

MONITORING THE WATER QUALITY AND HEAVY METALS PRESENT IN THREE DIFFERENT REGIONS OF THE VARDAR RIVER BY ATOMIC ABSORPTION SPECTROSCOPY (AAS)

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Abstract

The water quality of the Vardar river was monitored in the Taor-Pelince-Trnovec regions through water sampling by the Atomic Absorption Spectroscopy (AAS) method. The sampling sites were selected considering their potential for pollution due to anthropogenic factors like high levels of heavy metals, traffic, sewage waste etc., while sampling was conducted during the course of three months (February, March, and April) with comprehensive purpose. At the Hydro-Meteorological Institute, important physicochemical parameters, such as color, turbidity, pH, suspended solids, dissolved oxygen, biochemical oxygen demand, filtered dry residue, chemical oxygen demand and heavy metals were analysed. Important ions were also evaluated to show the mineral composition and nutrient status. Calibrated equipment and high-purity reagents were used to ensure preciseness. Our results concluded that the Vardar river in these respective regions, was highly polluted throughout all three months with Taor being the highest affected and Pelince the least affected. These findings, in turn highlight the vital need for water management and pollution reduction strategies in the Vardar river.

Keywords: Vardar river, heavy metals, pollution, AAS, physicochemical parameters.

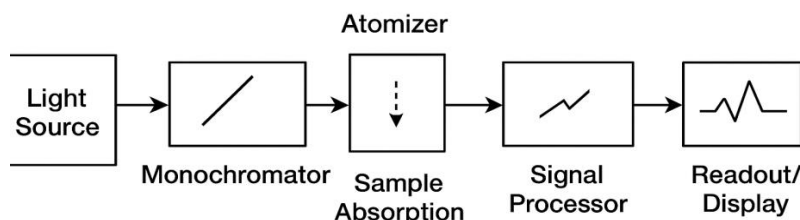
Introduction

In chemistry, water is known as the “universal solvent” owing to its involvement in almost all biochemical and physiological processes, which in turn underscore its importance for public health, flora and fauna [Pimentel et al., 2004]. Yet, despite its significance, global water resources are continuously faced with quality degradation. Pollution is one of the most dangerous environmental issues of the 21st century, which risks the health of the entire planet [Munteanu et al., 2021; Bhadarka et al., 2024].

The Vardar river representing the longest river in North Macedonia, supplies different crucial sectors with its water. However, the continuous presence of untreated waters, industrial discharges that carry heavy metals and other particulates has significantly diminished its quality [Dimoska et al., 2017; Stafilov and Levkov, 2007; WorldBank, 2015; Dehari et al., 2022]. Literature defines heavy metals as a group of elements with high molecular weight and density compared to water. At low concentrations, they can be essential for human health, nevertheless in high concentrations they are toxic and dangerous [Kassim et al., 2022; Chowdhury et al., 2016].

Atomic Absorption Spectroscopy (AAS) is an analytical method which can be used to determine the concentration of elements in environmental samples by measuring the absorption of

light. Atoms absorb energy and electrons move to higher levels, when exposed to ultraviolet or visible radiation. The absorbed light is measured, the detector compares the transmitted wavelengths to the original ones. In the end, the processor produces characteristic peaks that are unique to each element in the display screen [Idris et al., 2021; Ibrahim et al., 2023; Peñaloza et al., 2023; Ashirafu and Ntale, 2024].



Scheme 1. Symbolic schematic diagram of instrumentation for Atomic Absorption Spectroscopy (AAS) [Idris et al., 2021; Ibrahim et al., 2023; Peñaloza et al., 2023; Ashirafu and Ntale, 2024]

Materials and methodology

2.1. Area of study and study period

Water samples were collected in three different regions of the Vardar river, during February, March, and April 2024. At each site (Taor-Pelince-Trnovec), three surface water samples (0-30 cm depth) were collected in high-purity polyethylene bottles, at low temperatures, and transported to the laboratory for analyses.

Table 1. and Figure 1. Geographic coordinates and locations of Taor, Pelince, Trnovec in North Macedonia

SITE	LATITUDE (N)	LONGITUDE (E)	DESCRIPTION
Taor	41.8993°	21.6113°	Upstream site, near archaeological site Tauresium
Pelince	42.2869°	21.8474°	Midstream site, near ASNOM Memorial Center
Trnovec	41.8004°	22.6069°	Downstream site, near Vinica



2.2. Physicochemical and heavy metal analyses

Physicochemical analyses were performed following the *APHA Standard Methods*. To determine heavy metal concentration, water samples were acidified (pH <2) with concentrated nitric acid to avoid precipitation. Erlenmeyer flasks, volumetric flasks, beakers, and pipettes, were soaked in 10% HNO₃ for 24 hours and washed with deionized water before use. Certified standard solutions of Fe, Mn, Cu, Zn, Pb, and Cd were used for calibration in *Atomic Absorption Spectroscopy (AAS)* to obtain accuracy. Measurements of pH was conducted using *WTW S12 multiparameter probe*,

while turbidity was measured using an *AQUALYTIC PC Compact turbidimeter*. Laboratory verification of pH was determined by *CONSORT C830 digital pH meter*. Oxygen-related parameters were determined using standard titrimetric methods: a) for dissolved oxygen (DO) the *Winkler method*, b) biochemical oxygen demand (BOD₅) the *five-day incubation method*, and c) chemical oxygen demand (COD) the *permanganate titration*. Nutrient concentrations were determined using colorimetric and spectrophotometric techniques; with ammonia-N detected by the *indophenol blue method*, nitrite-N by the *sulphanilamide method*, nitrate-N by *UV spectrophotometry* at 220 nm, and phosphate-P using the *molybdenum blue method*. Important major ions were analysed with classical methods, including *argentometric titration* for chloride (Cl⁻), *acid-base titration* for bicarbonate (HCO₃⁻), *EDTA titration* for calcium (Ca²⁺) and magnesium (Mg²⁺), and *flame emission spectrophotometry* for sodium (Na⁺) and potassium (K⁺). Trace metal analysis included iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), lead (Pb), and cadmium (Cd), with samples digested in concentrated HNO₃ and analysed by *AAS*.



Figure 2. Hydrometeorological Institute (HI) in Skopje, North Macedonia (left) and Atomic Absorption Spectroscopy (AAS) apparatus used for heavy metal analysis found at HI (right)

The following table presents the minimal, maximal allowed limits and standard deviation for the calculated parameters as given by the EU directives, WHO standards, and the standard deviation is adapted on n=3 based on APHA [EU, 2020; WHO, 2022; APHA, 2017].

Table 2. Minimal, maximal and standard deviation values according to EU, WHO and APHA standards

No.	PARAMETERS	UNIT	MINIMUM VALUE	MAXIMUM VALUE	STANDARD DEVIATION (SD)
1.	Smell	N.A *	N.A *	N.A *	N.A *
2.	Colour	Pt-Co	0	15	± 0.5
3.	Turbidity	NTU	0	5	± 0.2
4.	pH	N.A *	6.5	8.5	± 0.1
5.	Dissolved oxygen (DO)	mg/L	5	13.99	± 0.3
6.	Suspended solids	mg/L	0	25	± 1.0
7.	Filtered dry residue	mg/L	0	500	± 10
8.	Biochemical oxygen demand (BOD ₅)	mg/L	0	5	± 0.3
9.	Chemical oxygen demand	mg/L	0	10	± 0.5

	(COD from KMnO_4)				
10.	Ammonia as N	mg/L	0	0.5	± 0.02
11.	Nitrites as N	mg/L	0	0.1	± 0.01
12.	Nitrates as N	mg/L	0	50	± 1.0
MAJOR IONS					
13.	Potassium (K^+)	mg/L	N.A [*]	12	± 0.3
14.	Sodium (Na^+)	mg/L	N.A [*]	200	± 5
15.	Chlorides (Cl^-)	mg/L	N.A [*]	250	± 7
16.	Calcium (Ca^{2+})	mg/L	20	100	± 3
17.	Magnesium (Mg^{2+})	mg/L	10	50	± 2
18.	Phosphates (PO_4^{3-})	mg/L	0	0.1	± 0.01
19.	Bicarbonates (HCO_3^-)	mg/L	N.A [*]	500	± 10
HEAVY METALS					
20.	Iron (Fe)	mg/L	0	0.3	± 0.01
21.	Manganese (Mn)	mg/L	0	0.05	± 0.003
22.	Copper (Cu)	mg/L	0	2	± 0.04
23.	Zinc (Zn)	mg/L	0	3	± 0.1
24.	Lead (Pb)	mg/L	0	0.01	± 0.001
25.	Cadmium (Cd)	mg/L	0	0.003	± 0.0002

Results and discussion

The results are presented in the following tables and graphs, which represent the essence of this study.

3.1. Month: February

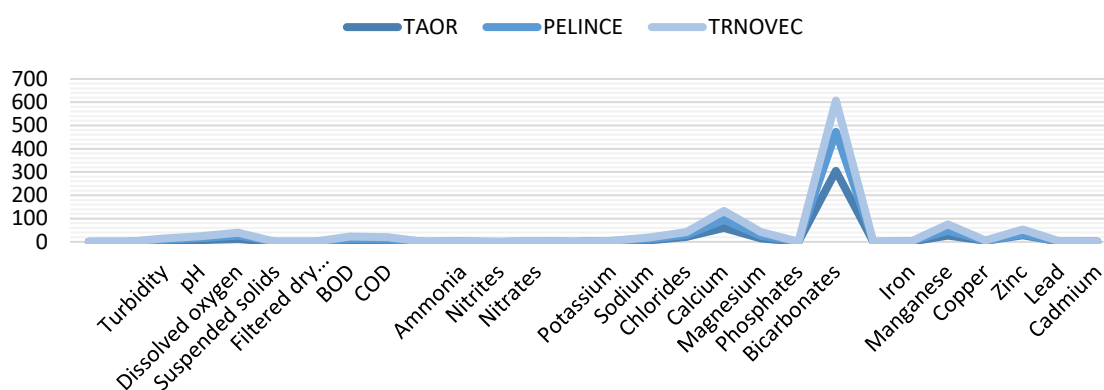
Comparison of relevant water quality parameters for the month February are presented in table 2 and graph 1.

Table 3. and Graph 1. Water quality parameters in Taor-Pelince-Trnovec regions. Month: February

No.	PARAMETERS	UNIT	TAOR	PELINCE	TRNOVEC
1.	Smell	N.A [*]	N.A [*]	N.A [*]	N.A [*]
2.	Colour	Pt-Co	3.7	4.1	4.1
3.	Turbidity	NTU	4	4.8	5.4
4.	pH	N.A [*]	7.95	7.9	7.73
5.	Dissolved oxygen (DO)	mg/L	12.25	13.99	13.15
6.	Suspended solids	mg/L	2	2	5
7.	Filtered dry residue	mg/L	150	155	200
8.	Biochemical oxygen demand (BOD_5)	mg/L	2	4	5
9.	Chemical oxygen demand (COD from KMnO_4)	mg/L	10.1	8.5	9.05
10.	Ammonia as N	mg/L	0.0189	0.0082	0.0130
11.	Nitrites as N	mg/L	0.0098	0.0042	0.0182
12.	Nitrates as N	mg/L	1.2419	0.5494	1.078
MAJOR IONS					
13.	Potassium (K^+)	mg/L	1.528	1.528	2.241

14.	Sodium (Na ⁺)	mg/L	6.584	5.088	7.527
15.	Chlorides (Cl ⁻)	mg/L	21.45	8.51	11.52
16.	Calcium (Ca ²⁺)	mg/L	60.12	34.07	38.08
17.	Magnesium (Mg ²⁺)	mg/L	14.59	10.94	15.81
18.	Phosphates (PO ₄ ³⁻)	mg/L	0.098	0.054	0.09
19.	Bicarbonates (HCO ₃ ⁻)	mg/L	305.1	167.8	134.2
HEAVY METALS					
20.	Iron (Fe)	mg/L	0.1	0.12	0.1
21.	Manganese (Mn)	mg/L	0.027	0.020	0.028
22.	Copper (Cu)	mg/L	0.013	0.016	0.015
23.	Zinc (Zn)	mg/L	0.028	0.049	0.051
24.	Lead (Pb)	mg/L	0.019	0.012	0.002
25.	Cadmium (Cd)	mg/L	0.003	0.002	0.002

*N.A -not applicable



3.2. Month: March

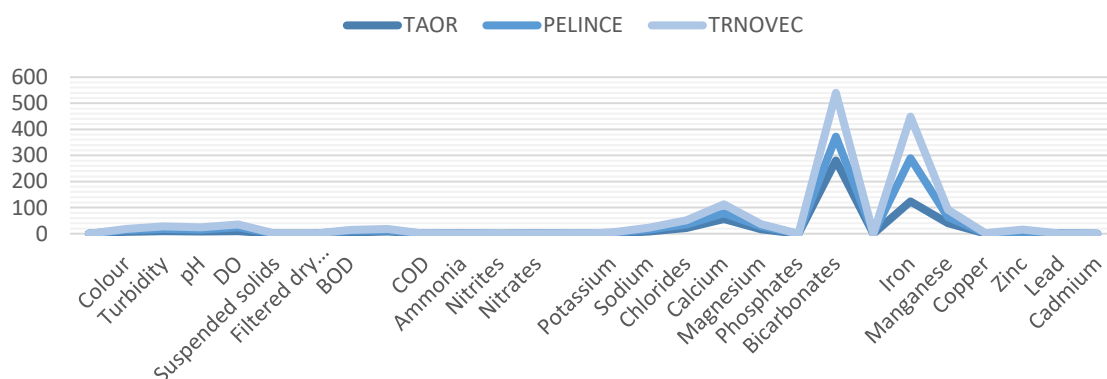
The following results recapitulate the water quality parameters for the Taor-Pelince-Trnovec regions in March.

Table 4. and Graph 2. Comparison of water quality parameters in Taor-Pelince-Trnovec regions. Month: March

No.	PARAMETERS	UNIT	TAOR	PELINCE	TRNOVEC
1.	Smell	N.A *	N.A *	N.A *	N.A *
2.	Colour	Pt-Co	4.1	4.0	3.7
3.	Turbidity	NTU	5	6	5
4.	pH	N.A *	7.8	7.98	7.96
5.	Dissolved oxygen (DO)	mg/L	12.56	14.61	12.77
6.	Suspended solids	mg/L	2	5	5
7.	Filtered dry residue	mg/L	150	200	250
8.	Biochemical oxygen demand (BOD ₅)	mg/L	4.14	4.37	4.29
9.	Chemical oxygen demand (COD from KMnO ₄)	mg/L	8.53	3.79	6.32
10.	Ammonia as N	mg/L	0.0615	0.0672	0.0258
11.	Nitrites as N	mg/L	0.0028	0.0021	0.0012

12.	Nitrates as N	mg/L	0.8323	0.1071	0.3502
MAJOR IONS					
13.	Potassium (K ⁺)	mg/L	1.62	1.628	1.602
14.	Sodium (Na ⁺)	mg/L	8.127	8.032	7.387
15.	Chlorides (Cl ⁻)	mg/L	21.27	14.18	16.31
16.	Calcium (Ca ²⁺)	mg/L	56.11	22.04	34.07
17.	Magnesium (Mg ²⁺)	mg/L	17.02	10.94	8.51
18.	Phosphates (PO ₄ ³⁻)	mg/L	0.061	0.009	0.051
19.	Bicarbonates (HCO ₃ ⁻)	mg/L	280.7	91.5	167.8
HEAVY METALS					
20.	Iron (Fe)	mg/L	0.124	0.165	0.160
21.	Manganese (Mn)	mg/L	0.020	0.024	0.028
22.	Copper (Cu)	mg/L	0.014	0.018	0.019
23.	Zinc (Zn)	mg/L	0.015	0.025	0.029
24.	Lead (Pb)	mg/L	0.017	0.012	0.015
25.	Cadmium (Cd)	mg/L	0.004	0.002	0.001

*N.A -not applicable



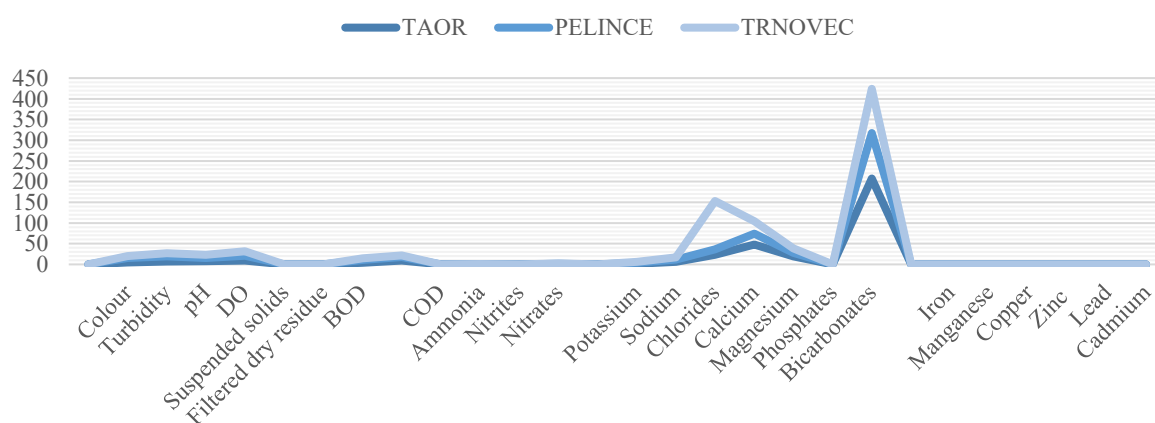
3.3. Month: April

Finally the results conducted in April are given in the below table and graph.

Table 5. and Graph 3. Comparison of water quality parameters in Taor-Pelince-Trnovec regions. Month: April

No.	PARAMETERS	UNIT	TAOR	PELINCE	TRNOVEC
1.	Smell	N.A*	N.A*	N.A*	N.A*
2.	Colour	Pt-Co	4.6	3.7	4.2
3.	Turbidity	NTU	6	8	9
4.	pH	N.A*	7.69	7.85	7.94
5.	Dissolved oxygen (DO)	mg/L	12.4	13.22	13.39
6.	Suspended solids	mg/L	5	5	4
7.	Filtered dry residue	mg/L	300	250	300
8.	Biochemical oxygen demand (BOD ₅)	mg/L	4.14	6.37	4.29
9.	Chemical oxygen demand (COD from KMnO ₄)	mg/L	9.05	9.05	3.56

10.	Ammonia as N	mg/L	0.0355	0.0242	0.0104
11.	Nitrites as N	mg/L	0.0317	0.0077	0.0139
12.	Nitrates as N	mg/L	0.9848	0.567	0.6571
MAJOR IONS					
13.	Potassium (K ⁺)	mg/L	1.47	2.23	2.25
14.	Sodium (Na ⁺)	mg/L	6.092	5.34	5.66
15.	Chlorides (Cl ⁻)	mg/L	23.05	13.28	11.28
16.	Calcium (Ca ²⁺)	mg/L	48.11	26.02	30.15
17.	Magnesium (Mg ²⁺)	mg/L	19.46	8.51	10.94
18.	Phosphates (PO ₄ ³⁻)	mg/L	0.017	0.024	0.068
19.	Bicarbonates (HCO ₃ ⁻)	mg/L	207.5	189.8	156.8
HEAVY METALS					
20.	Iron (Fe)	mg/L	0.10	0.12	0.14
21.	Manganese (Mn)	mg/L	0.028	0.028	0.027
22.	Copper (Cu)	mg/L	0.015	0.017	0.096
23.	Zinc (Zn)	mg/L	0.019	0.025	0.024
24.	Lead (Pb)	mg/L	0.002	0.025	0.012
25.	Cadmium (Cd)	mg/L	0.007	0.008	0.009



Conclusion

The above mentioned tables and graphs, show that the degree of water pollution by heavy metals in all three regions and months was moderately high. This can be confirmed by the values of turbidity (Pelince 4.8-8 NTU, Trnovec 5.4-9 NTU and Taor generally lower than in Pelince and Trnovec), BOD (Pelince approx. 4-6.37 mg/L, Trnovec approx. 4.29-5 mg/L and Taor approx. 2-4.14 mg/L) and COD (Pelince approx. 8.5-9.05 mg/L, Trnovec approx. 3.56-9.05 mg/L and Taor up to approx. 9.05 mg/L).

On the other hand this calculations can be further verified by dissolved oxygen levels which in Pelince remain relatively high, ranging from 13.22 to 13.99 mg/L. Taor shows higher level of nitrates with value approx. 0.95 mg/L, along with elevated bicarbonate concentrations more than 200 mg/L; at the same time, it has the highest concentrations of iron and manganese, with Fe reaching approximately 0.10 mg/L and Mn up to 0.028 mg/L, influenced by anthropogenic factors.

However, Trnovec is in between the two other regions in context of heavy metal pollution. It shows lower values of heavy metals than in Taor but slightly higher than in Pelince, particularly for Fe and Mn. As a result, it can be concluded that the water quality overall has stable physicochemical parameters with the limits falling in between the standards given by WHO and EU. However some parameters of the Vardar river sites exceed acceptable value (i.e. turbidity, heavy metals like Pb and Cd concentrations represent health concern), supporting the need for prior treatment before using the water, which was the main purpose of this study.

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