

Seasonal variation of dissolved oxygen in river water in an urbanized area: example of the Vladayska River

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Сезонна вариация на разтворения кислород в речни води в урбанизираните територии: по примера на р. Владайска

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Резюме. Настоящото изследване разглежда сезонните вариации в концентрациите на разтворен кислород в урбанизираните реки, с фокус върху река Владайска, град София. Изследвано е влиянието на ключови фактори като температура, биологична потребност от кислород (БПК₅), химическа потребност от кислород (ХПК), валежи и речен отток върху колебанията в нивата на разтворен кислород. Водите на река Владайска, подложени на значителен антропогенен натиск, показват значителни колебания в нивата на разтворен кислород, като най-ниските концентрации са регистрирани през лятото и есента. Тези периоди съвпадат с високи температури на водата, нисък речен отток и повишени нива на БПК₅ и ХПК, което предполага повишена консумация на кислород от органични и химически замърсители. Резултатите показват, че нивата на разтворен кислород в река Владайска падат под критичните прагове (5 mg/L) през лятото и есента, което представлява екологичен риск и намалява способността за самопочистване на речните води. През пролетта и зимата по-високите нива на разтворен кислород се свързват с по-ниски температури и увеличен обем на речния поток. Това проучване акцентира върху сезонния спад в нивата на разтворен кислород в урбанизираните реки, дължащ се както на естествени процеси, така и на интензивна антропогенна дейност, подчертавайки значението на непрекъснатия мониторинг на качеството на водата.

Ключови думи: качество на водата, физикохимични показатели, динамика, водни екосистеми, екологичен риск.

Abstract. This study investigates the seasonal variation of dissolved oxygen (DO) concentrations in urbanized rivers, with a focus on the Vladayska River in Sofia, and examines key influencing factors such as temperature, biological oxygen demand (BOD₅), chemical oxygen demand (COD), precipitation and river runoff. The waters of the Vladayska River, subjected to significant anthropogenic pressure, show significant fluctuations in DO levels, with the lowest concentrations recorded in summer and autumn. These periods coincide with high water temperatures, low river discharge, and elevated BOD₅ and COD levels, indicating increased oxygen consumption by organic and chemical pollutants. The results show that DO levels in the Vladayska River fall below critical thresholds (5 mg/L) in summer and autumn, representing an ecological risk and reducing river waters' self-purification capacity. In spring and winter, higher DO levels suggest a seasonal recovery associated with cooler temperatures and increased river flow volume. This study accentuates the seasonal decline in dissolved oxygen levels in urbanized rivers due to both natural processes and intensive anthropogenic activity, highlighting the importance of continuous water quality monitoring.

Keywords: water quality, physicochemical parameters, dynamics, water ecosystem, ecological risk.

Introduction

Rivers within urbanized territories are subjected to considerable anthropogenic impacts that alter their natural chemical composition, often leading to a decline in water quality (Glińska-Lewczuk et al.,

2016; Mallin et al., 2009). Worldwide, urban water ecosystems experience intense stress from anthropogenic pressures (Huang et al., 2017). Rivers in urban zones can become highly contaminated by domestic and industrial wastewater, which deteriorates their ecological status. Such pollution exerts a

functional toll on urban aquatic ecosystems, hindering the natural biological development of aquatic organisms and reducing the rivers' self-purification capacity (Rabalais, et al., 2002; Wang, et al., 2016). The primary driver of these adverse outcomes is the reduced concentration of dissolved oxygen (DO) (Wang et al., 2012). Over the past two decades, a global decline in dissolved oxygen has been observed, largely due to pollution, nutrient influx, and climate warming (Breitburg et al., 2018). This trend also affects rivers that flow through densely populated or heavily urbanized regions.

Dissolved oxygen is a critical variable for assessing water quality and is one of the most significant indicators of deteriorated surface water bodies (Rajwa-Kuligiewicz et al., 2015; Wang et al., 2003; Sánchez et al., 2007). It is vital for aquatic organisms and is involved in numerous biogeochemical processes (North et al., 2014). DO levels influence the metabolism, development, reproduction, and population dynamics of aquatic heterotrophic organisms (Hull et al., 2000). Within aquatic systems, DO is generally regulated by photosynthesis, aerobic respiration by microorganisms, and biological and chemical oxygen demand (Banerjee et al., 2019). Low DO concentrations directly impact the diversity and abundance of fish and other organisms, thus altering the ecological balance. The key causes of DO depletion include organic pollution, eutrophication, and nitrification (Rabalais et al., 2010; Li et al., 2022). Rapid decreases in DO lead to toxic algal blooms and loss of biodiversity, exacerbating the degradation of water ecosystems' overall ecological status (Bricker et al., 2007; Howarth et al., 2011).

Waters in good ecological status typically maintain DO concentrations above 6.5–8 mg/L (USEPA, 1986). Levels below 5 mg/L induce stress in aquatic organisms, while levels under 2 mg/L cause hypoxia and mortality in both lower and higher organisms (EPA, 2000; Lai et al., 2013). According to Ordinance № 4 on characteristics of surface waters in Bulgaria, dissolved oxygen must not be below 6 mg/L. DO concentration is not constant and varies over time (diurnal, seasonal, and annual fluctuations), influenced by factors like water temperature, atmospheric pressure, hydrodynamic processes, pollution, nutrient levels, and biological activity. Water salinity and pH also correlate with DO levels (Cox, 2003; Rajwa et al., 2014; He et al., 2011; Mandal et al., 2012; Banerjee et al., 2019). In the

study by Nakova et al. (2009) it was noted that the dynamics of dissolved oxygen in river waters depend on the processes of diffusion, microbial respiration, photosynthesis and aeration from tributaries. Precipitation and river runoff are also important factors that under different conditions can affect DO levels (Biggs and Close, 1989; He et al., 2011; Bello et al., 2017).

The present research aims to study the seasonal fluctuations in the content of dissolved oxygen in the waters of the Vladayska River, as well as to analyze the influence of temperature, biological and chemical oxygen demand, precipitation and river runoff on these fluctuations. This will help reveal the dynamics of dissolved oxygen and the conditions under which it is expected to decrease. The study is part of the project "Assessment of the water quality in urbanized areas based on the example of the Vladayska River, Sofia" and will support a more detailed study of the state of the waters of the Vladayska River.

Materials and methods

Study area

The Vladayska River originates from the northwestern slope of Vitosha Mountain, with its source located near Cherni Vrah at approximately 2250 m altitude. Initially flowing northwest, the river shifts direction near the village of Vladaya (900 m), turning north-northeast as it traverses the Sofia Basin. Near Kubratovo village, it merges with the Perlovska River due to riverbed modifications, before eventually joining the Iskar River. The river covers 33.2 km from its source to its confluence, with the majority of its course (22.3 km) running through the urbanized areas of Sofia. Along its route, the Vladayska River receives several smaller left- and right-bank tributaries, including the Planinitsa and Domuz Dere rivers, with its most substantial left tributary being the Sukhodolska River, which spans 21 km, of which 13.7 km also flow through urbanized areas (Fig. 1). The Vladayska River catchment area includes the northwestern slopes of Vitosha Mountain, the northeastern slopes of Lyulin Mountain, and part of the Sofia Basin, covering a total area of 145 km², with 65 km² classified as urbanized. The elevation range of the catchment extends from 500 to 2280 m, with an average altitude of 890 m. The total elevation drop from the source area

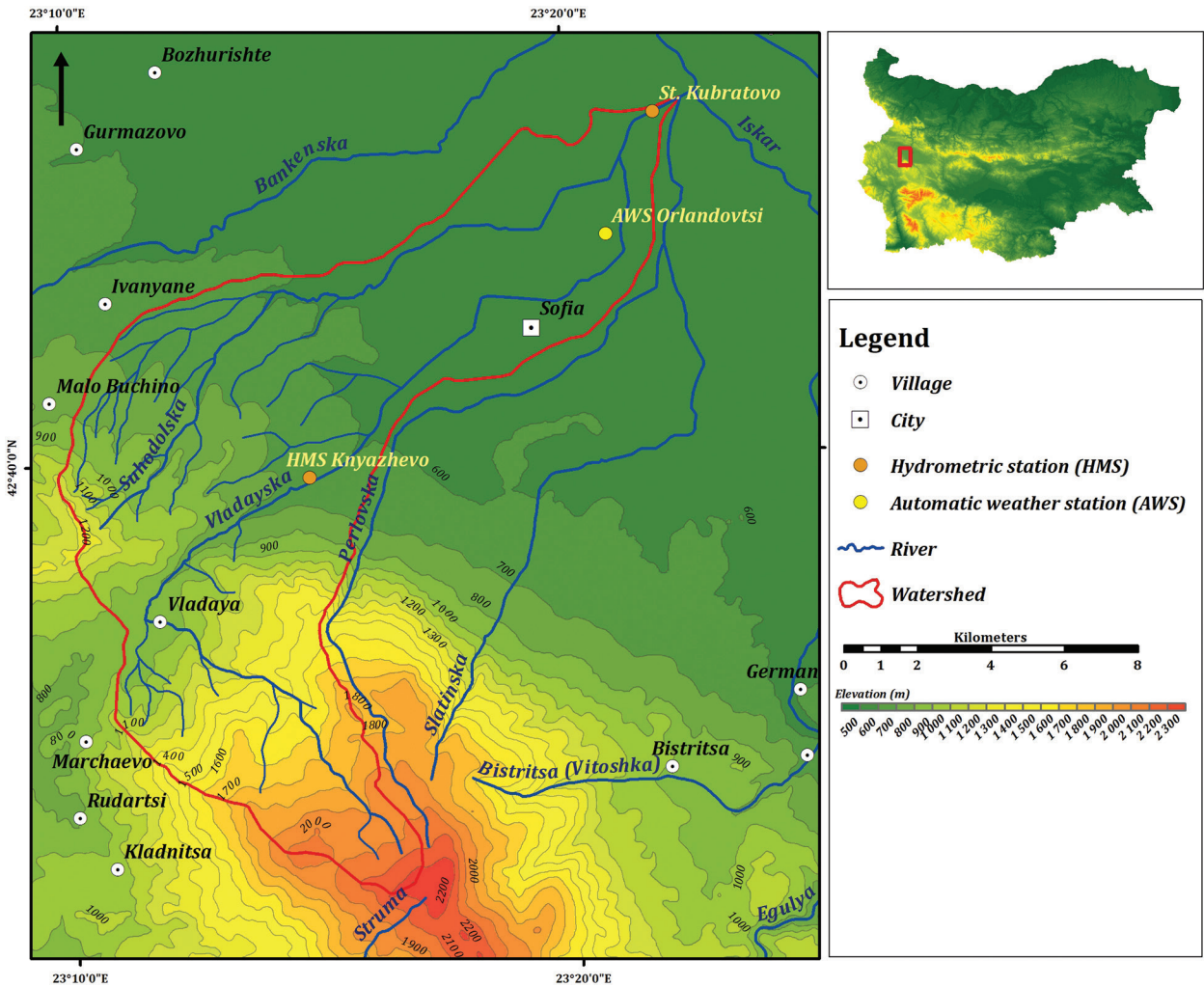


Fig. 1. Study area and sample sites

to the confluence follows a north-northeast trajectory, with an average terrain slope of 6° . The steepest gradients, reaching $40\text{--}45^\circ$, occur along the slopes of Vitoshka and Lyulin Mountains, while the gentlest slopes, approximately $2\text{--}3^\circ$, are found within the Sofia Basin.

The region is characterized by a temperate-continental climate in the lower part near the confluence with the Iskar River, gradually transitioning to a mountain climate with increasing altitude toward the source area (Rachev & Nikolova, 2009). Winter temperatures in the region are around or below 0°C , while summer temperatures approach 20°C ; however, temperatures in the mountainous part of the catchment decrease by approximately 0.6°C per 100 m (Velev, 2010). The distribution of precipitation by season is characterized by a rainy spring – 170 mm of seasonal total precipitation, followed by summer

with a total precipitation of 163 mm, autumn with 140 mm, and in winter only falling to 119 mm. Intense, torrential rainfall is typical of the study area during the warm half of the year, which can cause sudden increases in river levels and regional flooding. The Vladayska River has an average annual flow rate of $0.63\text{ m}^3/\text{s}$ (Hydrological reference book of the Rivers in Bulgaria, Vol. II, 1957). Most of its flow comes from rain and snow, with substantial groundwater contributions (up to 44.4%) in its upper course (Benderev et al., 2015). The river's flow regime is marked by high water levels in spring and low water levels in late summer and autumn, with peak discharge occurring in May and June, and the lowest flows observed in August and September. According to the Standardized Runoff Index (SRI), the Vladayska River basin is classified as moderately drought-prone (Hristova & Ivanova, 2018).

Output data

This study utilized data for six indicators commonly used to assess water quality and widely applied in quantitative and qualitative monitoring of river waters. These include dissolved oxygen, biological oxygen demand (BOD₅), chemical oxygen demand (COD), water temperature, rainfall amounts, and river discharge. Data for dissolved oxygen, BOD₅, COD, and water temperature consist of 45 measurements taken between 2011 and 2021, with sampling conducted four times a year, once in each season. These measurements were taken at the Kubratovo station and published by the Executive Environment Agency (EEA). The station is located in the lower course of the Vladayska River, before its confluence with the Iskar River, after the river has flowed through the urbanized area of Sofia.

Rainfall data are presented as monthly totals for the period 2011–2021, measured at the Orlandovtsi Automatic Weather Station (AWS) situated at an altitude of 525 m in the river's lower course, just before it exits the densely built-up area of Sofia. Average monthly river discharge was measured at the Knyazhevo Hydrological Monitoring Station (HMS No. 18420), located in the middle course of the Vladayska River as it enters Sofia. HMS Knyazhevo is part of the river discharge monitoring network of the National Institute of Meteorology and Hydrology (NIMH).

Data analysis

For the purposes of this study, widely used statistical methods were applied to analyze the data, including correlation analysis and the construction of a correlation matrix to examine linear relationships among the indicators. Data were grouped by season and presented through boxplot diagrams to observe the seasonal dynamics of dissolved oxygen and the

seasonal fluctuations of other indicators. This approach aids in assessing their influence on seasonal changes in oxygen levels in the aquatic environment. The correlation matrix and boxplots were generated in the programming language for statistical analysis and visualization R (R Core Team, 2023).

Results and discussion

Variation in Physicochemical Parameters

Table 1 presents the descriptive statistics for the indicators DO, temperature, BOD₅, COD, rainfall, and river discharge. During the study period, dissolved oxygen ranged between 10.6 and 1.6 mg/L, with an average value of 5.5 mg/L. Temperature varied from 23 °C to 1.8 °C, with an average of 12.7 °C. The biological oxygen demand over 5 days (BOD₅) reached a maximum of 69 mg/L and a minimum of 3.9 mg/L. The average concentration is 17.4 mg/L. Chemical oxygen demand (COD) values ranged from 200 to 17.2 mg/L, with an average of 55.9 mg/L. The maximum monthly rainfall total was 141.7 mm, while the minimum monthly rainfall was 1.4 mm. The average monthly river discharge ranged from 2.5 to 0.05 m³/s, with a mean value of 0.59 m³/s.

Correlation dependence between the studied indicators

In this study, a correlation analysis was conducted to establish the relationships among the indicators. The correlations are presented in a correlation matrix (Fig. 2) using Pearson's method. An autocorrelation was observed between dissolved oxygen (DO) and water temperature ($r = -0.59$). Higher water temperatures correspond to lower DO levels, while lower temperatures result in higher DO lev-

Table 1
Descriptive statistics

Parameters	Max	Min	Mean	SD
DO (mg/l)	10.6	1.6	5.5	2.01
Temperature (°C)	23	1.8	12.8	–
BOD ₅ (mg/l)	69	3.9	17.4	16.6
COD (mg/l)	200	17.2	55.9	44.1
Rainfall (mm)	142.4	1	49.4	30.6
River flow (m ³ /s)	2.5	0.05	0.5	0.59

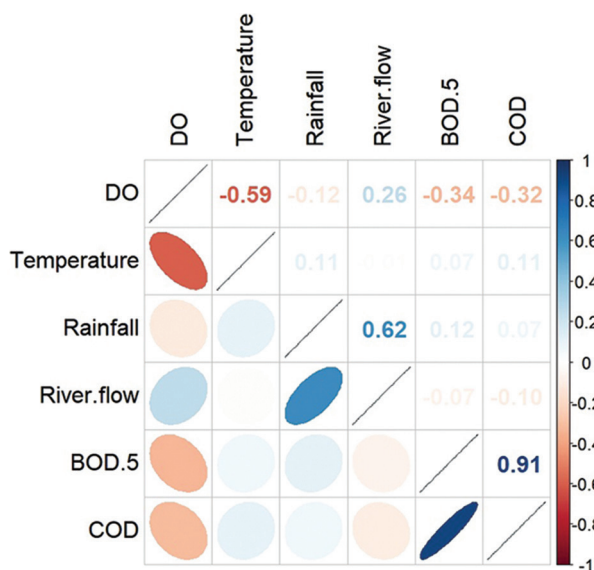


Fig. 2. Correlation matrix

els. Similar relationships between these indicators have been observed in studies by Bello et al. (2017) and Khani and Rajaei (2017). This is attributed to the fact that water temperature influences numerous biological, chemical, and physical processes in aquatic environments. River water temperature is determined by air temperature, solar radiation, and the nature of river recharge (Riđanović et al., 2010; Harvey et al., 2011). Higher temperatures increase microbial activity in the water, consuming more oxygen and thus reducing DO levels (Desmet et al. 2011, Rajwa-Kuligiewicz et al., 2015). Another reason is that oxygen dissolves more easily in colder water than in warmer water (Harvey et al., 2011).

Dissolved oxygen shows a weak negative correlation with biological and chemical oxygen demand, with correlation coefficients of $r = -0.34$ and $r = -0.32$, respectively. High oxygen demand tends to lower DO levels in water (Hasan et al., 2019), however, many other factors influence this relationship, so the correlation is not strong. DO shows a very weak correlation with rainfall ($r = -0.12$) and river discharge ($r = 0.26$). These are indirect factors that do not have a linear relationship with DO due to the complexity of dynamic processes occurring within river waters.

There is a high positive correlation dependence between BOD₅ and COD indicators ($r = 0.91$). An expected positive correlation with a coefficient of $r = 0.62$ also occurs between precipitation and river

runoff. As the rainfall increases, so does the river runoff. The not-very-high correlation coefficient indicates the influence of many other factors and environmental conditions that complicate this dependence.

Seasonal variation of dissolved oxygen and other parameters

This study analyzed intra-annual variations in dissolved oxygen and other key parameters over the study period. Seasonal variation graphs for each parameter are presented in Fig. 3. The top, middle, and bottom lines of the box in Fig. 3 represent the upper quartile (75%), median, and lower quartile (25%), respectively. The whiskers are used to determine the minimum and maximum values.

Dissolved oxygen concentrations in the waters of the Vladayska River show distinct seasonal patterns, with the highest levels observed in spring and winter. In spring, DO values range from 3.5 mg/L to 10.4 mg/L, while in winter, concentrations vary from 5.2 mg/L to 10.55 mg/L, reaching a peak of 10.55 mg/L in February. Summer and autumn display lower DO concentrations, ranging from 1.6 mg/L to 7.4 mg/L in summer and from 2.7 mg/L to 6.7 mg/L in autumn, with the minimum concentration of 1.6 mg/L recorded in August. The graph reveals that 75% of data points for summer and autumn are at or below the threshold of 5 mg/L, indicating oxygen deficits in river waters during these seasons. In contrast, all winter data points exceed the 5 mg/L threshold, while in spring, approximately 25% of the samples fall below this level. The seasonal dynamics of dissolved oxygen is addressed in the study by Liu et al. (2020), which also found a decrease in dissolved oxygen in summer at the surface of the Pearl River Estuary and at depth in autumn. In spring and winter, both at the surface and at depth, DO rises.

Biological oxygen demand (BOD) indicates the oxygen required by microorganisms in water. BOD₅ represents the amount of oxygen consumed by bacteria and other microorganisms as they decompose organic matter under aerobic conditions. BOD₅ is measured by determining the initial DO content of a certain volume of sample and after a five-day incubation period at 20°C, the sample is removed from the incubator and the final DO content is taken. The difference between the initial and final contents is

the oxygen consumption. Seasonal fluctuations in BOD₅ values in the waters of Vladayska Rivers show a significantly higher oxygen demand in autumn compared to other seasons. In spring, summer, and winter, BOD₅ values range between 4.4 and 14 mg/L, with occasional peaks up to 59 mg/L. In autumn, BOD₅ varies from 3.9 to 49.4 mg/L, with two instances of exceptionally high levels at 64.7 and 69 mg/L. In all seasons, BOD 5 values higher than the permissible content in surface waters of 2.5 mg/l are observed (Ordinance № 4). In

the present study, the biological demand for oxygen repeatedly exceeds the permissible standards for water quality. In the study of Varbanov et al. (2021) also reported 10- to 25-fold excesses of BOD₅ in the waters of the Vladayska River. Chemical oxygen demand (COD) is another indicator measuring oxygen consumption from microorganisms for the decomposition of organic matter and the oxidation of inorganic chemicals. Chemical oxygen demand is measured as a closed water sample is incubated, with a strong chemical oxidant under specific con-

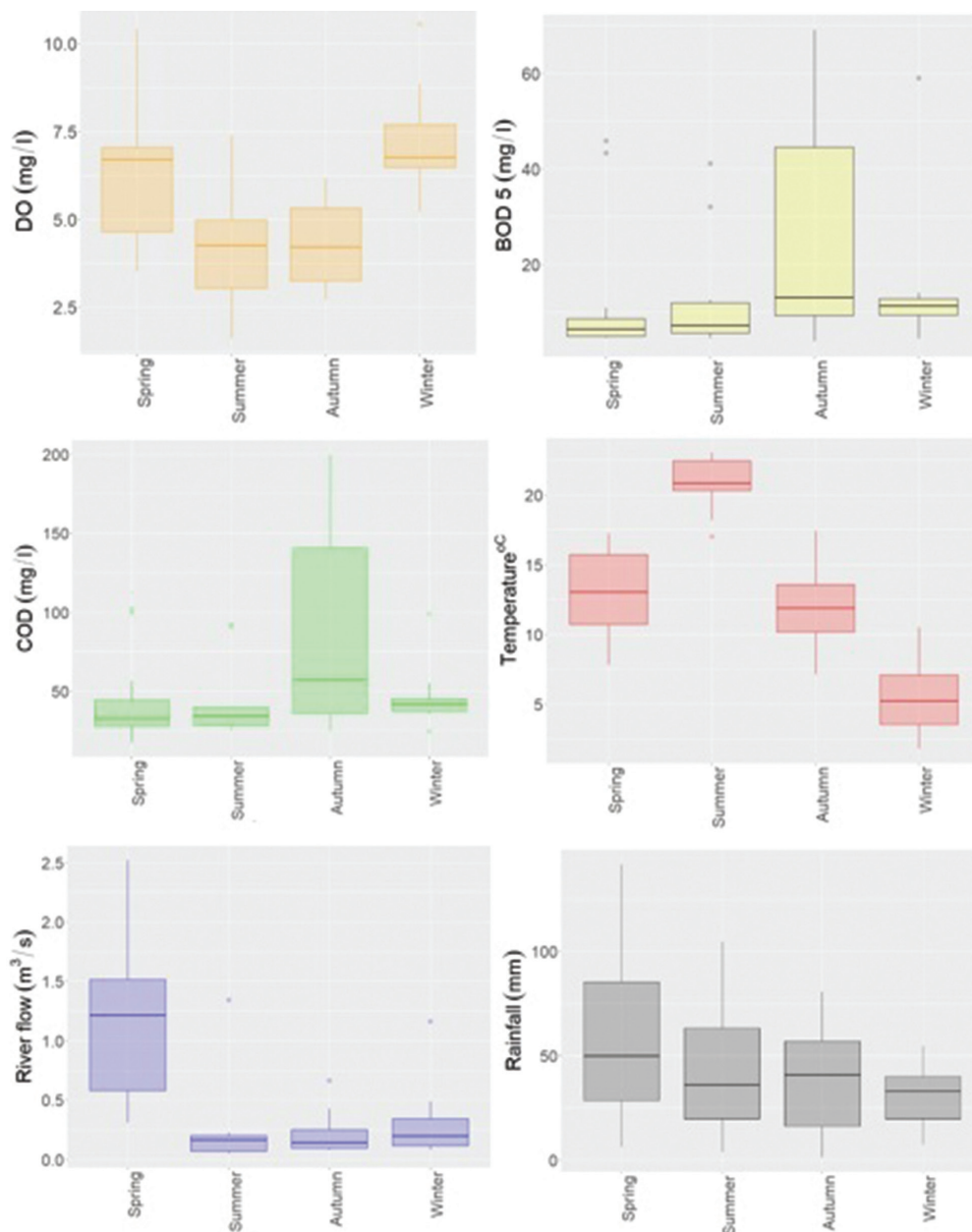


Fig. 3. Seasonal variation of dissolved oxygen and other indicators

ditions of temperature and for a particular period. COD measurements are commonly made on samples of wastewater or natural waters contaminated by domestic or industrial wastes. Seasonal fluctuations of COD in the waters of the Vladayska River are similar to those of BOD₅, with a sharp increase in autumn compared to other seasons. The high BOD₅ and COD levels in autumn coincide with a decrease in DO, although the minimum DO levels are registered during the summer. In autumn, COD reaches up to 200 mg/L, while in other months, it peaks at 102 mg/L. A number of studies have found an increase in biological and chemical oxygen demand during the dry season compared to the rainy season (Uddin et al., 2015, Liu et al., 2024, Wang et al., 2022). The concentration of pollutants in smaller volumes of river water, dilution of pollutants during the rainy season, reduced hydrodynamics during the dry season, and higher temperatures during the dry season have been cited as possible causes.

The seasonal dynamics of dissolved oxygen (DO) in water largely depend on water temperature. The World Health Organization reports that lower temperatures typically correlate with higher dissolved oxygen concentrations, while warmer, polluted waters have reduced DO levels (WHO, 2006).

In the lower course of the Vladayska River, water temperature follows the seasonal air temperature pattern. During spring, water temperatures range from 7.8 °C to 17.2 °C, reaching their highest values in summer, between 17 °C and 23 °C. Autumn temperatures, similar to spring, fluctuate between 7.1 °C and 17.4 °C, while winter months record the lowest water temperatures, ranging from 1.8 °C to 10.5 °C. In summer, when water temperatures peak, DO levels are at their lowest. Although water temperature gradually decreases in autumn, DO remains low throughout the autumn months, with a slight increase toward the end of the season. And in other studies, in which they investigated the dynamics of DO, they found that during the warm months the concentration of dissolved oxygen decreases (Rajwa-Kuligiewicz et al., 2015, Harvey et al., 2011).

The seasonal variations in Vladayska River discharge show high water volumes in spring, ranging from 0.3 m³/s to 2.5 m³/s. During the other seasons, discharge is significantly lower, varying between 0.05 m³/s and 0.67 m³/s, with occasional increases in winter up to 1.3 m³/s and in summer up to 1.2 m³/s. Reduced water volumes in the riverbed can lead to

higher pollutant concentrations, decreased flow dynamics, limited oxygen exchange with the atmosphere, and accelerated water warming, all of which increase microbial activity and oxygen consumption. They, in turn, lead to a reduction in DO.

Rainfall acts as an indirect factor in seasonal DO dynamics, potentially contributing to either oxygen saturation or depletion. The boxplot diagram of the seasonal distribution of precipitation for the studied period shows that the highest average monthly amount of precipitation is registered in the spring months, followed by the summer, autumn and winter months. Precipitation has a multidirectional effect on dissolved oxygen concentration. On the one hand, the small amount of precipitation implies a small river runoff and a correspondingly reduced concentration of dissolved oxygen during the dry season. On the other hand, they can influence with their intensity by supporting the transport and entry of pollutants from urbanized areas into the river bed (Liu et al., 2024, Zhang et al., 2022).

Conclusion

This study examines a small but essential set of factors influencing dissolved oxygen (DO) levels in the waters of the urbanized Vladayska River system. The indicators describing these factors are easy to measure and are typically included in most monitoring programs for quantitative and qualitative river water assessments.

The analyses performed in the present study show that the seasonal variation of dissolved oxygen is mainly due to natural factors, namely water temperature. This is evident by the significant correlation between DO and water temperature ($r = -0.59$). DO has a weak relationship with BOD ($r = -0.34$) and COD ($r = -0.32$), which indicates the secondary influence of pollutants entering the river. The lack of correlation dependence between river runoff and precipitation indicates their indirect importance for the dynamics of DO. The lowest DO levels are recorded during the summer and autumn, coinciding with the highest water temperatures, and the highest biological and chemical oxygen demand. During the summer, dissolved oxygen reaches critically low levels, posing a risk to aquatic ecosystems.

Summer and autumn are periods of pronounced water stress and reduced self-purification capacity for the river. The natural conditions, combined

with urbanization and high anthropogenic load, significantly worsen the quality of the waters of the Vladayska River, emphasizing the importance of effective monitoring and intervention measures to mitigate environmental impact and protect its ecological balance.

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