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ANALYSIS OF GROUNDWATER RESOURCES IN STARA ZAGORA DISTRICT, BULGARIA: QUALITY AND ENVIRONMENTAL RISKS

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Abstract

Groundwater, a vital resource in Bulgaria, is increasingly at risk of contamination from anthropogenic activities. A study in the Stara Zagora district for a year, situated in an area with strong anthropogenic pressure (urbanization, 4 TPPs, open-pit mining of lignite coal, large military training ground, intensive agriculture) assessed the groundwater quality of 6 wells (Ws) and 6 springs (Ss), based on 48 samples, analyzing 11 physicochemical (colour, taste, odour, pH, EC, TH, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, and OM) and 3 bacteriological (AMO, E.coli and Enterococci) parameters. The groundwater partly meets the Bulgarian standards as a natural resource (W1, W2 - summer, autumn and winter, W3 - summer and winter, S1, S2, S5 - autumn, and S6) and as a source for drinking (W1 and S2 - except for spring, W2 - except for spring and autumn, S1 and S6 - except for summer, autumn and winter). The deviation from the norms of groundwater as a natural resource results from pollution with NH_4^+, NO_3 and OM, and for drinking purposes: with E. coli, enterococci, AMO, OM, NH_4^+ and NO_3. Agriculture and livestock waste were identified as major pollution sources. Many positive and negative Pearson correlations existed between controlled groundwater parameters. Immediate treatment of contaminated Ws and Ss, and regular monitoring and health risk assessments are essential to mitigate groundwater pollution and ensure safe water for consumption.

***Key words**: environmental risk, groundwater, physico-chemical and bacteriological parameters, quality assessment.*

INTRODUCTION

Water equals life. No living thing on the planet can exist without water. Among all living organisms in the world, humans use the most water. That's why water is a critical resource for people's life as it is used for various purposes – human consumption, industrial processes, agriculture, and recreation (Saadatpour et al., 2021; Nadjai et al., 2024). In the last decades, the quality of water has been impacted by contamination with a wide range of pollutants (Adimalla & Qian, 2019; Taloor et al., 2024). In addition, water will become increasingly scarce as a result of population growth, urbani-zation, anthropogenic activities and climate change (Nawaz et al., 2023; Abdessamed et al., 2023). Water scarcity in many parts of the world is a serious problem. Groundwater seems to be the potential natural resource capable to reverse this situation (Taloor et al., 2020). Due to unavailability or inadequate quality of surface water, demand for groundwater resources has increased over the years and in present days constitutes about 20% of the world's supply (Barakat et al., 2018; Jyothilekshmi et al., 2019). In many countries, groundwater is a major source of water for drinking, irrigation and industry, and its quality is very important regarding its safe use for all these purposes (Sharma et al., 2017; Singh et al., 2022; Kumar et al., 2024). The poor quality of potable water is responsible for 80% of water-borne diseases in the world (Malik et al., 2012). Water quality illustrates the physical, chemical and biological condition of water bodies, aiming to identify and address concerns through a comprehensive approach tailored to specific uses (Giri, 2021). Numerous studies revealed different aspects of the groundwater quality used for drinking purposes: physicochemical and microbial status of spring/well water (Giao et al., 2023; Devolli et al., 2024); physicochemical characterization of ground-water in urban areas (Wakode et al., 2018; Ali et al., 2022; Subba et al., 2024); water quality and pollution sources in areas with mining activities (Mohammadpour et al., 2024), etc.

According to data from the EEA within the European Union (EU), 65% of water for drinking purposes and 25% for agricultural needs is provided by groundwater. At the same time, groundwater pollution and extraction is a serious threat to this resource: 24% of the total groundwater bodies are in poor chemical status and 9% - in poor quantitative status (EEA, 2023). A study of Sentek et al. (2024) shows that groundwater in the EU-27 is under significant pressure from excessive irrigation, industrial overexploitation, and a cocktail of pollutants, so that the resulting water scarcity is serious enough to affect livelihoods and even entire sectors.

Bulgaria has significant groundwater reserves, with a flow rate of about 193 millions m^3/year. In 2023, groundwater was 10.2% of the total amount of the extracted fresh water in the country (5336.1 million m^3), of which 79.3% were used for drinking, 14.2% for industry, 3.5% for agriculture and 2.9% for other purposes (National Statistical Institute, 2024). In the period 2003-2022, a gradual improvement in groundwater quality was observed for most of the analyzed indicators. Despite this positive trend, the main pollutants of groundwater with exceedance of the quality standards were nitrate (at 25% of all Monitoring points /MPs/) and partly sulfate, total Fe, Na and Mg (at 3.6-5% of MPs) (ExEA, 2024).

In some areas of Bulgaria, mainly semi-urban and rural, groundwater are single sources for water supply, especially in private farmyards and animal farms (Kostadinova, 2014). Usually, those sources are outside the National Monitoring System (NMS) and the lack of reliable information about the groundwater quality is a major concern. All the above have motivated conducting this study, aiming to assess the groundwater quality as a natural resource and for drinking purposes by physico-chemical and microbiological parameters from wells and springs out of the NMS in Stara Zagora district, exposed to strong anthropogenic pressure – urbanization, energetics, industry, transport and intensive agriculture.

MATERIALS AND METHODS

Study area

The study was conducted during the period July 2023 - June 2024 in Stara Zagora district, situated in South-Central Bulgaria (5.151 km^2), divided into 11 municipalities with 11 towns and 195 villages and population of 307,140 inhabitants (86 people/km^2). About 72% of the population lives in the cities, of which about 80% lives in the two largest cities – Stara Zagora (142,000) and Kazanlak (64,000) (National Statistical Institute, 2025). The region is characterized by a moderately continental climate (average annual maximum/minimum temperature +17.9°C and +8.0°C, respectively, average annual rainfall 598 mm), diverse and fertile soils, relatively good water resources and flat, hilly and low mountainous relief. Stara Zagora district is under strong anthropogenic pressure: the industry - the largest energy complex in the country Maritsa-Iztok (4 coal-fired Thermal Power Plants, 3400 MW, and open-pit mining of lignite coal) operates here as well as many other enterprises; transport - the region is an important road and railway center, connecting the eastern and western, northern and southern parts of Bulgaria; agriculture, characterized by intensive crop (mainly grain) and animal (milk, eggs and meat) production; in addition a large military training ground is also situated here (District administration - Stara Zagora, 2025). The region is rich in groundwater sources, with a significant portion of the population relying on groundwater for their daily needs. The depth of the aquifers varies from 30 to 200 m. Boreholes wells are a cost-effective and sustainable solution for accessing groundwater resources. They provide a reliable source of water for domestic, agricultural and industrial use (ExEA, 2024).

Monitoring Points

For the purpose of the study, 12 monitoring points (MPs), outside the National Monitoring System, covering 12 groundwater sources used for drinking purposes were selected: six open wells (Ws) and six springs (Ss), situated on the territory of Stara Zagora district (Table 1, Figure 1).

Table 1. Type, location and coordinates of underground water sources

No	Water source's location	Coordinates		a.s.l. (m)
		Latitude	Longitude	
A	*Wells (Ws)*			
1	W1	42.632	25.794	278
2	W2	42.382	25.432	349
3	W3	42.574	25.555	324
4	W4	42.299	25.937	111
5	W5	42.389	25.722	168
6	W6	42.401	25.652	174
B	*Springs (Ss)*			
1	S1	42.667	25.394	450
2	S2	42.671	25.787	354
3	S3	42.543	25.569	309
4	S4	42.489	25.689	334
5	S5	42.433	25.544	322
6	S6	42.381	25.540	280

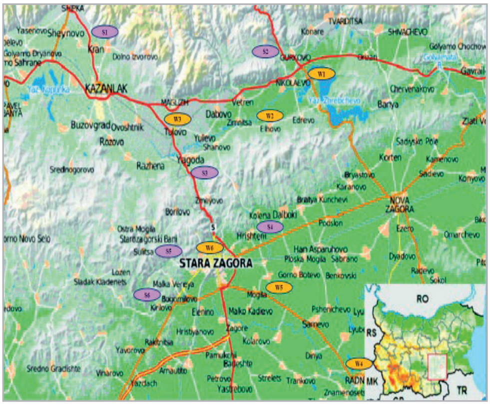

Figure 1. Map with monitoring points in Stara Zagora district, Bulgaria

Sampling and sample preparation

During the one-year monitoring period, groundwater samples were collected once in a season (March, June, September and December) from each MP, a total of 48 samples, including 24 samples from the wells and 24 samples from the springs. For water sampling and sample preparation for analyses, international references (ISO 5667-5, 11) were used. The samples for physicochemical analysis were collected in chemically clean polypropylene containers (1L) and for the microbiological analysis - in sterile glass containers (0.5L), transported in a cooler bag (2-5ºC), and processed for analysis within 2 hours after collection in the laboratories of the Environmental Center at Trakia University.

Physico-chemical parameters and analysis

All analyses were performed in triplicate. In the study, the following 11 physicochemical parameters were determined: colour, taste and odour (visual, organoleptic observation), pH and electrical conductivity (EC) - *in situ*, with portable Multi-340i/SET meter; the other parameters were analyzed in the laboratory: total hardness (TH) - titrimetrically, using standard EDTA, chloride (Cl^-) - by standard $AgNO_3$ titration (ISO 9297), sulfate (SO_4^{2-}) - by Bulgarian State Standard (BDS) 3588, ammonia (NH_4^+) - by BDS 3587 and nitrate (NO_3^-) - by BDS 3758, using UV-VIS Spectrophotometer JENWAY 6705, and oxidizability (organic matter, OM) - by titration method with $KMnO_4$.

Microbiological parameters and analysis

The bacteriological analyses included three microbiological parameters: total aerobic mesophilic bacteria (AMO) at 22°C - by ISO 6222, *Escherichia coli* - by ISO 9308-1 and enterococci - by ISO 7899-2. The total germs were counted after filtering the water using 0.45 µm pore size membranes, incorporated on selective chromogenic medium sheets (Rida® Count, R-Biopharm AG, Germany), and incubated at 22°C for 24 to 48 hours. The results are expressed in colony forming units (cfu/ml).

Assessment of groundwater quality

The assessment of groundwater quality from the monitored water bodies was conducted in two aspects:

a) the groundwater as a natural resource: the evaluation was based on eight physicochemical parameters (pH, EC, TH, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, and OM) as stipulated in Ordinance No. 1/2007. The chemical status of each groundwater body was classified as "good" if the parameter values were below the permissible limits, and "poor" if the values exceeded these limits. The overall ecological status of each water body was then determined by the lowest status recorded among the individual parameters assessed;

b) the groundwater as a source for drinking and domestic purposes by 14 parameters - 3 organoleptic (colour, taste and odour), 8 physicochemical (similar as in "a") and 3 microbiological (AMO, *E. coli* and Enterococci), according to Ordinance No. 9/2001.

Statistical analysis
All data ware analyzed by statistical software and data analysis tool XLSTAT, Version 2016.02, Addinsoft.

RESULTS AND DISCUSSIONS

Assessment of groundwater quality as a natural resource
The assessment was conducted using eight physicochemical parameters (Tables 2 and 3).
Among these, **pH**, which indicates the acidity or alkalinity of water, is a key parameter in groundwater quality assessment, as it influences the chemical and biological properties of groundwater. The pH values ranged between 6.89 and 8.22 and confirmed the results from previous studies that groundwater from wells/spring has natural or light alkalinity: 6.3-8.5 (Barakat et al., 2018, Ali et al., 2022, Abdessamed et al., 2023, Kumar et al., 2024). The coefficient of variation shows that pH is a conservative parameter with low variability - Cv = 2.41-3.47%. The same variation was reported by Nadjai et al. (2024), Cv = 2-5%.
Electrical Conductivity (EC) is an indicator of the total dissolved solids and salinity of the water. High salinity can affect the taste, sight, and smell of drinking water, and can worsen its quality. The EC values ranged between 382 and 5470 µS/cm for Ws, average 1487 µS/cm (Table 2), and within a much narrower range 298-910 µS/cm, average 627.4 µS/cm for Ss (Table 3). The coefficient of variation reflected those differences and demonstrated higher variability at Ws (Cv=88.8%) than at Ss (Cv=31.6%). The high EC values for Ws, except for W4 indicated high salinity and mineral content in groundwater with low runoff and high intensity of infiltration (Ravikumar & Somashekar, 2017).

Table 2. Physico-chemical and microbiological parameters of the wells (Ws) groundwater (n = 3)

MP*	Season	pH	EC, µS/cm	TH, mgeqv/l	Cl^-, mg/l	SO_4^{2-}, mg/l	NH_4^+, mg/l	NO_3^-, mg/l	OM, mg/l	AMO**, cfu/ml	*E.coli*, cfu/ml	*Ent.****, cfu/ml
W1	*Spring*	7.22	474	5.62	13.1	8.62	0.31	12.5	2.49	80	1	< 0.1
	Summer	7.46	718	5.11	14.2	8.20	0.08	13.1	2.30	< 0.1	< 0.1	< 0.1
	Autumn	7.91	478	2.49	11.7	8.36	0.06	11.3	3.31	2	< 0.1	< 0.1
	Winter	7.42	486	2.25	12.6	7.75	0.06	12.6	1.83	56	< 0.1	< 0.1
W2	*Spring*	7.19	1283	9.41	31.8	29.5	0.85	40.9	2.21	26	< 0.1	90
	Summer	7.21	1116	10.4	27.4	19.3	0.21	23.4	2.53	3	< 0.1	< 0.1
	Autumn	7.56	928	2.08	19.6	26.6	0.18	38.5	1.13	17	< 0.1	8
	Winter	7.27	1055	3.62	25.3	26.7	0.06	18.8	1.90	< 0.1	< 0.1	< 0.1
W3	*Spring*	7.40	388	5.88	11.6	7.84	1.33	42.4	1.28	210	5	45
	Summer	7.56	386	3.73	7.82	5.25	0.09	13.1	3.71	< 0.1	7	< 0.1
	Autumn	7.82	382	2.79	6.38	8.28	0.55	13.8	2.85	< 0.1	< 0.1	< 0.1
	Winter	7.63	392	1.83	10.4	8.42	0.37	28.4	3.93	90	< 0.1	192
W4	*Spring*	7.37	5470	38.0	398.5	394.2	1.85	96.1	2.31	267	< 0.1	50
	Summer	7.55	5180	27.3	269.6	385.5	3.82	511.8	7.35	100	103	208
	Autumn	8.18	4577	27.6	274.3	392.8	2.87	409.5	5.29	160	< 0.1	80
	Winter	7.47	3800	16.2	253.7	256.7	1.80	72.6	6.68	81	< 0.1	100
W5	*Spring*	7.59	513	3.75	10.6	15.7	0.92	48.8	2.31	5	1	3
	Summer	7.11	780	3.45	14.5	25.8	3.27	80.8	2.28	770	6	72
	Autumn	7.62	1243	2.66	43.0	28.5	1.03	43.3	0.81	4	< 0.1	2
	Winter	7.47	514	3.30	8.89	15.7	0.92	48.9	1.87	3	< 0.1	2
W6	*Spring*	7.41	1208	11.9	7.23	46.7	0.90	43.6	2.13	13	< 0.1	< 0.1
	Summer	7.17	1451	3.69	7.55	68.1	0.99	65.8	2.49	14	3	58
	Autumn	7.77	1406	2.67	7.37	59.6	0.92	48.7	2.06	30	< 0.1	2
	Winter	7.44	1452	3.09	7.73	64.9	0.70	45.5	1.48	76	1	4
Average (n=24) *Cv, %*		7.46± 0.18 *2.41*	1487± 1320 *88.8*	8.20± 8.28 *101.0*	62.3± 104.0 *167.0*	80.0± 112.1 *140.1*	1.00± 0.71 *71.0*	74.3± 48.1 *64.7*	2.77± 1.26 *45.8*	83.9± 90.9 *108.3*	5.41± 9.81 *181.3*	38.4± 50.5 *131.5*
***** Standards		6.5-9.5	2000	12	250	250	0.50	50	5.0	100/ml 22°C	0/100 ml	0/100 ml
			Meets the standard				*Deviation from the standard*					

*MP - Monitoring point; **AMO - Aerobic mesophilic microorganisms; ****Ent.* - Enterococci;
*****Ordinance No. 9/16.03.2001 (for drinking water - includes all tested parameters) and Ordinance No. 1/10.10.2007 (for groundwater as natural resource - includes only physicochemical parameters).

Table 3. Physico-chemical and microbiological parameters of the springs (Ss) groundwater (n = 3)

MP*	Season	pH	EC, µS/cm	TH, mgeqv/l	Cl^-, mg/l	SO_4^{2-}, mg/l	NH_4^+, mg/l	NO_3^-, mg/l	OM, mg/l	AMO**, cfu/ml	*E.coli*, cfu/ml	*Ent.****, cfu/ml
S1	*Spring*	7.15	304	4.56	10.6	12.7	0.17	8.98	1.75	< 0.1	< 0.1	< 0.1
	Summer	7.45	298	3.08	5.00	11.9	0.06	5.99	2.33	< 0.1	< 0.1	< 0.1
	Autumn	7.72	300	2.43	10.7	11.0	0.07	7.34	2.84	13	< 0.1	< 0.1
	Winter	7.31	306	3.06	11.9	9.64	0.12	5.52	2.14	< 0.1	< 0.1	< 0.1
S2	*Spring*	7.28	655	7.32	11.6	5.93	0.34	30.5	2.59	70	9	< 0.1
	Summer	7.26	645	5.11	6.33	5.25	0.16	24.9	2.87	1	< 0.1	< 0.1
	Autumn	7.91	421	1.86	3.97	3.38	0.23	33.5	2.90	13	< 0.1	< 0.1
	Winter	7.43	652	2.75	10.4	6.21	0.16	27.4	1.97	21	< 0.1	3
S3	*Spring*	7.63	844	3.34	47.0	26.8	0.55	19.7	2.52	< 0.1	< 0.1	< 0.1
	Summer	7.31	825	3.13	19.9	27.4	0.18	13.2	7.51	< 0.1	7	< 0.1
	Autumn	7.88	852	3.60	76.7	26.9	0.31	17.3	7.63	< 0.1	< 0.1	5
	Winter	7.72	849	2.91	35.4	27.5	0.14	18.6	5.67	< 0.1	< 0.1	< 0.1
S4	*Spring*	7.14	910	8.87	11.9	68.8	0.62	13.8	2.72	7	< 0.1	< 0.1
	Summer	6.89	768	2.76	16.6	52.1	1.48	18.5	6.37	< 0.1	< 0.1	< 0.1
	Autumn	7.99	452	3.54	8.23	53.2	1.13	33.6	3.41	60	50	118
	Winter	7.53	905	3.98	11.8	66.4	0.53	11.9	3.25	< 0.1	< 0.1	< 0.1
S5	*Spring*	7.28	693	5.70	25.1	49.1	0.50	49.9	1.81	67	6	100
	Summer	7.69	513	6.40	23.9	30.7	0.78	49.6	23.1	56	61	218
	Autumn	7.42	669	5.94	32.7	41.4	0.18	4.45	1.98	102	< 0.1	4
	Winter	7.43	693	5.36	25.8	46.5	0.50	48.1	1.85	109	< 0.1	52
S6	*Spring*	7.35	609	8.88	25.2	41.5	0.49	34.5	1.47	16	< 0.1	< 0.1
	Summer	7.34	762	7.60	3.99	51.2	0.33	36.4	2.58	8	< 0.1	4
	Autumn	8.22	366	2.39	8.63	56.3	0.32	41.0	4.23	26	< 0.1	3
	Winter	7.20	764	1.70	11.7	50.1	0.27	36.4	1.77	25	< 0.1	1
*****	Standards	6.5-9.5	2000	12	250	250	0.50	50	5.0	100/ml 22°C	0/100 ml	0/100 ml
		(blue)	*Meets the standard*			(red)	*Deviation of the standard*					

*MP - Monitoring point; **AMO - Aerobic mesophilic microorganisms; ****Ent. - Enterococci;
*****Ordinance No. 9/16.03.2001 (for drinking water - includes all tested parameters) and Ordinance No. 1/10.10.2007 (for groundwater as natural resource - includes only physicochemical parameters).

The low values for Ss could be related to high-elevation topography, high runoff, low infiltration, and recharge water type with low salt enrichment (Rao et al., 2012).

Previous studies also reported significant variation of that parameter: 220-8250 µs/cm, Cv = 35-51% (Barakat et al., 2018; Abdessamed et al., 2023; Kumar et al., 2024; Nadjai et al., 2024). The results obtained classified the ecological status of all tested groundwater as "good"; the exemption was W4, whose water's ecological status was determined as "bad".

TH in groundwater is computed as the total sum of Ca and Mg ion concentrations. The range of TH values in our study was between 1.83 and 38.0 mg/l, average 8.20 mg/l, Cv = 101.0% for Ws (Table 2), and between 1.83 and 8.88 mg/l, average 4.43 mg/l, Cv = 37.9% for Ss (Table 3). All concentrations were under the permissible level (<12 mg/l) according to the standard and classified the ecological status groundwater as "good"; the only exception was the W4, where concentrations were over the norm and determined the "bad" ecological status of water. In comparison to our results, other authors found higher levels of TH in groundwater: 90-940 mg/l (Barakat et al., 2018, Ali et al., 2022, Kumar et al., 2024), which is logical as the conditions of the studies were different than those in our study. **Chloride** is found in almost all-natural groundwater resources due to its high stability. The main sources of Cl^- include anthro-pogenic activities as well as leaching and weathering of different minerals. The chloride content imparts a salty taste to groundwater (Nag, 2009). The chloride concentration ranged from 6.38 to 398.5 mg/l for Ws (Table 2) and from 3.97 to 76.7 mg/l for Ss (Table 3). The coefficient of variation revealed a high variability of that parameter - Cv = 62.0-167.0% and indicated its sensibility to environmental factors.

The results obtained determine groundwater of all monitored water bodies as water in "good" ecological status (<250 mg/l) with one exception - W4, where Cl^- exceeded the norm in spring, summer, autumn and winter. Data from previous studies also reveal a large variation in the groundwater chloride concentration from differ-rent sources: 9-2400 mg/l, Cv = 63-74% (Ali et al., 2022, Kumar et al., 2024; Subba et al., 2024; Nadjai et al., 2024).

Sulfate ions are a natural component of groundwater, as they are the result of diverse processes - dissolution and precipitation of minerals, wastewater penetration from diffuse sources, deposition from the atmosphere (SO_2, H_2SO_4, and sulfate), others; the main source of SO_4^{2-} in groundwater are metallic sulfides (Tiwari et al., 2016). The indicator values varied from 5.25 to 394.2 mg/l, average 80.0 mg/l, Cv = 140.1% for Ws, and from 3.8 to 68.8 mg/l, average 32.6 mg/l, Cv = 64.4% for Ss. All SO_4^{2-} concentrations from Ss, and those from W1, W2, W3, W5, and W6 met the requirements of the standard for "good" ecological status, while the W4 groundwater was determined in "bad" ecological status. Some authors reported SO_4^{2-} concentrations in ranges close to ours: 7-421 mg/l, Cv = 76-81% (Ali et al., 2022; Panneerselvam et al., 2023; Kumar et al., 2024; Subba et al., 2024).

The **ammonium** is a common contaminant in groundwater, in many cases as result of human activities, mostly from the application of fertilizers, disposal of manure, discharge of sewage and leakage from landfills. That's why the traceability of ammonium in groundwater is of great importance (Liang et al., 2022; Liu et al., 2023). The range of NH_4^+ in groundwater of both water source types was 0.06 to 3.82 mg/l. Under the permissible level, determining "good" ecological status of the water body were the NH_4^+ concentrations for W1, W2 (summer, autumn and winter), W3 (summer and winter), S1, S2, S3 (summer, autumn and winter), S5 (autumn) and S6; in all other cases groundwater status was "bad". Devolli et al. (2024) found lower concentrations of NH_4^+ in spring and well water than in our study - 0.03-0.48 mg/l.

Nitrates are a major groundwater pollutant, especially in areas with high levels of industrialization, agricultural activities, and urbanization. Nitrate fertilizers, which are water-soluble (e.g., urea, ammonium sulfate), easily leach into the groundwater system, leading to serious NO_3^- pollution (Adimalla & Qian, 2019); septic tanks and leaks from wastewater pipes are other anthropogenic sources of nitrate in groundwater (Pawar & Shaikh, 1995). The NO_3^- concentration in the study area ranged from 11.3 to 511.8 mg/l, average 74.3 mg/l, Cv = 64.7% for Ws and from 5.52 to 49.9 mg/l, average 24.7 mg/l, Cv = 58.7% for Ss. The measured levels determine a "good" ecological status for groundwater from all monitored water bodies; the exceptions were W4 and W5 (summer) which fell in the "bad" ecological status category. Comparable to our results were data reported by Barakat et al. (2018), Panneerselvam et al. (2023), Subba et al. (2024), and Nadjai et al. (2024), (0.12-280 mg/l, Cv = 92-167%).

OM is an indicator characterizing the groundwater quality. Dissolved OM in groundwater is generally low compared to inland surface waters, but even traces of OM can lead to insipid taste of water and promote bacterial growth (Prasad et al., 2023). The ecological impact of OM inputs does not solely depend on its quantity but also by form of the constituents - dissolved or bound (Harjung et al., 2923). OM levels were between 0.81 and 23.1 mg/l and classified groundwater from all water bodies in the "good" ecological status category; exceptions were W4 and S3 (summer, autumn, winter), and S4 and S5 (summer) where the ecological status of groundwater was "bad".

Based on the assessments of the different physicochemical parameters, the final assessment determined W1, W2 (summer, autumn and winter), W3 (summer and winter), S1, S2, S5 (autumn) and S6 in "good" ecological status, meeting the Bulgarian standard quality requirements for a natural resource (Ordinance No. 1/2007). In all other cases, the water bodies were classified as the "bad" ecological status category. The status of W4 was particularly worrying, as throughout the entire monitoring period the levels of the analyzed physico-chemical parameters (except for pH) exceeded the permissible levels (Table 2). The poor state of the groundwater can be explained with the water body location, characterized with many anthropogenic activities: close vicinity to a TPP (908 MW), lignite coalmine and slag heap; in addition, intensive agriculture, involving fertilization and irrigation, is practiced in the area. Obviously, those activities influence the groundwater quality and determine the *bad* ecological status of that natural resource. It is necessary to conduct systematic monitoring of groundwater resources in order to identify the sources of pollution with a view to taking measures to improve the groundwater quality in the region.

Assessment of groundwater quality as a source for drinking purposes

The assessment was made by 14 physico-chemical and microbiological parameters as follows (Tables 2 and 3):

Physico-chemical parameters: The first group of those parameters included 3 organoleptic parameters - colour, taste and odour. By those parameters, all groundwater samples collected (total 48) met the requirements of the standard (Ordinance No. 9/2001), as they were "acceptable for users and without significant fluctuations from the usual for the indicator". The second group covered 8 parameters (pH, EC, TH, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, and OM), with permissible levels equal for both standards - for drinking water (Ordinance No. 9/2001), and for groundwater as a natural resource (Ordinance No. 1/2007). That's why, the assessments of the Ws and Ss as natural resources are also valid as sources of drinking water. Therefore, the groundwater resources in good ecological status can be used for drinking and conversely, the groundwater from water bodies in poor ecological status are not suitable for potable purposes (Tables 2 and 3).

Microbiological parameters: Microbes influence and often control geochemical processes and hence, are important to the quality of the natural water, they determine when the wells' clogging is a problem, and often whether anthropogenic chemicals (contaminants) disappear or persist in groundwater or not (Ferris, 2021). The quality assessment of the tested groundwater, made by three groups sanitary indicator microorganisms - Aerobic mesophilic microorganisms (AMO), *E. coli* and Enterococci, showed that the counts of all bacterial groups ranged within large limits: AMO - <0.1-770 cfu/ml, Cv = 108.3% for Ws, and <0.1-109 cfu/ml, Cv = 113.6% for Ss; *E. coli* - <0.1-103 cfu/ml, Cv = 181.3% for Ws, and <0.1-61 cfu/ml, Cv = 97.7% for Ss; enterococci - <0.1-208 cfu/ml, Cv = 131.5% for Ws, and <0.1 - 218 cfu/ml, Cv = 218.2% for Ss (Tables 2 and 3). Colony counts at 22ºC or AMO, provide a general idea of how contaminated the water is. Their presence in natural water can raise concerns regarding water quality and safety. *E. coli* and Enterococci indicate a fecal contamination of groundwater and the possible presence of disease-causing bacteria, viruses, and protozoa (Ateba & Maribeng, 2011; Tropea et al., 2021; Naily et al., 2023). Barakat et al. (2018) reported higher upper borders for *E. coli* (1-650 cfu/100 ml) and Enterococci (0-750 cfu/100 ml) for water from 8 springs in Morocco, while much lower variation for *E. coli* was established by Nawaz et al. (2023), 0-5 cfu/100 ml in groundwater from 10 different sites of Panjab city, Pakistan, and Devolli et al. (2024), 0-3 cfu/100 ml in groundwater form 7 wells in Albania. The established bacterial counts meet the requirements of the standard as follows: for AMO at W1, W2, W3 (except for spring), W4 (except for summer, autumn and winter), W6, S1, S2, S3, S4, S5 (except for autumn and winter), and S6; for *E. coli* at W1 and S2 (except for spring), W2, W3, W5 and S5 (except for spring and summer), W4, S3 and S4 (except for summer), W6 (except for summer and winter), S1 and S6, and for Enterococci at W1, W2 (except for spring and autumn), W3 (except for spring and winter), W4 (except for summer), W6 and S6 (except for summer, autumn and winter), S1, S2 (except for spring), S3 and S4 (except for autumn); in the other cases the quality of ground-water deviated from the norms for drinking water.

Considering that the final assessment of groundwater of the relevant water body is made based on the lower quality assessment for the tested physicochemical and microbiological parameters, it can be concluded that only groundwaters from W1 and S2 (except for spring), W2 (except for spring and autumn), S1 and S6 (except for summer, autumn and winter) meet the standard. In all other cases the groundwaters were not suitable for drinking. The most aggravating factor is the presence of *E. coli* and Enterococci and partly of AMO, OM, NH_4^+ and NO_3^- above the permissible limits. All these pollutants contribute to organic sources of pollution, most likely with wastewater from settlements and livestock farms, including farmyards in the villages. It is necessary to continue monitoring groundwater sources used for drinking purposes, aiming to develop measures to eliminate or reduce organic/microbial contamination within the limits set by the standard.

Correlation analysis

The correlation matrices, calculated using Pearson correlation coefficients, revealed strong and moderate relationships (both positive and negative) among the investigated parameters for both types of groundwater sources (Tables 4 and 5).

In **wells**, significant correlations were identified between EC and TH, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, *E. coli*, and Enterococci; between TH and Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, *E. coli*, and Enterococci; and between Cl^- and SO_4^{2-}, NH_4^+, NO_3^-, and Enterococci. Additional correlations were observed between SO_4^{2-} and NH_4^+, NO_3^-, *E. coli*, and Enterococci; between NH_4^+ and NO_3^-, AMO, *E. coli*, and Enterococci; as well as between NO_3^- and *E. coli* and Enterococci, and between *E. coli* and Enterococci, with correlation coefficients ranging from r = 0.40 to 0.99.

In **springs**, notable correlations included those between season and TH (r = -0.58); EC and Cl^- and SO_4^{2-}; SO_4^{2-} and NH_4^+; NH_4^+ and *E. coli* and Enterococci; NO_3^- and AMO, *E. coli*, and Enterococci; OM and *E. coli* and Enterococci; AMO and Enterococci; and *E. coli* and Enterococci, with correlation coefficients ranging from r = 0.44 to 0.90.

Table 4. Pearson correlation matrix for the open well's groundwater quality parameters

	Season	Ph	EC	TH	Cl^-	SO_4^{2-}	NH_4^+	NO_3^-	OM	AMO	*E.coli*	*Ent.*
Season	1.00											
pH	0.33	1.00										
EC	-0.07	0.18	1.00									
TH	-0.29	0.13	0.93	1.00								
Cl^-	-0.08	0.20	0.96	0.95	1.00							
SO_4^{2+}	-0.07	0.20	0.99	0.93	0.97	1.00						
NH_4^+	-0.18	0.07	0.70	0.63	0.64	0.72	1.00					
NO_3^-	-0.04	0.37	0.75	0.68	0.66	0.77	0.81	1.00				
OM	-0.17	-0.08	0.11	0.10	0.08	0.07	0.04	0.04	1.00			
AMO	-0.18	-0.27	0.18	0.21	0.22	0.20	0.63	0.20	-0.10	1.00		
E.coli	-0.13	0.02	0.48	0.40	0.37	0.52	0.60	0.75	0.09	0.07	1.00	
Ent.	0.03	0.03	0.51	0.44	0.48	0.54	0.62	0.61	0.30	0.29	0.60	1.00

Table 5. Pearson correlation matrix for the spring fountains groundwater quality parameters

	Season	pH	EC	TH	Cl^-	SO_4^{2-}	NH_4^+	NO_3^-	OM	AMO	*E.coli*	*Ent.*
Season	1.00											
pH	0.34	1.00										
EC	-0.03	-0.28	1.00									
TH	-0.58	-0.35	0.25	1.00								
Cl^-	-0.01	0.20	0.45	0.02	1.00							
SO_4^{2+}	0.02	-0.03	0.47	0.28	0.05	1.00						
NH_4^+	-0.20	-0.11	0.24	0.14	0.04	0.56	1.00					
NO_3^-	-0.05	0.21	0.06	0.22	-0.06	0.26	0.30	1.00				
OM	-0.04	0.21	0.03	0.05	0.24	0.01	0.30	0.26	1.00			
AMO	0.07	0.07	-0.04	0.31	0.05	0.20	0.16	0.48	0.04	1.00		
E.coli	-0.08	0.30	-0.18	0.13	-0.04	0.10	0.47	0.40	0.70	0.34	1.00	
Ent.	0.08	0.23	-0.14	0.19	0.05	0.18	0.44	0.58	0.70	0.48	0.90	1.00

There was overlap in certain correlations observed in both types of water bodies; for example, correlations were found between EC and Cl^- and SO_4^{2-}, as well as between NH_4^+ and NO_3^-, *E. coli*, and Enterococci, and between *E. coli* and Enterococci. However, notable differences were also identified. Some correlations observed in wells were not present in springs (e.g., TH with Cl^- and SO_4^{2-}; Cl^- with SO_4^{2-}; NH_4^+ with NO_3^-), while certain correlations present in springs were absent in wells (e.g., OM with *E. coli* and Enterococci; NO_3^- with AMO, *E. coli*, and Enterococci; AMO with Enterococci). Previous studies have also reported significant correlations among several monitored parameters, consistent with the findings of our study. For example, correlations between TH and NO_3^- and Cl^- have been reported by Ali et al. (2022); between EC and TH and SO_4^{2-}, and between TH and Cl^- and SO_4^{2-} by Abdessamed et al. (2023); and between EC and Cl^-, NH_4^+, and NO_3^-, as well as between

TH and Cl^-, NH_4^+, and NO_3^-, by Shrestha et al. (2023). Additionally, Giao et al. (2023) observed a correlation between NO_3^- and TH.

Several of the correlations identified in our study are logical and causally linked. For example, the correlations between EC and TH, Cl^-, and SO_4^{2-} can be attributed to the fact that higher EC reflects higher levels of dissolved salts in water, which correspond to increased concentrations of Ca^{2+}, Mg^{2+}, chloride, and sulfate (Schubert et al., 2024). Similarly, correlations between NH_4^+ and NO_3^- and AMO, *E. coli*, and Enterococci are expected, as nitrogen is an essential element for microbial growth, and higher nitrogen concentrations can support increased microbial populations (Mattoo & Suman, 2023). The correlation between NH_4^+ and NO_3^- is consistent with the nitrification process, in which ammonium is oxidized to nitrite and subsequently to nitrate, leading to higher NO_3^- concentrations in the presence of elevated NH_4^+ levels (Mattoo & Suman, 2023). Additionally, correlations between OM and *E. coli* and Enterococci are expected, as higher organic matter concentrations provide a substrate for microbial growth, resulting in increased microbial counts (Harjung et al., 2023). The correlation between *E. coli* and Enterococci is also logical, as both bacteria are indicators of fecal contamination, and their concentrations typically correspond in contaminated water sources (Wang et al., 2013). However, some observed correlations, such as those between TH and Cl^- and SO_4^{2-}, Cl^- and SO_4^{2-}, NH_4^+, NO_3^-, and Enterococci, EC and Cl^- and SO_4^{2-}, and SO_4^{2-} and NH_4^+, are more difficult to interpret. Further targeted research is needed to confirm or clarify the underlying mechanisms of these associations.

CONCLUSIONS

This study assessed the quality of groundwater from six wells (Ws) and six springs (Ss) in the Stara Zagora region, an area characterized by strong anthropogenic pressure, including high levels of urbanization, four thermal power plants (3400 MW), a large lignite coal mine, a military training ground, and intensive agriculture. The evaluation was conducted using 11 physicochemical parameters (colour, taste, odour, pH, EC, TH, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, and OM) and three microbiological parameters (AMO, *E. coli*, and Enterococci), considering groundwater both as a natural resource and as a source for drinking water.

The findings indicate that:

(i) Groundwater met the Bulgarian standards for ecological status (as a natural resource) based on pH, EC, TH, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, and OM in W1, W2 (summer, autumn, and winter), W3 (summer and winter), and in S1, S2, S5 (autumn), and S6. In all other cases, groundwater exhibited poor ecological status, with NH_4^+ identified as the main pollutant, followed by NO_3^- and OM.

(ii) Groundwater met the Bulgarian standards for drinking water for all tested parameters in W1 and S2 (except in spring), in W2 (except in spring and autumn), and in S1 and S6 (except in summer, autumn, and winter). Deviations from the standards in other cases were primarily due to contamination with *E. coli* and Enterococci, and to a lesser extent with AMO, OM, NH_4^+, and NO_3^-.

(iii) Numerous significant positive and negative Pearson correlations were identified among the monitored groundwater parameters, with 28 correlations observed in wells and 13 in springs.

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