DOI: 10.31577/ahs-2026-0027.01.0002

ACTA HYDROLOGICA SLOVACA

Volume 27, No. 1, 2026, 12 – 22

Groundwater quality assessment under different anthropogenic loading in a small Bulgarian sub-basin of the Danube watershed

Tsetska SIMEONOVA*, Milena KERCHEVA, Gergana KUNCHEVA, Margaritka FILIPOVA, Emil DIMITROV, Dimitranka STOICHEVA

This study aims to assess the quality of groundwater under the influence of land use activities within a small sub-basin of Danube watershed in Northern Bulgaria over three monitoring periods: 2007, 2008, and 2024. A total of 22 water sources were explored, located in the mixed urbanized area of Trastenik village, Ruse district (domestic home wells) and springs and wells in forests, arable fields, and pastures, occupied by Calcic Chernozems. Different physico-chemical parameters of groundwater samples were assessed to determine their quality. The Gibbs and Piper diagrams were used to characterize the hydro-chemical dynamics of groundwater. It was concluded that the weathering of minerals and evaporation concentration were the processes controlling the groundwater chemical composition. Based on the Water Quality Index (WQI) model the groundwater sources are categorized as good to unsuitable in the urban mixed areas. It was found that the groundwater under mixed urban areas (village) was characterized with higher content of chemical elements, especially in 2007 and 2008, while after a 15-year period (in 2024) lower values of most chemical elements in the waters and a 40–50% reduction in nitrates was reported, confirming that land-use changes notably affect groundwater quality.

KEY WORDS: groundwater sources, WQI model, Gibbs diagram, Calcic Chernozems, Danube watershed

Introduction

Globally, groundwater is used for drinking, domestic, irrigation and industrial purposes. Observed climate change and excessive human activity seriously threaten groundwater, with the deterioration of its quality and the depletion of water resources being one of the leading problems worldwide (Singhal et al., 2020; Yu et al., 2023). The chemical composition of groundwater depends on natural factors such as the hydrological characteristics of the terrain, the type of soils, geology profile and climate, as well as on the anthropogenic loads of the watersheds (Shaffer and Liwang, 2001). The studies on comparative analysis of groundwater quality under different types of land use are remains limited in scope and such studies remain critical to achieve the sustainable water resources management (Verma et al., 2020; Ayeni, 2024). For groundwater protection, constant monitoring of pollutants is necessary to minimize negative impacts. The monitoring of groundwater quality is a significant tool that promotes the sustainable development of agricultural regions and provides important data for water management (Ghazaryan et al., 2020). A lot of groundwater quality monitoring programs are developed in order to prevent water contamination due to intensive anthropogenic loading of the watersheds (Council Directive 91/676/EEC; Council Directive 98/83/EEC; Directive 2000/60/EEC).

In a study of Stoicheva et al., (2016), in the watershed of the Yantra River, a tributary of the Danube river, a wide variety of typical for the region agricultural practices were investigated and it was found a significant anthropogenic loading of waters from domestic wells. According to the authors, it is necessary to determine the maximum permissible loading with nitrogen on the arable lands, and the applied methodological approach can be used in future environmental impact assessment on a watershed level. A study, conducted by Dumbrovsky et al., (2015) in the same direction, found that environmentally friendly and sustainable agriculture, which takes into account the requirements of crops and at the same time adopts scientifically based technologies for growing and managing soils, are one of the ways to improve the quality of soils and waters in the areas of drinking water reservoirs. Identifying contaminants sources helps explain geochemical processes and contaminant transport patterns (Maliqi et al., 2020; Bridhikitti et al., 2021; Nawale et al., 2021). In the present day, with the development of technologies and their availability, real-time online monitoring can be implemented, as well as a variety of additional methods and water quality indicators and ecosystem risks as a result of extreme weather events can be assessed

spatially (Skala et al., 2017; Lyons et al., 2023).
The purpose of the study is to make a comparative monitoring of the groundwater quality in a small sub-basin of Danube watershed from 2007, 2008 and after 15 years (in 2024) in a mixed urbanized area of Trastenik village, Ruse district (domestic home wells) and its surroundings (springs and wells in forests, arable fields, pastures) occupied preliminary by Calcic Chernozems.

Material and methods

Study area

The study was conducted on the territory and surrounding fields of Trastenik village (43.678N, 25.899E, 120 m altitude), Ruse region, within a sub-basin of the Rusenski Lom River, part of the Danube watershed (Fig. 1a). The undulating relief is a factor for soil water erosion occurrence.
The climate is moderate-continental with an average annual air temperature of 11.2°C and a well expressed annual air temperature amplitude (up to 41–42°C). The average annual amount of precipitation is 606 mm (Fig. 2) with a maximum in June and a minimum in February (Stanev et al., 1991). The water percolation conditions were characterized by the annual (April-March) and fall and winter (October-March) precipitation amounts and the leaching index (LI) calculated in case of B hydrologic soil group (Williams and Kissel, 1991). As it is shown in Fig. 2, two of the years – 2007 and 2024 were drier than average, while 2008 was wetter. The LI during the dry years was negligible (less than 5 mm), while in 2008, it was higher than average. In case of B soil hydraulic group, the average LI (48 mm) can be classified as small (Williams and Kissel, 1991).
Calcic Chernozem (IUSS Working Group WRB 2015) is the dominant soil variety in the studied area. The parent material is loess with a high calcium carbonate content. The soil texture is relatively homogeneous along the depth of the soil profiles (Table 1). The data for two soil profiles, representative for the middle part of a sloping crop field and foothills, showed the dominance of silt fraction. The profile 2 is with a finer soil structure due to accumulation of the eroded material. The organic carbon content of the arable layer is medium (1.3–1.6%), and the soil reaction is slightly to moderately alkaline pH 7.7–8.4.
The content of soil mineral nitrogen and available potassium is high, but low in available phosphorus. The sorption capacities of the arable soil layers are 34 and 38 cmol kg^{-1}, correspondingly for Profile 1 and Profile 2 and the degree of saturation with bases is 94%. There is no exchangeable aluminium, the calcium cation is dominant (88%) in the sorption capacity. The soil field capacity of the arable layer is about 25%wt. Despite the presence of subsoil compaction which typically limits vertical drainage, the well-developed soil structure allows for rapid bypass (macropore) flow through desiccation cracks, increasing the vulnerability of

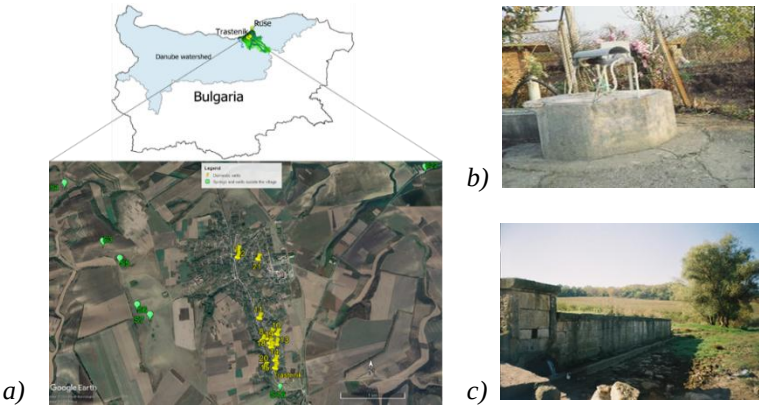


Fig. 1. Study area and sampling locations: a) Geographic map of Trastenik village and surroundings; b) representative domestic home well; c) representative spring in the surrounding fields.

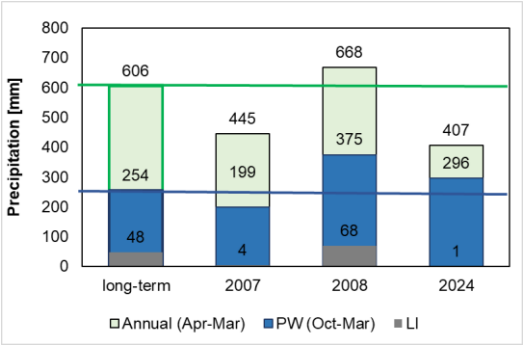


Fig. 2. Precipitation and leaching index (LI) in the region of Trastenik, Ruse.

Table 1. Physical and chemical properties of two representative Calcic Chernozem soil profiles in Trastenik, Ruse (Kercheva et al., 2021)

Hor.	Sampling depth [cm]	SOC [%]	Total carbonates, [%]	pH H_2O	Sand 2–0.063 mm [%]	Silt 0.063–0.002 mm; [%]	Clay <0.002 mm [%]	Texture class	Kf [cm h^{-1}]
Profile 1, middle part of sloping crop field, near to groundwater source S22									
Apk	0–10	1.32	6.9	8.1	6.6	67.3	26.1	SiL	
	10–20	1.30	6.3	8.2	6.7	67.1	26.2	SiL	4.0
Ak	30–40	0.9	6.8	8.2	8.2	65.7	26.2	SiL	
Ck	60–70	0.4	16.3	8.4	6.7	68.8	24.4	SiL	9.0
	80–95	0.3	17.7	8.4	6.3	69.7	24	SiL	
Profile 2, foothills of sloping crop field, near to groundwater source S4									
Ap	0–5	1.63	0.76	7.7	5.1	64.5	30.4	SiCL	
A	20–25	1.26	0.76	7.7	5.1	63.8	31.1	SiCL	2.6
Ab	45–50	1.03	0.26	7.8	5.9	63.1	30.9	SiCL	
bCk	110–150	0.5	4.33	8.3	4.7	66.0	29.4	SiCL	

** SiL- Silt Loam; SiCL- Silty Clay Loam*

shallow groundwater to surface-derived contaminants of shallow groundwater with nitrogen and other elements of agricultural sources. The characteristics of the relief, such as the varying slopes of the terrain, can lead to soil water erosion and enrichment of the waters with nitrates, phosphates, which can be the cause of the appearance of eutrophication of the open water bodies. During the conducted field survey, the level of the underground water in the wells was determined with an electronic sensor. It has been established that the depths of the aquifers from which water were taken is between 3.75–20 m. The survey of the groundwater sources was carried out during the spring-summer period of 2007, 2008 and 2024. The monitoring studies included 22 water sources (springs and domestic wells), located both in the village (14 of them) and outside – in forests, fields, orchards, etc. (7 of them) (Fig. 1b and 1c).

Land use: At the beginning of the study period – 2007, 2008 land use in the village included farmyards with a large number of animals, and or vegetable gardens, greenhouses, etc. In 2024, a change in land use was observed through a reduction or cessation of animal husbandry, and the vegetable gardens were replaced with grassy areas. The water samples from the central water supply (CWS) is included in the study. It is important to mention that the CWS in most settlements in Ruse region is achieved by pumping of groundwater and their chemical composition is quite close to that of the investigated springs in the fields.

Experimental methods

The water samples were analyzed for pH, EC, K^+, Na^+, Ca^{2+}, Mg^{2+}, NO_3^-, HCO_3^-, Cl^- by the following methods: pH – potentiometrically by a pH meter, EC electro conductivity meter (Arinushkina, 1970); nitrogen content, sulfates and chloride was measured by "Spectroquant Pharo 100"; Merck Millipore (PHARO 100). The potassium and sodium were determined by flame photometer, calcium and magnesium – by atomic absorption spectrometry – AAS (Page et al., 1982), hydrocarbonate by titration with 0.02n H_2SO_4 to pH 4.4 (Arinushkina, 1970). TDS – Total dissolved solids is a quantitative indicator of total dissolved substances contained in the water, which are found in the form of inorganic salts and a small amount of soluble organic substances. It was found that the relationship between this parameter TDS and EC for groundwater is linear and can be calculated by the formula (Weaver et al., 2007):

$$TDS\ [\text{mg L}^{-1}] = A \cdot EC \qquad \text{in mS m}^{-1} \tag{1}$$

where A is a coefficient that can take different values between 5.5 and 9, (we used the coefficient 6.4.) Total hardness TH($CaCO_3$) is the concentration of Ca^{2+} and Mg^{2+} ions expressed as $CaCO_3$ equivalent (Pal et al., 2018). They are presented in different units of measurement, but when calculating the WQI, in this material, the results are presented in mgeqv L^{-1}.

Gibbs diagram

To identify the geochemical processes affecting the chemical composition of groundwater, the Gibbs diagram is used (Ye et al., 2022). The mechanisms managing the main processes of dissolved elements and ions are summarized in three dominant processes – precipitation, rock weathering and evaporation (Gibbs, 1970). The Gibbs diagram uses the logarithm value of TDS as a coordinate and the ratio of cations or anions as the abscissa (Qu et al., 2024).

Piper's diagram

The Piper's diagram is constructed in Excel using a template workbook (Halford, 2024) and a modification with adding nitrate on chloride axes (Yu et al., 2021), for better distinguishing the hydrochemical characteristics of

domestic wells from the springs in the surrounding fields.

Calculation of the Water Quality Index (WQI)

The Groundwater quality index (WQI) is the most widely used approach for comprehensive waters quality assessment. The WQI calculation method has been described in detail by many researchers (Saeedi et al., 2009; Bharti and Katyal, 2011 and others). The model is based on weighing and evaluation of various parameters for their quality, as a result of which a numerical evaluation expression with values from 0 to 100 is obtained, which expresses the combined impact of the studied parameters on the overall state of water quality. Five or six groups are thus categorized, which classify groundwater quality based on the relevant index range, i.e. excellent (0–25), good (26–50), poor (51–75), very poor (76–100), unsuitable (>100). The parameters obtained from the laboratory analyzes were used to calculate the WQI using the method of Horton (1965). The calculations go through several stages:
1) Calculation of q_i, which is a measure of the quality rating for each parameter (i) involved in the model;

$$q_i = 100\ [(v_i - v_{i0}) / (S_i - v_{i0})] \quad (2)$$

$$q_i = 100\ [v_i / S_i] \quad (3)$$

where
v_i – is value of the i^{th} parameter,
S_i – is standard permissible value of the i^{th} parameter,
v_{i0} – is the ideal value for each parameter, which is assumed to be 0 for drinking water, with the exception of the pH parameter, for which a value of 7.0 is assumed, for naturally pure waters, and for dissolved oxygen, for which a value of 14.6 mg L^{-1} is assumed (Boah et al., 2015), for pH is have used the following equation:

$$q_{pH} = 100\ [(v_{pH} - 7.0)/(8.5 - 7.0)] \quad (4)$$

2) Calculation of W_i weight coefficient (normalized weight) of each parameter. The weights for the water quality parameters were assumed to be inversely proportional to the recommended standards for the corresponding parameters by the following equation:

$$W_i = K / S_i \quad (5)$$

where
W_i – is unit weight for the i^{th} parameter S_i is standard value of the i^{th} parameter,
K – is constant of proportionality and is given by the following equation:

$$K = 1 / [\ 1/vs_1 + 1/vs_2 + \ldots\ldots + 1/vs_n] \quad (6)$$

The overall water quality index is estimated by linearly aggregating the quality score with a weight unit:

$$WQI = \Sigma\ q_i W_i / \Sigma\ W_i \quad (7)$$

Results and discussion

Understanding the processes of formation, the chemical elements present in groundwater, and the quality of groundwater requires taking into account the natural factors on which their formation depends, and land use, which is influenced by agricultural practices in adjacent territories reflecting different levels of anthropogenic loading. The main agricultural practices in this region include intensive crop rotation, irrigation in home gardens, manuring, frequent soil cultivation, animals breeding on a small area, etc. The results for physico-chemical composition were based on the values of individual wells (the range refers to individual sampling points), while Table 2 only presents their average values for the respective year.

Groundwater physico-chemical composition

From the obtained results for the pH values of groundwater during all monitoring periods, it is established that the waters in this region have a neutral to slightly alkaline pH (Table 2), which is typical for groundwater (perfect pH range is in the range of 6.5–8.5 (Regulation 9/2001).
Electrical conductivity (EC) is a proxy for total dissolved inorganic solids; it reflects the ionic strength and mineralization of the water. It has been established that higher electrical conductivity is a characteristic of waters with a higher amount of dissolved substances and, accordingly, a higher concentration of ions (Jeyakumar et al., 2017) and water is unavailable to plants regardless of the applied irrigation. Domestic wells exhibited the highest electrical conductivity in 2007, ranging from 570 to 1890 µS cm^{-1} (mean: 1084 µS cm^{-1}). Conversely, the lowest mineralization was recorded in 2008, with values fluctuating between 165 and 254 µS cm^{-1} (mean: 209 µS cm^{-1}) (Table 2). Substantially lower average values were measured in the springs, in 2007 and 2008 – 448 and 144 µS cm^{-1}, correspondingly, in contrast to 2024, where the electrical conductivity was 828 and reached 1770 µS cm^{-1} in the groundwater source S22 (Table 2). However, the maximum permissible concentration level (MPCL) for drinking water of 2000 µS cm^{-1} (Regulation 9/2001) was not exceeded. In our case the waters can be referred to the following three groups: below <250 µS/cm are of excellent quality and correspondingly low salt content, from 250-750 µS cm^{-1} are good with a medium content of dissolved salts, while between 750–2250 µS cm^{-1} are acceptable for use, but with a high content of dissolved salts Wilcox (1955).
The total mineralization of the waters or the total dissolved substances (TDS, mg L^{-1}) include mainly the dissolved mineral substances as well as some organic substances. They depend notably on various sources of pollution such as agricultural practices, domestic runoff, the industrial or wastewater treatment, etc. The TDS values in domestic wells were observed to be highest in 2007 (between 365 and 1209, mean: 694 mg L^{-1}) and lowest in 2008 (mean:134 mg L^{-1}), while in 2024, the average values of TDS (636 mg L^{-1}) are close to those – in 2007 (Fig. 3a). The data showed that the average

Table 2. **Mean physico-chemical parameters, calculated weighting factors (S_i- standard permissible value, W_i- weight coefficient (normalized weight), K- constant of proportionality), and Water Quality Index (WQI) for groundwater sources in Trastenik, Ruse region (2007, 2008, and 2024)**

Monitor. period	pH	EC [µS cm^{-1}]	TDS [mg L^{-1}]	TH$_{(CaCO3)}$ [mgeqv L^{-1}]	K^+	Na^+	Ca^{2+}	Mg^{2+}	NO_3^- [mg L^{-1}]	HCO_3^-	Cl^-	WQI
Domestic wells												
2007	7.55	1083.9	693.7	14.2	34.6	117	95.0	115.6	370	569	75.1	153.1
2008	7.70	208.7	133.6	14.6	44.7	129	112.4	109.5	301.4	548	58.7	169.3
2024	7.60	993.5	635.8	10.4	11.9	135	82.4	76.6	141.5	414	30.2	79.1
Springs, outside the village												
2007	7.75	448.3	286.9	5.6	1.5	77	29.9	49.9	12.6	548	19.0	39.5
2008	7.70	144	92.2	7.9	1.5	86	77.7	48.6	27.5	464	14.0	44.3
2024	7.60	962.1	615.8	8.5	6.8	122	93.5	47.1	26.4	463	19.7	49.2
$1/S_i$	0.15	0.0005	0.001	0.08	0.08	0.005	0.006	0.01	0.02	0.003	0.004	
K	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	
W_i	0.41	0.001	0.003	0.22	0.22	0.01	0.02	0.03	0.05	0.009	0.01	ΣW_i= 1.0
S_i	6.5–8.5[a]	2000[a]	1000[c]	12[a]	12[b]	200[a]	150[a]	80[a]	50[a]	300[a]	250[a]	

[a] *Regulation 9/2001;* [b] *WHO (2004);* [c] *WHO (2017)*

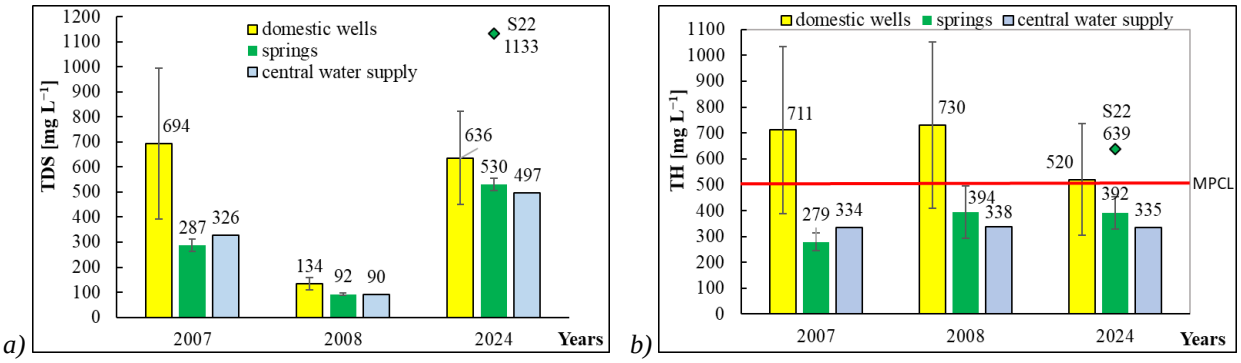


Fig. 3. TDS (a) and TH (b) values in groundwater sources during monitoring periods (2007, 2008, 2024). S22 indicates the outlier from the erosion control field.

values of total dissolved solids in springs outside the urban area, were low during the initial monitoring periods – 287 and 92 mg L^{-1} in 2007 and 2008, and higher in 2024 (530 mg L^{-1}, excluding source S22 with the highest TDS of 1133 mg L^{-1}). The well (S22) is located in close proximity to the experimental field, on a steep slope near a roadside vehicle turnoff. It is subject to contamination as a result of erosion and roadside garbage. In a number of water quality standards, TDS ranges between 500–1000 mg L^{-1}. Although according to this indicator the studied water sources fit within these limits, several wells (No. 12, 18, 9, and S22) exhibited concentrations exceeding the general trend in 2024. The others can be classified as excellent and with good quality according to this indicator.

The total hardness TH (expressed as $CaCO_3$) is the amount of dissolved calcium and magnesium in the water. It can be expressed in different measurement units and according to WHO 2006, MPCL is 500 mg L^{-1}, while in Bulgarian water regulations it is expressed as mgeqv L^{-1} and MPCL is 12 mgeqv L^{-1} (Regulation 9/2001). From the examined samples it is found that during the three monitoring periods the total hardness varies between 279 and 730 mg L^{-1}, whereby the springs outside the urban area do not exceed the MPCL (Fig. 3b). It should be noted that the soil parent material contained markedly amount of carbonates (Table 1). Water is known to be a good solvent for such type of minerals. According to Sawyer and McCarty (1967), waters can be classified into 4 groups according to their total hardness. In our study between 5% and 25% of waters fall in the hard water group (150–300 mg L^{-1}) while the main part (75%–95%) of water sources are classified as very hard waters (>300 mg L^{-1}).

As can be seen from the Fig. 4, the potassium content varies substantially. The average potassium content of domestic wells was found to be the highest in 2008 (44.7 mg L^{-1}), followed by 2007 (34.6 mg L^{-1}), and notably decreased in 2024 (11.9 mg L^{-1}) (Fig. 4a). While nearly all (100%) samples from arable land stayed below 10 mg L^{-1}, domestic wells showed high variability. Notably, the proportion of domestic wells with low potassium (0–

10 mg L^{-1}) increased from roughly 55% in 2007/2008 to 76% in 2024. Conversely, high-concentration wells (>50 mg L^{-1}) became rare, dropping from a 30% frequency in 2008 to only 8% in 2024. This cation also has the largest coefficient of variation, despite physico-chemical fixation by the soil, which can be explained with a different anthropogenic loading (fertilizers and pesticides were applied, vegetables were grown, etc). It should also be noted that the water sources with the highest potassium content are relatively shallow between 3–5 m.

Sodium is an element with a high geochemical mobility and transitional status in the geochemical cycle of the elements. Sodium content in groundwater depends mainly on cation exchange, weathering of minerals and anthropogenic impact (Ye et al., 2022). The large fluctuations in the dynamics of sodium may be due to a large extent to the specific geological characteristics and the location of the aquifers. As can be seen in Fig. 4b, there are substantially dynamics in its concentrations during the monitoring periods of 2007, 2008, and after 15 years in 2024. It was found that for sodium, unlike potassium, higher average values were measured in 2024 in domestic wells (135 mg L^{-1}) and lower in 2007 and 2008 – 117 and 129 mg L^{-1}. It was observed that the sodium content in the dominant part of wells (67–88%) under cultivated areas and fields was mainly in the range of 50–100 mg L^{-1}, except in 2024, where the proportion of wells above 100 mg L^{-1} increased. In 2024 the concentration exceeding the MPCL of 200 mg L^{-1} for drinking water (Regulation 9/2001) was recorded only in one water source – S22.

Based on the data collected from the studied water sources, calcium concentrations showed markedly fluctuations during each monitoring period. As can be seen from Fig. 5a the lowest values of calcium in the springs outside urban area was found in 2007 (mean 30 mg L^{-1}), while the highest concentration was measured in 2024 (mean 81 mg L^{-1}). It was found that 100% of the wells in 2007 contained calcium up to 100 mg L^{-1}, in 2008 and 2024 it was 84% and 57% of the investigated wells. It was found that almost all wells do not exceed the MPCL for calcium content in drinking water of 150 mg L^{-1} (Regulation 9/2001) with some exceptions for domestic wells and S22. The latter is situated on a sloping terrain, subjected to soil water erosion. It should be noted that lower values were recorded in water sources, which are around forests, fields, orchards, etc., outside the village (Fig. 5a), while higher concentrations of calcium were found in domestic wells especially in 2008. A high content can be related on the one hand to the carbonate content throughout the soil profile, on the other hand it can be due to the ion exchange between Na^+ and Ca^{2+} (Deepali et al., 2021).

The magnesium content in the groundwater also showed substantially variation and high concentrations in domestic wells, that exceeded the MPCL of 80 mg L^{-1} for this element for drinking water (Regulation 9/2001),

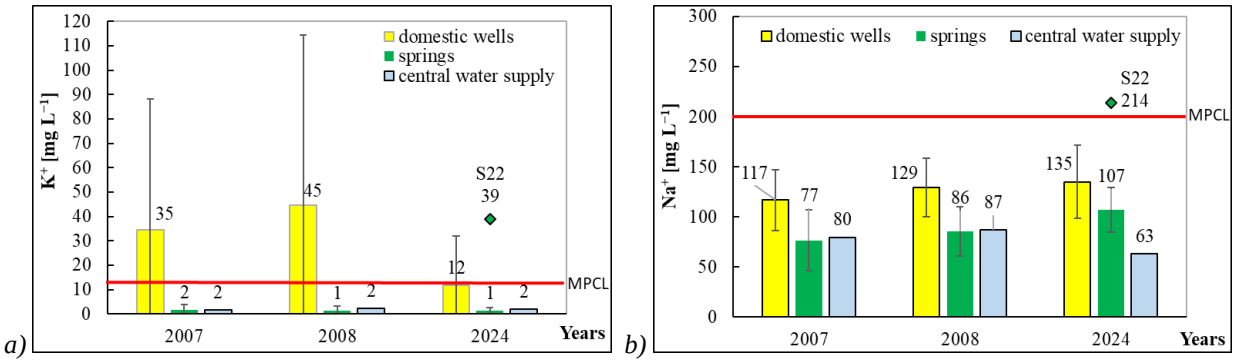


Fig. 4. Potassium (a) and sodium (b) concentration in the investigated water sources for the period 2007, 2008, 2024, Trastenik village, Ruse region. S22 indicates the outlier from the erosion control field.

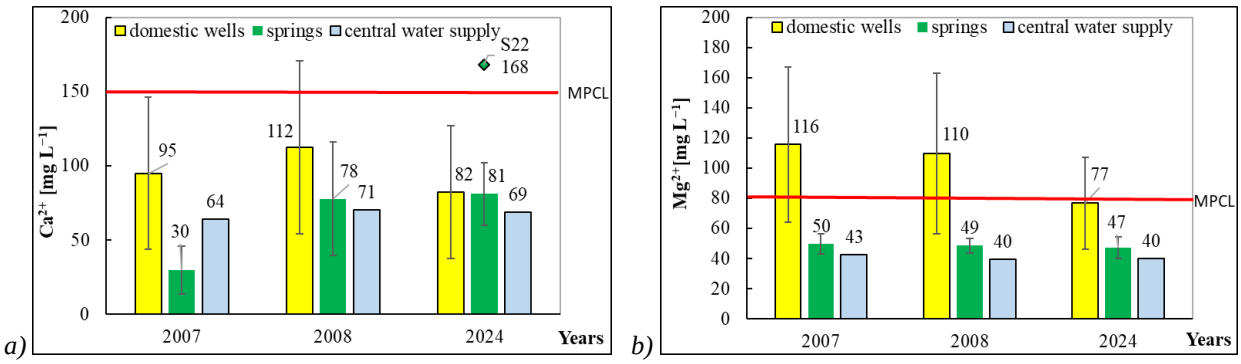


Fig. 5. Calcium (a) and magnesium (b) concentrations in the investigated water sources for the period 2007, 2008, 2024, Trastenik village, Ruse region. S22 indicates the outlier from the erosion control field.

especially in 2007 and 2008, reaching to 200 mg L^{-1}. As can be seen from Fig. 5b, magnesium values were lower in the wells outside the village, throughout the monitoring period. The main part of the wells (over 80%) contained magnesium up to 50 mg L^{-1}. It has been found that in domestic wells, magnesium concentrations are about 3–4 times higher, and about 60–70% of them fall in the range of 50 to 150 mg L^{-1}. Higher Mg^{2+} contents may occur due to the presence of both magnesium minerals and municipal waste (Sakram et al., 2022). Notably, by 2024, magnesium concentrations in domestic wells had declined by a factor of 1.5 to 2 compared to 2007/2008 levels and the average values do not exceed the MPCL.

The anions $NO3^-$ and Cl^- serve as anthropogenically derived tracers, as they are not primary components of the local loess parent material and are typically introduced via fertilizers and domestic waste (Badeenezhad et al., 2020; Egbueri, 2020; Subbra Rao et al., 2022 a, b). Research conducted by Kováčová (2015) and Siman and Velísková (2020) found that nitrogen transformations create ecological risks, such as soil and water pollution and increase nitrogen emissions when in watersheds with a high proportion of agricultural land. The nitrate content was found to vary widely, with a substantially similar coefficient of variation to that of potassium. The highest maximum and average nitrate values were recorded in domestic wells in 2007 and 2008, while the 2024 data after a 15-year monitoring period confirmed a decreasing trend in nitrate concentrations between 2.5 and 3.5 times. In 2007 and 2008, nearly all domestic wells (90–100%) failed to meet the drinking water standard, recording concentrations above 50 mg L^{-1}. By 2024, water quality improved notably, with only 46% of domestic wells exceeding this limit. The studied domestic wells exceed the MPCL of 50 mg L^{-1} for nitrate content in drinking water (Fig. 6). It was observed that the springs outside the village contained much lower values of nitrates throughout the studied period 8.25–45.20 mg L^{-1} and that a large part of them (65–70%) contained nitrates between 25 and 50 mg L^{-1}, about 15–30% between 10–25 mg L^{-1}, and there were not found springs with concentrations above 50 mg L^{-1} (Fig. 6).

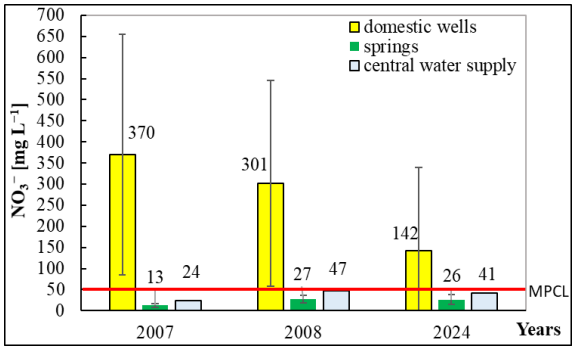


Fig. 6. Nitrate (NO_3^-) concentrations in the investigated water sources for the period 2007, 2008, 2024, Trastenik village, Ruse region.

It was observed that the hydrocarbonate concentrations were the highest in the domestic wells in 2007 and 2008, with average values of 569 and 548 mg L^{-1}, respectively, followed by 2024 – 414 mg L^{-1} (Table 2). Hydrocarbonate concentrations were lower in groundwater source in fields, except for 2024, where the average values were higher than those of the domestic wells. According to the data, hydrocarbonate is the most prevalent anion in the groundwater of the studied wells and less variable.

The chloride concentrations varied widely in domestic wells in 2007 (ranging from 31.6 to153.8 mg L^{-1}, mean – 75.1 mg L^{-1}) and 2008 (between 13.86 and130.63 mg L^{-1}, mean – 58.7 mg L^{-1}), while in 2024 decreased markedly, (from 17 to 88 mg L^{-1}, average – 30.2 mg L^{-1}). It was found that in the water sources outside the village, the chloride content was much lower and varied little (Table 2). More than half of the domestic wells in 2007 and 2008 had chloride content in the 50–100 and 100–150 mg L^{-1}ranges, while in 2024 the values were substantially decreases. It is possible that the anthropogenic loading intensifies the dynamics of chloride, because there is no mechanism in the soil to absorb chloride from the water. Chloride, like sodium, has high mobility and transit status in the biological cycle of substances.

It was found that in 2007, the cations in the studied water sources were arranged in the following order $Na^+ > Mg^{2+} > Ca^{2+} > K^+$, while the anions were in the following sequence: $HCO_3^- > NO_3^- > Cl^-$. In 2008 and 2024, the order of cations is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, while there is no change for anions. The groundwater is characterized by two primary hydrochemical facies: Na-Mg-HCO_3-NO_3 and Na-Ca-HCO_3-NO_3. This suggests that while rock weathering (providing Ca and Mg) is a factor, the high levels of Na and NO_3 point toward significant anthropogenic influence. However, it is possible the agricultural practices to strengthen the weathering of soil-forming materials. A similar observation was done in a study by Simeonova et al. (2017). In all cases, sodium is the predominant cation, while HCO_3^- is the major anion. According to Sakram et al. (2020) the sodium-hydrocarbonate (Na^+ - HCO_3^-) ionic composition of the waters determines the freshwater type, which refers to the dissolution of calcium feldspars and CO_2 in the soil and indicating the prevailing conditions of weathering and dissolution of minerals.

Hydro-geochemical facies and groundwater types

As can be seen from the Gibbs diagram (Fig. 7), most cation ratios ($Na^+/(Na^+ + Ca^{2+})$) and anion ratios ($Cl^-/(Cl^- + HCO_3^-)$) fall in the rock and mineral weathering region where TDS ranges from 100 to 1000 mg L^{-1} (Fig. 7a and 7b). Very few water samples spread from the rock weathering region to the evaporation region where TDS is more than 1000 mg L^{-1}. It should be noted that the studied water sources are not observed in the area of precipitation/ sedimentation where TDS is less than 100 mg L^{-1}. It can be seen that the chemical composition of groundwater in study area was mainly affected by water-

rock weathering and evaporation concentration. However, in 2008, the significant amount of precipitation above the average for the region had some effect on the chemical composition of the groundwater.

According to Marandi and Shand (2018) the Piper diagram is a more appropriate tool for understanding of the complex hydrogeochemical processes of groundwater. Piper trilinear diagram (Piper, 1994) consists of two triangles and one diamond. Three sides of the lower left triangle represent the milliequivalent percentages of Na^+ K^+, Ca^{2+} and Mg^{2+} in the cations, respectively. The three sides of the lower right triangle represent the milliequivalent percentage of HCO_3^-, Cl^-, and SO_4^{2-}. The anions and cations are shown by separate ternary plots, which were projected onto a diamond. Although the samples were not analyzed for sulfates content, we put the other data on Piper diagram in order to visualize their grouping in the years (Fig. 8). The difference between two figures is in addition of NO_3^- on chloride axes in Fig. 8b, which demonstrates the greater anthropogenic load of domestic wells in 2007 and 2008 years. As can be seen from the diagrams, the processes of dissolution and weathering of the rocks predominate. The soil parent material is loess with a high content of calcium carbonates, which are easily dissolved and washed into the deep layers. Therefore, sodium-magnesium-calcium ions predominate in the composition, while in the case of anions, nitrates related to anthropogenic activity affect their concentrations.

According to the Water Quality Index (WQI) the water in the domestic wells at the beginning of the monitoring periods in 2007 and 2008 had similar and substantially deteriorated quality (Table 2). In 2024 although the waters remained of unsatisfactory quality, an almost two-fold decrease in the index was observed. This finding is also confirmed by the 2.5-3 times decrease in the concentrations of a large number of the investigated chemical elements. As can be seen from the results, the anthropogenic load (irrigation, fertilizing with organic fertilizers, raising animals on small territories) has a notably impact on the composition and quality of water from domestic wells. The possible change of land use, as well as the characteristics of the soil and climatic conditions are the reasons for the observed change in

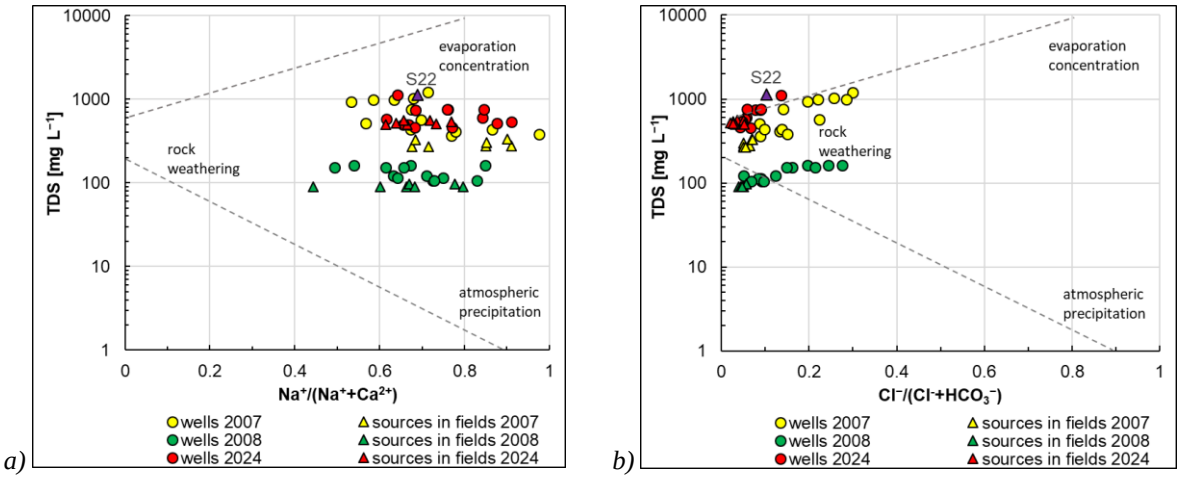


Fig. 7. Gibbs diagrams identifying dominant hydrogeochemical processes based on (a) cation ratios and (b) anion ratios across all monitoring years. S22 indicates the outlier from the erosion control field.

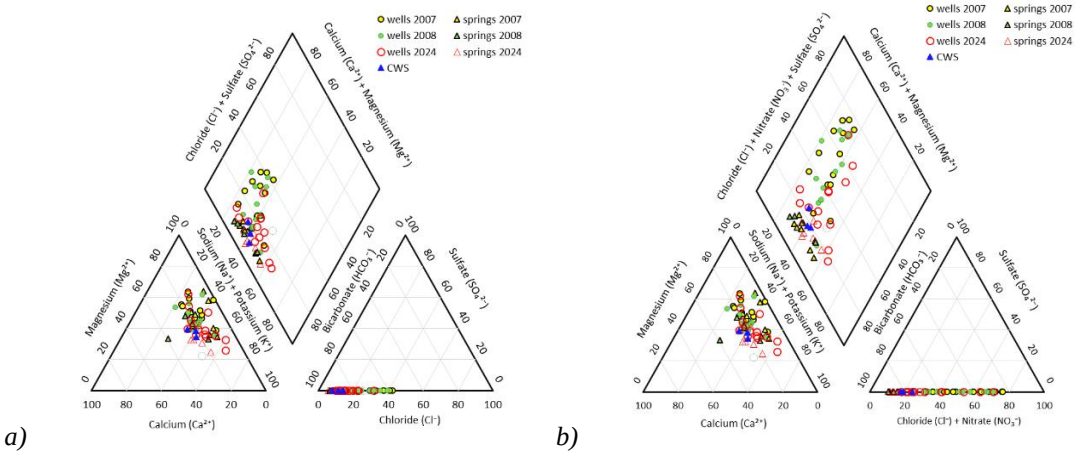


Fig. 8. Piper trilinear diagrams illustrating groundwater facies: (a) standard configuration; (b) modified configuration incorporating nitrate on the chloride axis to highlight anthropogenic impacts.

the water quality of the domestic wells. It is established that the springs and wells outside the settlement, located on arable fields, fields, meadows, etc., have similar lower indices during the three studied years. This is attributed to the fact that these sources integrate recharge from larger, less intensively managed catchment areas, reflecting diffuse rather than point-source loading.

Conclusion

The waters in the studied region have an alkaline reaction and a mixed Na-Mg-HCO3-NO3 composition. Hydrochemical compositions was influenced mainly by the dissolution and weathering of the rocks. A substantially, variation of the chemical elements and a high content of some of them (K^+, Ca^{2+}, Mg^{2+}, NO_3^-), that exceeded the MPCL for drinking water was observed, especially in the initial stages of the monitoring period. Their higher content was observed in the household gardens and wells designated as (point sources) of load. It has been observed that the springs outside the urban mixed area (diffuse sources of load) have a weaker influence on the enrichment of water with elements. The data show that after a 15-year period in 2024, lower values are reported in the waters for a large part of the investigated elements. After calculating the Water Quality Index, it was found that in the domestic wells it varied between 79 and 169, while WQI of springs changed less from 39.5 in 2007 to 49 in 2024. A significant change is observed in the groundwater index from domestic wells precisely in 2024. This state of the waters indicates the significant impact of anthropogenic loading throughout the watershed level and especially at domestic wells. Reducing nitrogen and other biogenic elements leaching from the soil profile and decreasing groundwater load can be achieved by applying less amounts of organic fertilizer and irrigation, and compacting crops.

Acknowledgements

The funding of the research activities was received from the Bulgarian National Science Fund under grant agreement КП-06-Н76/2 2023 (project "Integration of satellite derived and ground-based data for soil water balance components and crop cover into models for assessment of agroecological risks and agricultural practices for their mitigation").

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Assoc. Prof. Tsetska Simeonova, PhD. (*corresponding author, e-mail: cecka_simeonova@abv.bg),
Prof. Dimitranka Stoicheva
Department of Agrochemistry, Agroecology and Farming systems
"N. Poushkarov" Institute of Soil Science, Agrotechnologies and Plant Protection
Agricultural Academy
7 Shosse Bankya str.
1331 Sofia
Bulgaria

Prof. Milena Kercheva
Assoc. Prof. Gergana Kuncheva, PhD.
Assoc. Prof. Emil Dimitrov, PhD.
Department of Physics, Erosion and Soil biota
"N. Poushkarov" Institute of Soil Science, Agrotechnologies and Plant Protection
Agricultural Academy
7 Shosse Bankya str.
1331 Sofia
Bulgaria

Assoc. Prof. Margaritka Filipova, PhD.
Department of Heat, Hydraulics and Environmental Engineering
Agrarian and Industrial Faculty
University of Ruse "Angel Kanchev"
8 Studentska str.
7017, Ruse
Bulgaria