

Assessment of Surface Water quality in Highly Urbanized Areas: A Case Study of the Vladayska River in Sofia

Kalina Radeva^A, Zvezdelina Marcheva^A, Simeon Matev^A, Ilia Tamburadzhiev^A

^A Sofia University "St. Kliment Ohridski" Sofia, Bulgaria; ORCID KR: 0000-0002-7192-3385; ZM: 0000-0003-1539-9248; SM: 0000-0001-8192-558X; IT: 0000-0001-7365-9082

KEYWORDS

- water pollution
- urban river
- ► PCA
- water quality index
- Bulgaria

ABSTRACT

This study investigates the impact of Sofia's urban areas on the physicochemical parameters of water quality along the Vladayska River. Two sections of the river were analyzed: (1) an upper, relatively uppolluted section from the source to the Vladaya district, used as a reference due to limited data availability, and (2) a lower section (Kubratovo), downstream of Sofia, influenced by anthropogenic activities. Based on the results, significant changes in the physicochemical parameters were observed in the lower section. Principal component analysis (PCA) was conducted on data for 15 water quality indicators, precipitation, and river runoff under different hydrological conditions (high flow, low flow, and winter season) for the lower section (Kubratovo). The PCA results identified nutrient and organic matter pollution and mineral content as key drivers of water quality variability. Additionally, hydrological factors were found to indirectly influence water quality in the downstream section at Kubratovo. As revealed by the CCME WQI index, the Vladayska River's upper section also experienced poor water quality between 2013 and 2015, improving to good in 2016–2018, likely due to reduced pollution from tourism and residential sources. In contrast, the downstream section at Kubratovo consistently exhibited poor water quality from 2010 to 2021, reflecting ongoing urban pollution with no observed trend of improvement.

Introduction

River water quality is one of the current topics of theoretical and applied hydrology, ecological and urban hydrology, and one of the main problems in the planning and management of water resources. The chemical, physical, and biological characteristics of surface water, based on standards for its use, are related to human health, food production, wetland ecosystems, economic development and social growth in our communities (Jha et al. 2020). Questions about the protection of watercourses from the introduction of anthropogenic ingredients in undissolved and dissolved state have been raised for several decades. According to UNESCO's report (International Initiative on Water Quality, 2015), water quality problems pose new threats to water security and sustainable development and represent a major challenge in both economically developed and developing countries. The question of the quality of surface water in urban areas, where a combination of point and diffuse sources of pollution is registered, is particularly acute (Strokal et al., 2021). Rivers in cities perform important ecological and economic functions. They are a reliable source of water for various economic needs, an important element of na-

^{*}Corresponding author: Kalina Radeva; <u>kradeva@gea.uni-sofia.bg</u>

doi: 10.5937/gp29-54683

Received: November 10, 2024 Revised: February 28, 2025 Accepted: March 10, 2025

ture and specific ecological corridors in the urban landscape (Przyjazny et al., 2006; Viji et al., 2014).

Many studies show that the state of urban rivers is strongly influenced by human activities, especially changes in land use and cover in the process of urbanization (Giri et al., 2016). Under the influence of urbanization, pollution from non-point sources, caused by the runoff of rainwater, has become one of the main reasons for the deterioration of the water environment in cities (Muschalla et al., 2008; Egodawatta et al., 2009; Van Der Hoek et al., 2011; Van der Sterren et al., 2013). Determining the relative influence of these factors on water quality remains a serious challenge for science and water management (Interlandi & Crockett, 2003).

The impact of urban areas on water quality is mainly due to two key factors - significant pollutant production and a reduction in the retention capacity of river basins as a result of an increase in impervious surfaces (Sun & Lockaby, 2012). The conversion of parts of water catchments from natural to urban cover increases the concentrations of sediments and nutrients from tens to hundreds of times in surface waters. The imperviousness threshold, at which changes in water quality and runoff regime occur, varies from 5% to 20% of the catchment area (Medupin, 2020). In addition to sediments and nutrients, urban waters often contain pharmaceuticals, pesticides, heavy metals, pathogenic microbial populations and organic pollutants (USGS, 1999; Paul & Meyer, 2001). The release of nutrients (especially nitrogen and phosphorus), which originate mainly from agriculture and domestic wastewater, can cause eutrophication of surface waters (Newman et al., 2006). Point sources are the main source of river pollution in cities (Medupin et al., 2020). Some point sources, such as domestic sewage, release pollutants at relatively constant rates, while others, such as leaks and accidental spills, are variable or intermittent. Wastewater treatment plants serving permanent populations contribute continuous nutrient discharges to watercourses, further impacting water quality.

Both organic pollution and heavy metal contamination remain unresolved issues facing the water resources management sector in Bulgaria. This concerns rivers in urbanized areas, which face significant environmental challenges, mainly related to urbanization, pollution and insufficient wastewater treatment infrastructure. Another form of pressure is hydromorphological, related to changes in the physical characteristics of river channels. A specific problem is also the rectification of river channels, which leads to the loss of their ecological functions and biodiversity. Instead of using environmentally friendly solutions, rivers are often treated as engineering structures, which limits their potential to support the ecology and living conditions of the city. In addition, frequent dumping of waste into river channels and lack of effective monitoring further deteriorate their condition.

To better understand these challenges, the objective of this study is to analyze the quality of river water in a highly urbanized area by examining the current physicochemical status of a small river course, the Vladayska River in Sofia. This is achieved by applying the water quality index and statistical analysis in R, considering both urbanized and non-urbanized areas of Sofia to identify the main pollutants and factors affecting the river water.

Materials and methods

Study area

The Vladayska River, with a drainage area of 151 km² and a length of 37 km, originates below Cherni Vrah and Selimitsa, draining the western Vitosha Mountain. Its basin comprises three sections: the upper part in the Vitosha and Lyulin Mountains, the middle part in the foothills, and the lower part in the Sofia Valley (Fig.1). Flowing through Sofia, Bulgaria's capital with over 1.2 million residents, the river passes neighborhoods like Knyazhevo, Ovcha Kupel, and Orlandovtsi before merging with the Perlovska River. Within Sofia, the riverbed and drainage network are heavily modified by human activity.

The river lies in a temperate-continental climate zone, with winter temperatures around 0°C and summer averages near 20°C. Peak precipitation occurs in May and June, with the lowest in February, increasing with altitude (Velev, 2010). Snowmelt, primarily in April, contributes significantly to peak flows, while torrential summer rainfall often causes rapid water level rises and localized flooding, which has intensified in recent years (Bocheva & Malcheva, 2020). The multi-annual average flow was 0.727 m³/s from 1961–2002, decreasing to 0.48 m³/s during 2010–2021. In the seasonal distribution of runoff, there is a pronounced spring high water period, during which up to 70% of the annual flow occurs, followed by a summer-autumn and less pronounced winter low water period.

Water quality and hydrological data

In this study, data from the Environmental Executive Agency's control monitoring were used. Monitoring was conducted at two points: before the city of Sofia (Vladayska River – Vladaya) and at its exit (Vladayska River – Kubratovo) (Table 1). The available data cover different periods: for the Vladaya station, monitoring was conducted from 2013 to 2018 before being discontinued, while the Kubratovo station has a longer dataset covering eleven years from 2010 to 2021. River Vladayska has been studied and evaluated for 15 physicochemical parameters:



Figure 1. Study area with the location of the measuring stations.

- 1. General physicochemical parameters temperature, dissolved oxygen, electrical conductivity, total hardness, total dissolve solids, chlorides and sulfates.
- Indicators of organic pollution ammonium nitrogen (N - NH₄⁺), nitrite nitrogen (N–NO₃), nitrate nitrogen (N–NO₂), total nitrogen, total phosphorus, orthophosphates (P–PO₄), biochemical oxygen demand (BOD₅), and chemical oxygen demand (COD).

The data on river flow includes average monthly values for the period 2010-2021 at Knyazhevo hydrological station. The data was provided by NIMH (National Institute of Meteorology and Hydrology). Precipitation data are presented by monthly precipitation sum for the same period from the Orlandovtsi station. The station is located at 525 m above sea level, on the right bank of the Vladayska river, on a coastal slope above an extensive river floodplain. The station is automatic, model WS2816, and started operation in March 2015 (Table 1).

Data analysis and water quality analysis

In this study, correlations between water quality indicators were examined, and Principal Component Analysis (PCA) was applied to the Kubratovo monitoring station, located downstream of Sofia, to identify key factors influencing water quality. PCA was employed to reduce dimensionality and extract the most significant variance from

Table 1. Information about the Location of Water Sampling Points, Gauging,and Meteorological Stations

Location and description	Elevation (m)	Latitude (°)	Longitude (°)
Vladayska – Vladaya (upstream) - water sampling station	891.5	42.62609	23.20245
Vladayska – Kubratovo (downstream) - water sampling station	671	42.75417	23.37417
Kniazevo – gauging station	525.3	42.6563	23.2316
Orlandovtsi - meteo station	525.3	42.75056	23.34668

multiple water quality parameters. This site was selected for analysis due to its extended monitoring period (2010– 2021) and the availability of a more comprehensive dataset, providing a robust foundation for statistical evaluation and interpretation.

PCA is a widely used method for identifying significant contributors to river water quality and potential pollution sources (Nasir et al., 2011; Olsen et al., 2012; Glińska-Lewczuk et al., 2016; Zeinalzadeha & Rezaeib, 2017; Tripathi & Singal, 2019). It is particularly effective for analyzing relationships among water quality indicators and assessing the importance of various factors under different hydrological conditions, including high-flow, low-flow, and winter periods. The PCA was conducted in the R environprincipal components. This approach facilitated the identification of the most significant factors contributing to water quality variability.

Furthermore, the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) was applied for an integrated assessment of the Vladayska River's water quality. The calculations were performed using nine physicochemical parameters, in accordance with regulatory requirements for achieving "good quality status", as well as the reference values for surface water bodies of type R2 (Vladayska River before Vladaya) and R5 (Vladayska River at Kubratovo), as specified in Ordinance No. H-4/14.09.2012 on the characterization of surface waters (Table 2).

Table 2. Reference threshold values defining the good state for water parameters in surface water bodies of types R2 and R5, as specified in Regulation 4/2012.

Code	Water quality status	Variables										
		EC	DO2	N-NH ₄	N-NO ₃	N-NO ₂	N	Р	P-PO ₄	BOD _s		
		μS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l		
R2	Good	750	8-6	0.04-0.4	0.2-0.5	0.01 - 0.025	0.2 -0.8	0.012- 0.03	0.01-0.02	1-2.5		
R5	Good	750	8–6	004 -0.4	0.5 –1.5	0.01 - 0.03	0.5 -1.5	0.025-0.075	0.02-0.04	1.2-3		

ment using the prcomp function, with standardized data to ensure comparability. A scree plot (fviz_eig()) was used to visualize the contribution of principal components, while factor rotation was applied to improve interpretability. Additionally, a biplot (fviz_pca_var) illustrated the relationships between variables and their influence on the The CCME WQI index consists of three significant factors: scope (F1), frequency (F2), and amplitude (F3). The final result of the CCME is a dimensionless number that describes the state of water quality from 0 (poor quality) to 100 (high quality) (CCME, 2003; Sutadian et al., 2016) (Table 3).

able 3. Ranking system and	interpretation of	water quality based on	CCME WQI (CCME, 2001)
----------------------------	-------------------	------------------------	-----------------------

Rating	WQI values	Interpretation
Excellent	95–100	Water quality is protected with a virtual absence of threat or impairment; conditions very closer to natural or pristine levels
Good	80–94	Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels
Fair	65–79	Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels
Marginal	45–64	Water quality is frequently threatened or impaired; conditions usually depart from natural or desirable levels
Poor	0-44	Water quality is almost always threatened or impaired; conditions very often depart from natural or desirable levels

Results

Physicochemical Characteristics

The main statistical data on the water quality of the Vladayska River at two monitoring stations are summarized in Table 4, presenting the ranges, mean values, and standard deviations for the 15 physicochemical parameters analyzed. Temperature ranged from 2.5 to 23.8 °C, with conductivity values of 48–540 μS/cm before Vladaya and 213–933 μ S/cm at Kubratovo. Water hardness ranged from 0.5 to 6.6 mg/L, and suspended solids averaged 8.38 mg/L before Vladaya, compared to 4–596 mg/L at Kubratovo. Dissolved oxygen (DO) varied between 4.2–9.82 mg/L before Vladaya and 1.6–10.8 mg/L at Kubratovo, while chloride concentrations ranged from 1.2–94 mg/L before Vladaya and 20.2–180 mg/L at Kubratovo. Sulfate concentrations

Parameters	Min		Max		Me	an	Me	dia	SD	
	А	В	А	В	А	В	А	В	А	В
Temperature	2.5	1.8	22.1	23.8	9.03	13.1	7.6	12.5	-	-
EC, (μS/cm)	48	213	540	933	193.8	471	133	480	90.7	113.9
Hardness, (mg/L)	0.5	1.3	3.1	6.08	1.67	2.95	1.77	3.0	0.67	0.86
TDS, (mg/L)	1	4.0	33.6	596	8.38	44.04	4	14.4	9.49	97.05
DO, (mg/L)	4.2	1.6	9.8	10.55	7.27	5.48	7.35	5.2	1.43	2.01
Cl, (mg/L)	1.2	20.2	94	180	30.4	43.7	15	35.8	16.6	28.5
SO ₄ , (mg/L)	4.23	20.5	31.8	52.7	17.6	33,56	15.5	33.1	6.36	8.661
$N - NH_4^+ (mg/L)$	0.05	0.7	4.03	18.3	0.97	6.17	0.59	5.19	1.07	4.19
NO ₃ , (mg/L)	0.01	0.01	0.96	1.68	0.34	0.66	0.25	0.62	0.14	0.44
NO ₂ , (mg/L)	<0.01	<0.01	0.12	0.23	0.03	0.09	0.025	0.08	0.03	0.05
Total N, mg/L	0.23	1.88	6.55	23.7	2.15	8.78	2.3	7.7	0.78	5.24
Total P, (mg/L)	0.004	0.19	1.37	4.99	0.30	1.21	0.21	0.85	0.42	0.99
P- PO ₄ , (mg/L)	0.003	0.11	0.98	1.67	0.17	0.65	0.12	0.58	0.32	0.39
BOD ₅ , (mg/L)	0.6	3.9	14.5	69	4.64	17.4	4.7	10.1	1.31	17.9
COD, (mg/L	8	17.2	79	200	22.5	57.2	21	39	7.5	44.1

Table 4. Descriptive Statistics of Water Quality Indicators for the Vladayska River – Vladaya (A) and Kubratovo (B).

were 4.23-33.6 mg/L before Vladaya and 20.5-52.7 mg/L at Kubratovo. Nutrient content showed significant differences, with higher organic loads downstream at Kubratovo. Ammonium nitrogen $(N - NH_4^+)$, ranged from 0.05-4.3 mg/L before Vladaja and 0.7–18.3 mg/L at Kubratovo, facilitating nitrifying bacteria growth due to wastewater pollution. Nitrate nitrogen (N-NO₃) ranged from 0.01-0.12 mg/L before Vladaya and 0.01–0.68 mg/L at Kubratovo. Nitrite nitrogen (N–NO₂) was 0.01–0.12 mg/L before Vladaya and 0.01-0.23 mg/L at Kubratovo. Total nitrogen (N) concentrations before Vladaya ranged from 0.33 to 6.55 mg/L, with a clear improvement noted after 2017. However, total nitrogen values indicated significant pollution of river waters in the downstream section (1.88-23.7 mg/L at Kubratovo). The content of total phosphorus (P) and phosphates (P-PO₄) in the upper part of Vladayska River also varied, showing large fluctuations during the study period, with a significant reduction in concentrations after 2016 ($PO_4 - 0.003$ to 0.98 mg/L, and total phosphorus (P) between 0.010 and 1.37 mg/L). Phosphate values exceeded the "good" status threshold in almost all samples during the study period at Kubratovo, ranging from 0.11 to 1.67 mg/L for PO_4 , and from 0.19 to 4.99 mg/L for total phosphorus (P). The chemical oxygen demand (COD) before Vladaya ranged from 8 to 792 mg/L, while the biochemical oxygen demand over five days (BOD₅) varied from 0.6 to 14.5 mg/L, with improvements in water quality observed after 2016. COD values at Kubratovo varied between 17.2 and 200 mg/L, while BOD values ranged from 3.9 to 69 mg/l, indicating severe organic pollution of the river wa-

ters. Overall, Kubratovo showed significantly higher levels of ammonium nitrogen, nitrites, total phosphorus, orthophosphates, total nitrogen, BOD₅, and COD, reflecting strong anthropogenic influences such as untreated stormwater, industrial and domestic wastewater discharges.

Correlation matrix - physicochemical indicators

For the purposes of the present analysis, the correlation coefficients between the water quality indicators were calculated for the lower section (Kubratovo), presented in a correlation matrix (Fig. 2). Dissolved oxygen (DO) shows a negative correlation with temperature (r = -0.6), indicating lower oxygen levels as water temperature rises. DO also has a negative correlation with COD (r = -0.3) and nutrients like total nitrogen, total phosphorus, and NO₂, similar to trends observed in the urbanized part of the Pearl River estuary (Li et al., 2020). Temperature and electrical conductivity (EC) show a negative correlation (r = -0.4), likely due to groundwater inflow during summer low flow. Chlorides, sulfates, and electrical conductivity have a high positive correlation, with values of r = 0.9 and r = 0.6, respectively, indicating that as the concentration of these ions increases, so does electrical conductivity. Total phosphorus, total nitrogen, and orthophosphates exhibit very high correlations (r = 0.7-0.8), suggesting these ions often increase simultaneously due to common pollution sources. Ammonium ions (N - NH_4^+), strongly correlate with total nitrogen (r = 0.9), total phosphorus (r = 0.8), orthophosphates (r = 0.9), and both chemical and biological oxygen demand (r = 0.6). Orthophosphates (PO_4) positively corre-



Figure 2. Correlation matrix of water quality indicators

late with total nitrogen and total phosphorus (r = 0.8) and with BOD₅ and COD (r = 0.6), while negatively correlating with NO₃ (r = -0.6) and dissolved oxygen (r = -0.5). Nitrates (NO₃) show a strong positive correlation with dissolved oxygen (r = 0.7) and a negative correlation with water temperature (r = -0.7), consistent with Kermorvant et al. (2023). BOD5 and COD have a strong positive correlation (r = 0.9), as noted by Lee et al. (2016), emphasizing their role in identifying organic and inorganic pollution. Dissolved oxygen correlates positively with NO₃ (r = 0.7), with NO₃ identified as a significant predictor for dissolved oxygen concentrations (Wen et al., 2013). Precipitation shows weak correlations with all indicators, while river flow negatively correlates with EC, total nitrogen, and orthophosphates due to dilution during high flows.

Principal Component Analysis (PCA)

In this study, three periods of annual variations in the Vladayska River at the Kubratovo station have been defined based on the hydrograph of the average monthly river runoff for the period from 2010 to 2021.The first period encompasses the river's high water, recorded during March, April, May, and June. The second period includes the low water phase during the summer and autumn months of July, August, September, October, and November. The annual distribution of river runoff also allows for the definition of a



Figure 3. Hydrograph of average monthly water quantities for the period 2010–2021

third transitional period during winter, when a partial increase in water quantity is observed (Fig. 3). This period includes the months from December to February. Based on these defined periods in the river's annual regime, subsequent principal component analysis was performed to reveal differences in indicator loadings during each period.

The principal component analysis technique was used in this study to assess the seasonal variation of water quality parameters. Principal Component Analysis (PCA) was performed on standardized data for 15 water quality indicators, precipitation, and river runoff for the high-flow period, low-flow period, and winter seasons. In PCA, it is important to determine the number of principal components that enter the subsequent analysis. This is done by calculating the eigenvalues of the principal components (PC). A scree plot of the eigenvalues obtained in this study



Figure 4. Scree plot of the eigenvalues of principal components in high-water, low-water period and winter

|18|

shows a distinct slope change after the third eigenvalue in the PCA for all three periods studied. (Fig. 4). As a rule, the post-slope component is also taken (Vega et al., 1998). Four components will be included in the subsequent analysis. For the high-water period, the first four components explain 92,1 % of the total variation of the information contained in the source data set (Fig. 4). In the low-water period, the first four components explain respectively 74.3% of the total variation. In the winter season, the first four components explain 87,7% of the total variation.

The first component (PC1) in the PCA for the high-flow period accounts for 48.1% of the total variance, with the highest loadings for (N - NH₄⁺), total nitrogen, NO₂, BOD₅, total phosphorus, orthophosphates, and COD, all positively correlated. The second component explains 22.6% of the variance and includes indicators such as NO₃, EC, SO₄, and chlorides, all negatively correlated (Fig. 5). The third component explains 14% of the variance, characterized by positive loadings for TDS, DO, and precipitation, with a negative loading for temperature. The fourth component explains 7.4% of the variance and is associated with total hardness and river flow. The results indicate that during the high-water period, water quality variability is largely influenced by nutrient loading (e.g., ammonia, nitrogen, phosphorus), mineral content (e.g., nitrates, conductivity, sulfates, chlorides), and hydrological factors. Precipitation and river flow positively impact dissolved oxygen levels, while temperature has an opposing influence. TDS and total hardness were not significant factors during this period.

For the low-flow period, PC1 accounts for 35.2% of the variance and includes nutrient and organic pollution indicators, such as (N - NH₄⁺), total nitrogen, total phosphorus, and orthophosphates, all positively correlated (Fig. 5). PC2 explains 16.4% of the variance, characterized by positive loadings for BOD₅, TDS, DO, and COD, and a negative loading for EC. PC3 accounts for 11.6% of the variance, with significant factors including NO₃, total hardness, SO₄, and temperature, all negatively correlated. PC4 explains 11.1% of the variance, with the greatest loadings for NO2, chlorides, rainfall, and river flow (Tab. 5). During the low-flow period, water quality variability is primarily influenced by nutrient and organic matter pollution, similar to the highflow period. The first component highlights nutrient pollution as the main factor affecting water quality, while the second emphasizes the role of oxygen demand, dissolved oxygen, and ion content. Hydrological factors and mineral content have less influence, and water temperature shows a negative relationship with other indicators.

For the winter period, PC1 represents 47.1% of the total variation, including (N - NH_4^+), total nitrogen, total phosphorus, orthophosphates, NO_2 , BOD_5 , COD, and TDS. PC2 explains 21.7% of the variance (Fig. 5), with the highest loadings for NO_3 , total hardness, EC, SO_4 , chlorides, and



Figure 5. Results of principal component analysis performed with water quality data for a period of high water, low water, and winter seasons, Kubratoto station, Vladayska river

river flow. Unlike other periods, river flow is a significant indicator in the first two components. All significant indicators in PC1 and PC2 have negative loadings. PC3 accounts for 11% of the total variance, with DO and precipitation as key indicators. DO is not a significant factor for water quality during this season. PC4 explains 8% of the variance, with water temperature as the primary indicator (Tab. 5). While precipitation and temperature do not fall into the first two components, they have significant positive loadings. The indicators with the greatest loadings across the first and second components in all seasons include inorganic nutrients such as (N - NH₄⁺), N-NO³, N-NO₂, total phosphorus, total nitrogen, and orthophosphates. These are significant indicators throughout the year, with NH₄ serving as an indicator of domestic wastewater and industrial discharge (Furukawa et al., 2020). N-NO₂ reflects pollutants from household and land-use activities (Glińska-Lewczuk et al., 2016). BOD₅ and COD consistently have high loadings in all seasons, especially during high-flow and winter periods, due to organic and chemical pollutants that deplete dissolved oxygen and deteriorate water quality (Anh et al., 2023). Significant differences across the individual periods are observed in the influence of hydrological indicators and water temperature. The results indicate that river runoff has the highest loading during the low-water period, followed by the winter and high-water periods (Table 5). Precipitation, while not among the top two principal components in any of the analyses, shows the highest loading during the low-water period, followed by the high-water period. The prominence of these two indicators during the low-water period indicate their critical role in influencing water quality during dry conditions. Short-term intense rainfall and episodic increases in river discharge facilitate the entry of pollutants into the river, particularly in urban areas (Chow et al., 2019; Yang et al., 2021). During winter, precipitation and indicators related to nutrient and organic pollutants exhibit negative loading, likely due to lower precipitation levels and reduced temperatures. These conditions slow down biochemical self-purification processes, resulting in higher pollutant concentrations.

Water Quality Assessment Using Water Quality Index

The CCME WQI analysis for the Vladayska River was conducted as a summary assessment for each monitoring station providing an overall evaluation of water quality trends over time. The CCME WQI categorizes waters of Vladayska River in the upper section into two quality classes. Both applied indices confirm pollution of the Vladayska River upstream of Vladaya in the years 2013, 2014, and 2015, classifying the river water as being in poor condition. Notable improvement in water quality is observed in 2016, 2017, and 2018, reaching good condition. The main source of pollution in the studied section is pollution from human tourism activities or sewage from homes and septic tanks. Monitoring at this point was discontinued after 2018 (Fig. 6). The CCME WQI for the period 2010-2021 shows that the downstream section of the Vladayska Riv-

Description		High-wat	er period			Low-wat	er period		Winter			
Parameters	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
$N - NH_4^+$	0.31	-0.14	-0.06	-0.13	0.36	0.00	0.09	-0.11	-0.34	-0.01	0.00	0.16
NO ₃	-0.20	-0.37	0.13	-0.03	-0.30	0.06	0.37	-0.02	0.23	-0.33	0.21	0.18
Total N	0.37	-0.02	0.08	0.02	0.35	0.25	0.11	-0.11	-0.34	-0.04	-0.03	0.13
NO ₂	0.28	0.06	-0.19	-0.22	-0.18	-0.16	0.29	-0.32	-0.22	-0.08	0.30	0.18
Total P	0.36	-0.06	0.05	-0.02	0.32	0.01	-0.20	-0.02	-0.33	0.01	0.12	0.21
Total hardness	-0.02	-0.21	-0.11	0.68	-0.10	0.00	0.39	0.22	-0.14	-0.38	-0.19	-0.24
BOD₅	0.33	0.09	0.19	0.09	0.29	0.34	0.13	0.04	-0.35	0.05	-0.10	0.00
EC	0.14	-0.44	0.12	0.03	0.27	-0.33	0.26	0.10	0.06	-0.41	-0.30	0.28
TDS	0.05	0.18	0.46	-0.42	0.01	0.52	0.06	-0.04	-0.32	0.07	-0.21	-0.13
Orthophosphates	0.36	-0.03	0.03	0.10	0.34	-0.12	-0.03	-0.17	-0.34	0.06	0.03	0.05
DO	-0.27	-0.14	0.31	-0.18	-0.24	0.31	0.10	0.02	0.07	-0.11	0.44	0.44
SO ₄	0.23	-0.27	0.03	0.12	0.16	-0.19	0.47	-0.15	-0.19	-0.32	-0.05	-0.27
Water temp	0.08	0.20	-0.48	-0.19	0.08	-0.17	-0.43	0.11	-0.02	0.36	-0.04	0.45
Chlorides	0.02	-0.43	0.26	-0.12	0.22	-0.24	0.22	0.35	0.06	-0.36	-0.35	0.36
COD	0.34	0.12	0.20	0.05	0.29	0.38	0.09	-0.03	-0.34	0.00	-0.13	0.15
Rainfall	0.01	0.30	0.34	0.20	0.09	-0.01	0.03	0.61	0.17	0.08	-0.48	0.28
River flow	-0.05	0.36	0.37	0.32	-0.08	0.17	0.04	0.50	0.09	0.42	-0.31	0.04

Table 5. The factor loadings after the varimax rotation of the water quality data



Figure 6. CCME WQI values for the Vladayska River before Vladaya and at Kubratovo monitoring points

er, influenced by the urban activities of Sofia, has consistently poor water quality, with no trend of improvement during the study period.

CCME WQI values remained below 44 for most of the study period, indicating that water quality in this urban-influenced section is almost always threatened or impaired, with conditions frequently deviating from natural or desirable levels (Fig. 6). The CCME WQI values for the Vladayska River – Kubratovo indicate consistently poor water quality, with only minor seasonal fluctuations across different hydrological conditions. The index remains critically low during high water, low water, and winter periods, suggesting that increased flow does not significantly improve water quality.

Discussion

Urbanization of the catchment is associated with significant water quality deterioration, particularly in smaller watercourses like the Vladayska River. The ecological status of these waters is influenced by both natural and anthropogenic factors, with chemical changes being more pronounced during low flow conditions. Smaller rivers, with reduced flow, are especially vulnerable to significant changes in chemical parameters, which amplifies the impact of pollutants (Hellwig et al., 2017) The PCA results indicate that nutrients and organic pollution are the primary contributors to water quality variability under different flow conditions. During high-flow periods, increased nutrient loading (e.g., ammonia, nitrogen, phosphorus) and organic pollution (BOD₅, COD) degrade water quality, likely due to higher runoff from urban areas. Mineral content (nitrates, conductivity, sulfates, chlorides) also plays a role, though its impact is mitigated by dilution. Hydrological factors, such as rainfall and river flow, influence dissolved oxygen, while temperature has an inverse effect. In lowflow periods, the effects of nutrient and organic pollution

are exacerbated due to limited dilution capacity. The interaction between streamflow, dissolved oxygen, and mineral content is crucial for determining water quality during these conditions. In winter, nutrients and organic pollution continue to be key factors, with seasonal changes in river flow and temperature affecting dissolved oxygen and mineral content, resulting in distinct water quality dynamics. These findings highlight the critical link between urban development and water quality degradation, emphasizing the need to improve urban runoff management and wastewater treatment infrastructure. The results also indicate an improving trend in water quality at the monitoring point upstream of Sofia, while downstream water quality remains poor, showing no signs of improvement. CCME WQI for the Vladayska River at the Kubratovo monitoring point from 2010 to 2021 consistently indicates poor water quality, with no observed improvement trend. This suggests a gradual degradation of the aquatic environment in the Vladayska River. These observations are consistent with the study by Vyrbanov et al. (2021), which reported nutrient concentrations exceeding regulatory limits by more than 25 times, and BOD5 and dissolved oxygen levels exceeding norms by 10 to 25 times. The primary causes of water pollution in the Vladayska River are as follows:

- Untreated wastewater from neighborhoods with incomplete or non-existent sewage systems. These waters contain high levels of contaminants such as coliform bacteria, nitrates, phosphorus, various household chemicals, pharmaceuticals, and other harmful microorganisms.
- Discharge of treated industrial wastewater.
- Leaky or damaged sewage systems.
- Rainwater runoff carries oils, rubber, heavy metals, and other pollutants from vehicles off the streets.

• Illegal dumping of waste into riverbeds and the use of unauthorized landfills.

The Vladayska River faces significant challenges related to wastewater management, particularly due to the inadequate or completely absent sewage systems in certain areas on the outskirts of the city. In the southern parts of Sofia, where urban expansion has been rapid, wastewater from households is often discharged directly into the river without proper treatment. As a result, a significant portion of untreated wastewater flows directly into the Vladayska River, contributing to its pollution and further degrading the water quality in this important urban waterway.

Conclusion

Based on the conducted water quality analysis of the Vladayska River using R and the Water Quality Index (WQI), several key conclusions can be drawn:

The PCA results showed that nutrient and organic pollution (eg ammonia, nitrogen, phosphorus, BOD, COD), mineral content (nitrate, conductivity, sulfate, chloride, TDS) and physical factors (dissolved oxygen) were the main indicators affecting the water quality variability of the Vladayska River under different discharge conditions. Factors such as river flow, precipitation, and water temperature affect water quality to a lesser extent and have opposite effects according to season.

The results show that among the 15 observed chemical parameters, the majority of them do not meet the requirements of Bulgarian Water Quality Standards for Surface Water Environmental Quality at the monitoring point downstream of Sofia, indicating the negative impact of urban activities on water quality.

The results from the CCWQI indicate an improvement in water quality at the monitoring point upstream before Sofia, where the river achieved good water status. In contrast, the monitoring point at Vladayska River – Kubratovo, located at the city's exit, consistently recorded poor water quality, demonstrating a lasting impact of urban pollution.

This study highlights that urbanization has a profound effect on the river's water quality. While relatively good water quality was observed in the peripheral areas of the urban environment, significantly degraded water quality was detected at the river's exit from the city. These findings underscore the urgent need for improved water management and pollution mitigation measures within the urbanized sections of the river. Detailed observation, consistent monitoring and comprehensive assessment are essential to improve our understanding of the impact of different urban areas and the dynamics of their pollutant inputs. Strict control of industrial and domestic wastewater discharge sources is urgently needed to improve the river's ecological status.

Acknowledgments

We are very grateful for the support from the project No. BG-RRP-2.004-0008-C01. (SUMMIT-Sofia University Marking Momentum for Innovation and Technological Transfer), funded by the European Union—NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria.

References

- Anh, N. T., Can, L. D., Nhan, N. T., Schmalz, B., & Luu, T. L. (2023). Influences of key factors onriver water quality in urban and rural areas: A review. *Case Studies in Chemical and Environmental Engineering*, 8, 100424. https://doi. org/10.1016/j.cscee.2023.100424
- Bocheva, L., & Malcheva, K. (2020). Climatological assessment of extreme 24-hour precipitation in Bulgaria during the period 1931–2019. Proceedings of the 20th International Multidisciplinary Scientific GeoConference SGEM, 20(4.1), 357–366. <u>https://doi.org/10.5593/sgem2020/4.1/s19.045</u>
- CCME (Canadian Council of Ministers of the Environment). (2001). Canadian water quality guidelines for the protection of aquatic life: CCME Water Quality Index 1.0. In Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment.
- Chow, M. I., Lundin, J. I., Mitchell, C. J., Davis, J. W., Young, G., Scholz, N. L., & McIntyre, J. K. (2019). An urban stormwater runoff mortality syndrome in juvenile coho salmon. *Aquat. Toxicol.*, 214, 105231. <u>https://doi. org/10.1016/j.aquatox.2019.105231</u>
- Egodawatta, P., Thomas, E., & Goonetilleke, A. (2009). Understanding the Physical Processes of 639 Pollutant Build-up and Wash-off on Roof Surfaces. *Science of The Total Environment*, 406(6). 10.1016/j.scitotenv.2008.12.027
- Executive Environment Agency. (n.d.). NSMOS National System for Environmental Monitoring. Retrieved from http://eea.government.bg/en/nsmos/index.html
- Furukawa, K., Ichimatsu, Y., Harada, C., Shimozono, S., & Hazama, M. (2000). Nitrification of polluted Urban River waters using zeolite-coated nonwovens. *Journal of Environmental Science and Health, Part A*, 35(8), 1267–1278. <u>https://doi.org/10.1080/10934520009377035</u>
- Giri, S., & Qiu, Z. (2016). Understanding the relationship of land uses and water quality in Twenty First Century: A review. *Journal of Environmental Management*, 173, 41– 48. 10.1016/j.jenvman.2016.02.029
- Glińska-Lewczuk, K., I. Gołaś, J. Koc, Gotkowska-Płachta, A., Harnisz, M. & Rochwerger, A. (2016). The impact of urban areas on the water quality gradient along a lowland river. *Environment Monitoring and Assessment*, 188, 624. https://doi.org/10.1007/s10661-016-5638-z
- Hellwig, J., Stahl, K., & Lange, J. (2017). Patterns in the linkage of water quantity and quality during low flows. *Hydrological Processes*, 31(23), 4195-4205. <u>https://doi.org/10.1002/hyp.11354</u>
- Interlandi, S., & Crockett, C.S. (2003). Recent water quality trends in the Schuylkill River, Pennsylvania, USA: a preliminary assessment of the relative influences of climate, river discharge and suburban development. *Water Research*, 37(8), 1737-1748. 10.1016/S0043-1354(02)00574-2

- Jha, M.K., Shekhar, A., & Jenifer, M. A. (2020). Assessing Groundwater Quality for Drinking Water Supply Using Hybrid Fuzzy-GIS-Based Water Quality Index. *Water Research*, 179, 1–16. <u>https://doi.org/10.1016/j.</u> watres.2020.115867
- Kermorvant, C., Liquet, B., Litt, G., Mengersen, K., Peterson, E., Hyndman, R. J., Jones, J.B., & Leigh C. (2023).
 Understanding links between water-quality variables and nitrate concentration in freshwater streams using high frequency sensor data. *PLoS One*, 18(6): e0287640.
 10.1371/journal.pone.0287640
- Lee, J., Lee, S., Yu, S., & Rhew, D. (2016) Relationships between water quality parameters in rivers and lakes: BOD5, COD, NBOPs, and TOC. *Environmental Monitoring Assessment*, 188. 10.1007/s10661-016-5251-1
- Li, X., Lu, Ch., Zhang, Y., Zhao, H., Wang, J., Liu, H., & Yin, K. (2020). Low dissolved oxygen in the Pearl River estuary in summer: Long-term spatio-temporal patterns, trends, and regulating factors. *Marine Pollution Bulletin*, 151, 110814, <u>https://doi.org/10.1016/j.marpolbul.2019.110814</u>
- Medupin, C. (2020). Spatial and temporal variation of benthic macroinvertebrate communities along an urban river in Greater Manchester, UK. *Environmental Monitoring and Assessment*, 192, 84. <u>https://doi.org/10.1007/</u> <u>s10661-019-8019-6</u>
- Muschalla, D., Schütze, M., Schroeder, K., Bach, M., Blumensaat, F., Klepiszewski, K., Pabst, M., Press, A., Schindler, N., Wiese, J., & Gruber, G. (2008). The HSG guideline document for modelling integrated urban wastewater systems. In Proceedings of the 11th International Conference on Urban Drainage, Edinburgh, Scotland, UK.
- Nasir, M. F. M., Samsudin, M. S., Mohamad, I., Awaluddin, M. R. A., Mansor, M. A., Juahir, H., & Ramli, N. (2011). River Water Quality Modeling Using Combined Principle Component Analysis (PCA) and Multiple Linear Regressions (MLR): A Case Study at Klang River, Malaysia. World Applied Sciences Journal, 14, 73-82.
- National Institute of Meteorology and Hydrology. (2024). *Hydrological report.* Sofia.
- Newman, B. D., Wilcox, B. P., Archer, S. R, Breshears, D., Dahm, C.N., Duffy, C. J., McDowell, N.G., Phillips F. M., Scanlon, B. R., & Vivoni, E. R. (2006). Ecohydrology of water-limited environments: A scientific vision, *Water Resources Research*, 42(6). 10.1029/2005wr004141
- Olsen, R. L., Chappell, R. W., & Loftis, J. C. (2012). Water quality sample collection, data treatment and results presentation for principal components analysis – literature review and Illinois River watershed case study. *Water Research*, 46(9), 3110-3122. <u>https://doi.org/10.1016/j.</u> watres.2012.03.028

- Paul, M. J., & Meyer, J. L. (2001). Streams in the urban landscape. Annual Review of Ecology and Systematics, 32, 333-365. <u>https://doi.org/10.1146/annurev.ecol-</u> sys.32.081501.114040
- Przyjazny, A., Namiesnik, J. (2006). Chemometrics in monitoring spatial and temporal variations in drinking water quality. *Water Research*, 40(8), 1706–1716. <u>https:// doi.org/10.1016/j.watres.2006.02.018</u>
- R Core Team. (2023). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing. https://www.R-project.org/
- Rachev, G., & Nikolova, N. (2009). Climate of Bulgaria. *Yearbook of SU "St. Cl. Ohridski*", 101(2), 17–30. [In Bulgarian].
- Strokal, M., Bai, Z., Franssen, W., Hofstra, N., Koelmans, A. A., Ludwig, F., Ma, L., van Puijenbroek, P., Spanier, J. E., Vermeulen, L. C., van Vliet, M. T. H., van Wijnen, J., & Kroeze, C. (2021). Urbanization: An increasing source of multiple pollutants to rivers in the 21st century. npj Urban Sustainability, 1(24). <u>https://doi.org/10.1038/</u> <u>s42949-021-00024-5</u>
- Sun, G., & Lockaby, B. G. (2012). Water quantity and quality at the urban-rural interface. In D. N. Laband, B. G. Lockaby, & W. C. Zipperer (Eds.), Urban-rural interfaces: Linking people and nature (Chap. 3). <u>https://doi.org/10.2136/2012.urban-rural.c3</u>
- Sutadian, A.D., Muttil, N., Yilmaz, A., & Perera, C. (2016). Development of River Water Quality Indices – A Review. *Environmental Monitoring and Assessment*, 188, 56. https://doi.org/10.1007/s10661-015-5050-0
- Tripathi, M., & Singal, S. K. (2019). Use of Principal Component Analysis for parameter selection for development of a novel Water Quality Index: A case study of river Ganga India. *Ecological Indicators*, 96(1), 430-436. <u>https://doi.org/10.1016/j.ecolind.2018.09.025</u>
- United Nations Educational, Scientific and Cultural Organization. (UNESCO). (2015). International initiative on water quality (IIWQ).
- U.S. Geological Survey. (1999). *The quality of our nation's waters: Nutrients and pesticides*. U.S. Geological Survey Circular, 1225.

- Van Der Hoek, J.P., Hofman, J.A.M.H., & Van Someren, T.C.R. (2011). Integration and Innovation of the Urban Water Cycle: The Waternet Experience. *Journal of Environmental Science and Engineering*, 5, 533-544.
- Van Der Sterren, M., Rahman, A., & Dennis, G.R. (2013). Quality and quantity monitoring of five rainwater tanks in Western Sydney, Australia. *Journal of Environmental Engineering*, 139(3), 332-340. <u>https://doi.org/10.1061/</u> (asce)ee.1943-7870.0000614
- Varbanov, M., Gartsiyanova, K., Tcherkezova, E., Kitev, A., & Genchev, S. (2021). Analysis of the quality of river water in Sofia city district, Bulgaria. *Journal of Physics: Conference Series*, 1960, 012019. <u>https://doi.org/10.1088/1742-</u> <u>6596/1960/1/012019</u>
- Vega, M., Pardo, R., Barrado, E., & Deban, L. (1998). Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. Water Research, 32(12), 3581-3592. <u>https://doi.org/10.1016/S0043-1354(98)00138-9</u>
- Velev, S. (2010). *The climate of Bulgaria*. Heron Press. [In Bulgarian].
- Viji, J., Priyanka, J., Manish, R., & Pawan, L. (2014). Assessment of deterioration in water quality from source to household storage in semi-urban settings of developing countries. *Environmental Monitoring Assessment*, 186(2), 725–734. http://dx.doi.org/10.1007/s10661-013-3412-z
- Wen, X., Fang, J., Diao, M., & Zhang, Ch. (2013) Artificial neural network modeling of dissolved oxygen in the Heihe River, Northwestern China. *Environmental Monitoring and Assessment*, 185, 4361–4371. 10.1007/s10661-012-2874-8
- Yang, L., Li, J., Zhou, K., Feng, P., & Dong, L. (2021). The effects of surface pollution on urban river water quality under rainfall events in Wuqing district, Tianjin, China. *Journal of Cleaner Production*, 293, 126136. <u>https://doi. org/10.1016/j.jclepro.2021.126136</u>
- Zeinalzadeha, K., & Rezaeib, E. (2017). Determining spatial and temporal changes of surface water quality using principal component analysis. *Journal of Hydrology: Regional Studies*, 13, 1–10. <u>http://dx.doi.org/10.1016/j.</u> ejrh.2017.07.002