proportionally with mineralization and agricultural contamination. On the other hand, oxidability measures the amount of oxidizable organic matter, while alkalinity is correlated with the salt content. In this sense, this first principal component has a general chemical character.

Table 5. Results of t-test values for Nitrates

Group 1 vs. Group 2	Mean Group 1	Mean Group 2	t-value	*p*
2014 NO_3 vs. NO_3 2015	**7.279**	**5.233**	**9.578**	**0.000**
NO_3 2015 vs. NO_3 2016	**5.233**	**4.504**	**3.430**	**0.001**
NO_3 2016 vs. NO_3 2017	4.504	4.614	-0.594	0.553
NO_3 2017 vs. NO_3 2018	**4.802**	**5.080**	**-2.40**	**0.016**
NO_3 2018 vs. NO_3 2019	**5.080**	**4.138**	**8.82**	**0.000**
NO_3 2019 vs. NO_3 2020	**4.138**	**5.866**	**-16.0**	**0.000**
NO_3 2020 vs. NO_3 2021	**5.866**	**5.096**	**5.897**	**0.000**
NO_3 2021 vs. NO_3 2022	**5.096**	**4.267**	**7.363**	**0.000**
NO_3 2022 vs. NO_3 2023	**7.279**	**5.233**	**9.578**	**0.000**

The second principal component includes parameters such as NH_4, transparency, ammonium, and suspended matter. PC2 can be interpreted as the factor that evaluates the degree of organic pollution and the content of suspended particles.

Last but not least, significant differences are observed between the PCA diagrams corresponding to the years 2022 (Figure 10) and 2023 (Figure 11) respectively - for example: Nitrites are in Factor 1 in 2022 and then their contribution is added to Factor 2 in 2023.

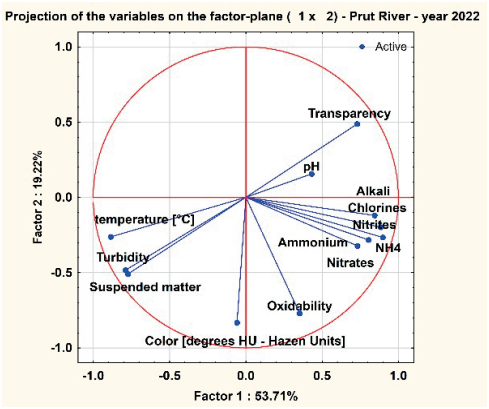


Figure 10. PCA diagram for 2022 database study case

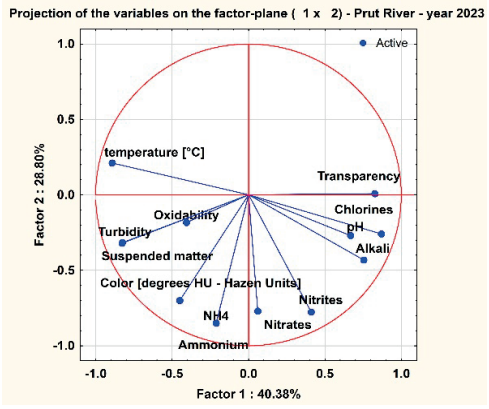


Figure 11. PCA diagram for 2023 database study case

In a short conclusion there are severe modification in these dynamics: in Figure 6, the two groups exhibit a switching, which means that the two processes associated with these groups have changed their relative importance in an inversely proportional manner.

Figure 12 presents the response surface for the dependence of pH on temperature and alkalinity for the dataset corresponding to the year 2014. The obtained surface shows a decreasing dependence of pH values on temperature (a fact also reported in the literature). What is interesting, considering that alkalinity determines how much pH can change when the equilibrium is altered, is that in this case the slope of the pH dependence on alkalinity is small (Figure 12).

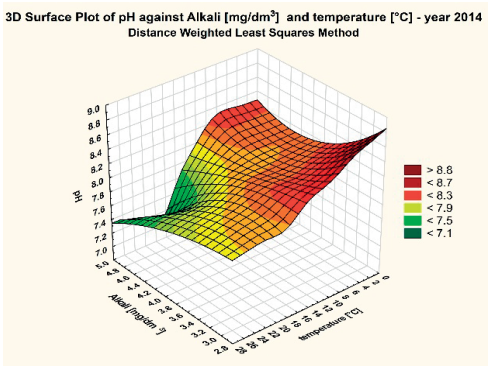


Figure 12. Surface plot pH against temperature and alkalinity for 2014 database study case

Figure 13 presents the response surface for the dependence of pH on temperature and alkalinity for the dataset corresponding to the year 2015. The obtained surface shows a completely different dependence of pH on temperature and alkalinity. However, it can be observed that in this case there is a stable dynamic equilibrium. Alkalinity determines a proportional increase in pH, which is contrary to the previous case.

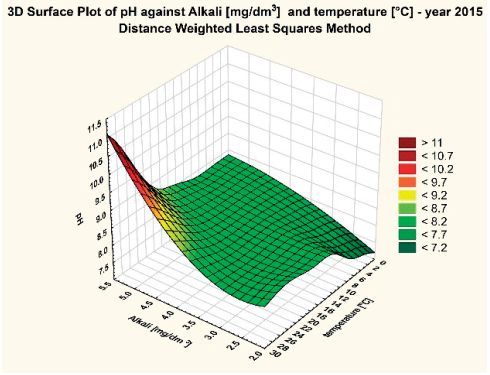


Figure 13. Surface plot pH against temperature and alkalinity for 2015 database study case

Figure 14 presents the response surface for the dependence of pH on temperature and alkalinity for the dataset corresponding to the year 2016. In this case, the surface is characteristic of an unstable dynamic equilibrium. Alkalinity determines a proportional decrease in pH, similar to the situation observed in 2014.

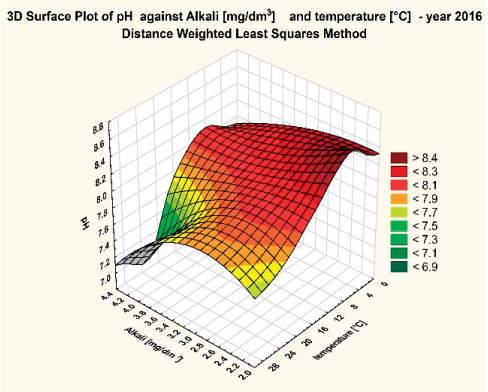


Figure 14. Surface plot pH against temperature and alkalinity for 2016 database study case

Figures 15 and 16 present the response surfaces for the dependence of pH on temperature and alkalinity for the datasets corresponding to the years 2017 and 2018.

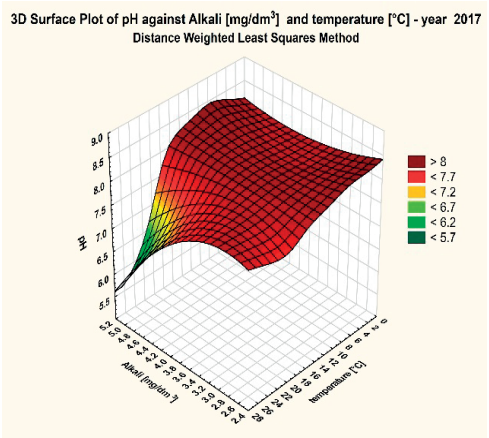


Figure 15. Surface plot pH against temperature and alkalinity for 2017 database study case

In these cases, as well, the surfaces are characteristic of an unstable dynamic equilibrium. Alkalinity determines a decrease in pH, similar to the situation observed in 2014.

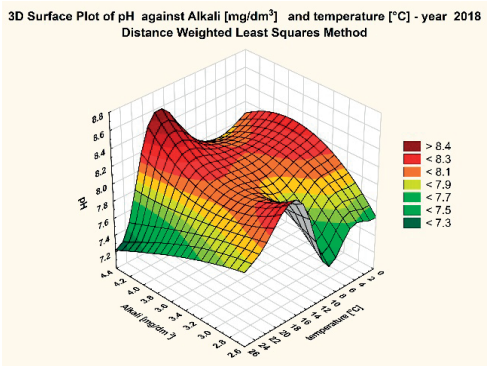


Figure 16. Surface plot pH against temperature and alkalinity for 2018 database study case

Figures 17 and 18 present the response surfaces for the dependence of pH on temperature and alkalinity for the datasets corresponding to the years 2019 (Figure 17) and 2020 (Figure 18).

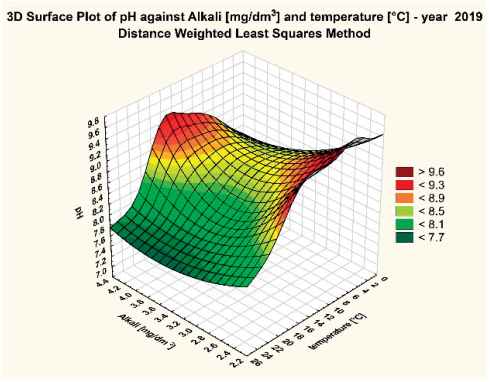


Figure 17. Surface plot pH against temperature and alkalinity for 2019 database study case

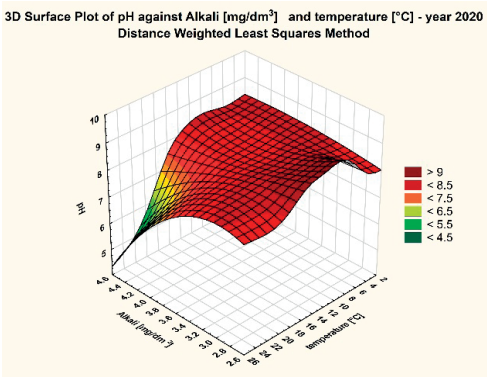


Figure 18. Surface plot pH against temperature and alkalinity for 2020 database study case

In the period 2021 - 2023, a dramatic change in the dependence of pH on the concentration of alkane as a function of temperature is observed (Figure 19, Figure 20 and Figure 21).

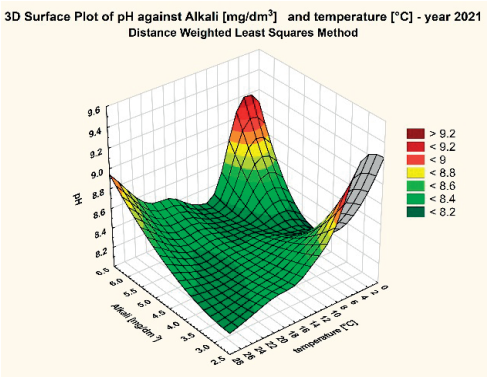


Figure 19. Surface plot pH against temperature and alkalinity for 2021 database study case

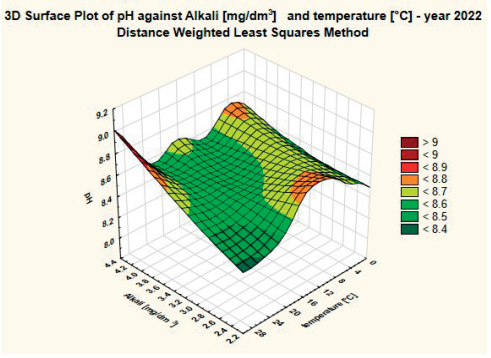


Figure 20. Surface plot pH against temperature and alkalinity for 2022 database study case

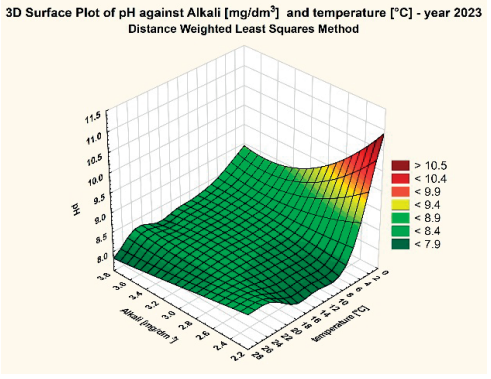


Figure 21. Surface plot pH against temperature and alkalinity for 2023 database study case

The present study aims to integrate a series of investigations conducted in the Prut River area (Dumitran, 2011). Many previous works have addressed heavy metal pollution (Matache et al., 2018) or the Water Quality Index (WQI) for this river (Duca et al., 2019). Furthermore, studies objectively describing the primary pollutants in the region where the river forms a natural border must also be considered (Teodosiu et al., 2009; Hrytsku & Hrytsku-Andriyesh, 2016). Naturally, research has also been conducted on the dynamics and interrelationships of key pollutants - such as NO3-N and NH4-N (Timofti et al., n.d.) - as well as on the environmental impacts of precipitation and temperature fluctuations (Corobov et al., 2021; Sava & Marusic, 2022).

In this context, we analyzed a 10-year period using a method capable of consistently addressing the entire dataset. The measured values correlate with those recorded for NO3-N, NO2-N, and NH4-N, generally aligning with observed trends regarding spatial variability and the gradient of this variability along the river's course (Neamtu et al., 2021). However, the present study clearly highlights significant differences between annual mean values, indicating that the processes specific to this natural aquatic system are undergoing changes. While previous studies focused on shorter timeframes - such as the five-year period from 2015 to 2019 (Neamtu et al., 2021; Duca et al., 2019) or even shorter intervals (Dumitran, 2011) - our study, utilizing a standardized dataset spanning a longer period, clearly revealed the existence of significant variations. It is also worth noting the strong correlation between N-NO2, N-NO3, and NH4, suggesting an underlying mechanism driving this relationship - a phenomenon previously observed using complementary methods (Timofti et al., n.d.). A particularly interesting finding emerges from the PCA analysis: the factors explaining the dataset's variability shift in relative importance over time. Specifically, during the 2014-2016 period, the primary factor (F1) encompasses turbidity, suspended matter, transparency, temperature, alkalinity, and chlorides; this represents a mixed physicochemical determinant - dominated by turbidity and suspended particles but also influenced by mineralization (alkalinity and chlorides) and temperature effects on these processes. Meanwhile, the secondary factor (F2) -comprising oxidability, nitrates, nitrites, ammonium, and pH - acts as a biochemical factor reflecting nitrogen transformations and organic matter degradation, essentially serving as a redox/organic and nitrogenous pollution factor. Starting in 2017, an interesting phenomenon was observed: the relative weights of the two previously identified factors shifted. This indicates that the biochemical factor - associated with nitrogen transformations and organic matter degradation - gained significance regarding data set variability, whereas the mixed physicochemical factor showed a stronger correlation along the Oy axis.

In the subsequent period (2018-2020), factors F1 and F2 reverted to their initial weightings; the mixed physicochemical factor became the dominant driver, contributing 45-46% to the overall variability, while factor F2 played a much smaller role, contributing 13-20%.

Finally, it is worth noting that between 2021 and 2023, the relative weights of the two main factors shifted once again. This periodic fluctuation reinforces a concept previously highlighted in the literature: the existence of two fundamental mechanisms explaining these correlations - pollution of industrial/anthropogenic origin and pollution resulting from natural and agricultural processes. Basing on the response surfaces shown in Figures 16, 18 and mainly on figures 19 and 20 - which represent stable equilibrium surfaces - we can conclude that the system is undergoing a "time-dependent oscillatory evolution," characterized by shifting contributions from organic and nitrogenous pollutants.

CONCLUSIONS

The statistical analysis of the physicochemical parameters of the Prut River water in the Cahul sector for the period 2014-2023 highlights a pronounced thermal stability, concomitant with significant variations in nitrogen compounds and pH, indicating a high sensitivity of the aquatic system to anthropogenic pressures and regional biogeochemical dynamics. The average annual temperature did not show significant differences except in the period 2019-2021, which confirms that the thermal regime of the river is predominantly controlled by climatic factors and less by local influences.

In contrast, pH recorded statistically significant variations over almost the entire analysed period, with a single point exception (2017-2017), suggesting continuous changes in the processes of mineralization, photosynthesis and nutrient loading. The annual variability of nitrite concentrations (2014-2020) and the significant variations of nitrates in all analysed years indicate an unstable regime of nitrogen compounds, compatible with fluctuating nutrient inputs from agricultural activities, hydrological processes and microbial transformations.

Overall, the results show that, although the physical parameters of the water remain relatively constant, the chemical parameters relevant for the assessment of eutrophication show a pronounced dynamic, which reflects an ecosystem in a fragile balance, influenced by both natural conditions and anthropogenic pressures. These findings highlight the need for continuous monitoring and implementation of nutrient source management measures to maintain the ecological status of the lower Prut River. Dramatic changes are observed regarding the internal processes of the studied hydrological system.

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