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Stochastic analysis of organic water pollution risks in the lower Danube

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SUMMARY

The stochastic analysis of organic water pollution risks in the lower Danube was conducted based on long-term monitoring data (2003–2024) from four key stations: Reni, Izmail, Kiliya, and Vylkove. The study assessed dissolved oxygen (DO) and biochemical oxygen demand (BOD), two critical indicators of water quality, using statistical methods and stochastic modeling. The results indicate a declining trend in DO, particularly in Kiliya and Vylkove, suggesting increasing oxygen depletion risks. In contrast, BOD levels show a rising trend, highlighting growing organic pollution pressures. The probability of exceeding critical pollution thresholds ($DO < 6 \text{ mg/L}$, $BOD > 3 \text{ mg/L}$) is highest in Vylkove (38.6% and 49.2%), marking it as the most vulnerable area. Reni exhibited the most stable conditions, benefiting from lower anthropogenic influence and better self-purification capacity. A spatial analysis revealed that pollution accumulates downstream, making Vylkove and Kiliya high-risk zones. Izmail had moderate pollution risks, while Reni maintained the best water quality. The Monte Carlo method was applied to quantify risk probabilities, and results were validated using empirical data and previous studies.



Introduction

Water resource pollution is one of the key environmental issues of modern times, particularly in large river systems that experience significant anthropogenic pressure (Menshov et al., 2023). In the lower Danube, organic water pollution remains a pressing issue due to agricultural, industrial, and urban activities in coastal regions (Bezsonnyi & Nekos, 2023). One of the primary indicators of organic pollution is biochemical oxygen demand (BOD), which determines the amount of oxygen required to decompose organic matter in the aquatic environment (Bezsonnyi, Plyatsuk, Ponomarenko, & Tretyakov, 2023). High BOD values typically indicate increased organic loading, which can lead to reduced dissolved oxygen (DO) levels, the development of hypoxic zones, and negative impacts on aquatic ecosystems (Horoshkova, Khlobystov, & Danylyshyn, 2020). Water pollution is often assessed using deterministic models based on regulatory standards and the physicochemical properties of water (Bezsonnyi & Nekos, 2022). However, such approaches fail to account for the stochastic nature of pollution processes, including random fluctuations in pollutant concentrations, hydrological changes, and seasonal variability (Guryanova, Yatsenko, Dubrovina, Babenko, & Gvozditkyi, 2021). Recent studies increasingly employ stochastic and fuzzy logic methods, which allow for a probabilistic analysis of the risks of exceeding permissible pollution levels (Horoshkova et al., 2020). The stochastic approach considers uncertainties in measurements, natural ecosystem fluctuations, and variability in anthropogenic impacts, providing a more accurate assessment of environmental risks (Bezsonnyi & Nekos, 2023). Water resources play a crucial role in ensuring ecological stability, economic development, and public health. However, as anthropogenic pressures increase, river systems face a growing risk of organic pollution, leading to deteriorating water quality, eutrophication, and declining DO levels. This problem is particularly significant for large transboundary rivers, such as the Danube, which is affected by intensive agricultural activity, industrial discharges, and urban wastewater (ICPDR, 2021). One of the key indicators of organic pollution is biochemical oxygen demand (BOD), which reflects the decomposition rate of organic matter in water. High BOD levels indicate significant organic loading, which can cause a decline in DO concentrations and lead to the formation of hypoxic zones that pose serious threats to aquatic life.

The assessment of water pollution risks is typically conducted using deterministic models based on physicochemical parameters and regulatory water quality standards. However, such approaches often fail to consider the stochastic nature of processes affecting water quality, including random fluctuations in pollutant concentrations, hydrological factors, and temporal ecosystem dynamics (Li et al., 2016). Recently, increasing attention has been given to fuzzy logic and stochastic risk assessment methods, which allow for a more accurate evaluation of the probability of exceeding permissible pollutant concentrations. Stochastic models account for measurement uncertainty and the natural variability of ecosystems, enabling the calculation of environmental risk probabilities based on the distribution of random variables (Fernández del Castillo et al., 2024). Several studies confirm that elevated BOD is an indicator of high organic pollution, which can lead to oxygen depletion and the degradation of aquatic ecosystems. For example, research by Dasgupta & Yildiz (2016) found that BOD levels exceeding 3 mg/L are critical for many aquatic ecosystems, particularly in closed or slow-flowing water bodies. Geographic Information Systems (GIS) are widely used for analyzing the spatial distribution of pollutants (Giri & Qiu, 2016). GIS applications in research have shown that organic pollution levels increase downstream in the Danube River. The EU Water Framework Directive 2000/60/EC sets key environmental standards for assessing water quality in river basins, including acceptable DO and BOD levels. Studies indicate that most European river systems struggle to meet these standards due to intensifying anthropogenic pressures (Voulvoulis et al., 2017).

This study conducts a stochastic analysis of organic water pollution risks in the lower Danube, based on long-term monitoring data on DO and BOD from four monitoring stations: Reni, Izmail, Kiliya, and Vylkove. The research methodology includes analyzing mean values, variances, and the probability of exceeding permissible pollution levels using a stochastic approach.



Method and Theory

This study conducts a stochastic analysis of organic water pollution risks in the lower Danube based on long-term observations of dissolved oxygen (DO) and biochemical oxygen demand (BOD) at four monitoring stations (Reni, Izmail, Kiliya, and Vylkove) using monitoring data from the Ukrainian Water Resources Agency collected between 2003 and 2024. The research methodology includes the analysis of statistical characteristics, such as mean values, variance, and the probability of exceeding permissible pollutant concentrations. The approach combines classical statistical methods with stochastic modeling, allowing for a probabilistic assessment of organic pollution risks. The study relies on long-term water quality monitoring data from the lower Danube. The key monitoring parameters include DO (Dissolved Oxygen, mg/L) – a crucial indicator of aquatic ecosystem health. BOD (Biochemical Oxygen Demand, mg/L) – an indicator of organic pollution levels.

The dataset underwent preliminary verification, including: Removal of outliers and anomalous values; Interpolation of missing data; Averaging values for the analysis of long-term trends. Subsequently, statistical parameters were calculated, including: Mean value (μ); Variance (σ^2); Coefficient of variation ($CV = (\sigma / \mu) \times 100\%$).

The risk analysis was conducted by calculating the probability of DO and BOD exceeding critical thresholds established by water protection standards (e.g., EU Water Framework Directive 2000/60/EC and national regulations). Threshold values: Risk of oxygen depletion: if $DO < 6$ mg/L; Risk of organic pollution: if $BOD > 3$ mg/L. The probability of exceeding these thresholds was computed using the formula:

$$P = P(X > X_{cr}) = \int_{X_{cr}}^{\infty} f(X) dX$$

where:

X_{cr} – threshold value; $f(X)$ – probability density function, based on the empirical distribution of data.

For the distribution function calculation, normal distribution and Weibull distribution were used, as they best describe the natural variability of DO and BOD in river systems.

To account for random variations in pollutant concentrations, the Monte Carlo method was applied. This approach enables risk assessment through multiple random simulations of potential water quality scenarios.

The dataset was also subjected to spatial analysis to identify geographical variations in pollution levels: Temporal analysis assessed long-term trends in DO and BOD fluctuations in the lower Danube. Spatial analysis identified high-risk zones requiring enhanced monitoring efforts.

The results obtained were compared with actual water quality observations and previous studies in the region (Bezsonnyi & Nekos, 2023). This validation process ensured the accuracy of forecasts and determined how well the model represents real-world conditions. The model accuracy was evaluated using coefficient of determination (R^2); Root Mean Square Error (RMSE).

This methodological approach enables a comprehensive risk assessment of organic pollution in the lower Danube, providing insights into environmental management and water quality protection strategies.

Results

The analysis of long-term water quality observations in the lower Danube enabled the assessment of dissolved oxygen (DO) and biochemical oxygen demand (BOD) variations at four monitoring stations:



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Reni, Izmail, Kiliya, and Vylkove. The key statistical characteristics of these parameters are presented in Table 1.

Table 1 Statistical parameters of DO and BOD at different monitoring stations

Station	Mean DO (mg/L)	DO Variance	Mean BOD (mg/L)	BOD Variance	DO Coefficient of Variation (%)	BOD Coefficient of Variation (%)
Reni	7.2	1.1	2.8	0.7	15.3	25.4
Izmail	6.9	1.3	3.2	0.9	18.8	28.1
Kiliya	6.4	1.5	3.5	1.0	23.4	30.5
Vylkove	5.8	1.8	4.1	1.2	31.0	35.7

The lowest average DO concentration was recorded in Vylkove (5.8 mg/L), indicating an increased risk of oxygen depletion in this section of the Danube. Similarly, the highest BOD level was also observed in Vylkove (4.1 mg/L), suggesting significant organic pollution pressure. The most stable conditions were found in Reni (DO = 7.2 mg/L, BOD = 2.8 mg/L), indicating a better oxygen regime.

To assess the risk of organic pollution, the probability of exceeding critical levels was calculated oxygen depletion risk: $DO < 6 \text{ mg/L}$; increased organic pollution risk: $BOD > 3 \text{ mg/L}$.

Table 2 Probability of exceeding DO and BOD standards

Station	P($DO < 6 \text{ mg/L}$)	P($BOD > 3 \text{ mg/L}$)
Reni	10.5%	20.2%
Izmail	15.8%	27.3%
Kiliya	23.4%	35.9%
Vylkove	38.6%	49.2%

The highest pollution risk was identified at Vylkove, where the probability of DO dropping below 6 mg/L reached 38.6%, and BOD exceeding 3 mg/L was 49.2%. Kiliya also falls into the high-risk zone, particularly for organic pollution (35.9%). Reni had the most favorable conditions, with the lowest probability of oxygen depletion.

To assess water quality changes over time, long-term trends in DO and BOD were analyzed: DO exhibits a gradual negative trend, especially in the lower reaches (Vylkove, Kiliya), indicating increasing anthropogenic pressure. BOD shows an upward trend, reflecting a growing presence of organic pollutants in the river. The most critical period for DO and BOD levels occurs during summer months, attributed to higher water temperatures and reduced ecosystem self-recovery capacity.

The most problematic area is the lower section (Vylkove, Kiliya), which has the highest BOD levels and lowest DO concentrations. Pollution levels increase downstream, indicating a cumulative effect of anthropogenic impacts. The middle Danube (Reni, Izmail) shows better water quality, but a gradual deterioration trend is still observed. These findings highlight the necessity of enhanced monitoring efforts, particularly in the lower Danube, where oxygen depletion and organic pollution pose significant environmental risks.

Conclusions

The study revealed a declining trend in dissolved oxygen (DO), particularly in the lower Danube (Kiliya, Vylkove), indicating a deterioration of the oxygen regime. Conversely, biochemical oxygen demand (BOD) shows an increasing trend, suggesting rising organic pollution and its accumulative effect. The highest probability of exceeding critical thresholds ($DO < 6 \text{ mg/L}$, $BOD > 3 \text{ mg/L}$) was recorded in Vylkove (38.6% and 49.2%), highlighting a significant environmental risk in this area. The most stable conditions were observed in Reni, where DO and BOD concentrations were more balanced.



The geographical pollution analysis indicated that Vylkove and Kiliya are high-risk zones, as they are located in the lower river section, where organic pollution accumulates. Izmail represents an intermediate zone, with moderate risks of DO depletion and increased BOD levels. Reni exhibited the best water quality, benefiting from the river's self-purification capacity and lower anthropogenic impact. These findings emphasize the need for enhanced water quality monitoring, particularly in the lower Danube, to mitigate the risks of oxygen depletion and organic pollution accumulation.

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