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Assessment of groundwater quality-case study, Suharekë Municipality, Kosovo

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ABSTRACT

Water is essential for the survival of all living beings on Earth, and they can thrive only if they consume high-quality water in sufficient amounts. Groundwater is a vital scource for drinking water; however, its quality has become concerning in recent decades due to human activities. This paper aimed to assess the quality of groundwater in the territory of the Municipality of Suharekë. To achieve this, 16 water samples were taken from dug and drilled wells used by the community for various purposes, from which the physical and chemical parameters of the water were analyzed. The groundwater analyzed in this study area generally showed parametric values within the standards for safe drinking water. The water quality index was calculated using the weighted arithmetic water quality index method, which is an easily applicable method for this purpose. The well water in the study area showed mostly excellent and good quality indices. Additionaly, the study identified seven hydrochemical types of water, with the most prevalent being the hydrochemical types Ca-Mg-HCO_3-CO_3 and Mg-Ca-HCO_3-CO_3.

Keywords: assessment, quality, groundwater, Suharekë, Kosovo.

INTRODUCTION

Water is a unique and vital natural resource on Earth, essential for human survival and for all living beings (Adimalla et al., 2022; Ugwu et al., 2017; Weight and Sonderegger, 2000). Water is a fundamental necessity for life (Ferrer et al., 2020), important for the maintenance of human life and development (Yang et al., 2016). According to (Giao et al., 2023), groundwater is an integral source of freshwater that serves various human needs in many parts of the world. It supports all forms of life and generates jobs (Yirged et al., 2023) for many sectors as industry, tourism, recreation, etc. It is estimated that groundwater supplies water to 2.5 billion people, who are completely dependent on this water source to meet their needs (Zektser et al., 2004). According to (Yang et al., 2016) about 30% of the global human population depends on groundwater for drinking water. Velis et al. (2017) emphasize that groundwater is a vital resource for human development. They represent a major source of human food, agriculture, and industry (Luvhimbi et al., 2022). According to (Desta et al., 2022; Wheeler et al., 2021) groundwater is a key component of human development, because it represents the main source of drinking water in many countries around the world. Kumar (2014) emphasizes that groundwater is used for various purposes, including irrigation, water for production, etc., so knowing its chemical composition takes on particular importance. The chemical composition of groundwater varies from the recharge zone to the drainage zone, as a result of a series of geochemical processes and the duration of its residence in the aquifer. In general, the chemical composition of groundwater is the result of several factors that develop under certain conditions of the geological environment. The main factor of chemical composition is the lithological composition of rocks, while factors such as physical-geographical, geological and hydrogeological conditions, the participation of living organisms as well as anthropogenic actions cooperate in the formation of the chemical composition of groundwater. The extraction and use of groundwater are constantly increasing, but their conservation and protection remains the main problem. The quality of groundwater is determined based on its chemical composition and physico-chemical properties, it depends on such factors as: lithology, depth of extension, water-rock contact surface, length of circulation path, hydraulic connection with surface waters, etc. The most popular definition of water quality is "water quality is its physical, chemical, and biological characteristics" (Hassan et al., 2017). Deterioration in drinking water quality also occurs during processing, storage, and distribution (Akoto et al., 2017). According to (Yang et al., 2014) socio-economic development and human population growth contribute to the increase in the production of household solid waste, which affects the water quality. This is because a large number of developing countries continue to deposit waste in landfills, while the runoff from these landfills often seeps into groundwater, resulting in groundwater pollution and threatening its quality (Eslami et al., 2019; Gao et al., 2020; Qian et al., 2020; Liu et al., 2019). Water quality, especially from a microbiological perspective, can be compromised during the collection, transportation, and storage of water at home. A deterioration in water quality is also due to various sources of organic and inorganic pollutants coming from agricultural, commercial and domestic activities (The Star Online, 2019). WHO (2012) emphasizes that water is related to human health; it is a mechanism to reduce diseases, but also a vehicle through which disease-causing agents are transported. Thus, the consumption of the water that is not within the standard hygienic-sanitary values for drinking water, cooking, etc., causes problems that manifest themselves in diseases as well as poor personal and household hygiene. Therefore, it is necessary to monitor, assess and control the quality and quantity of water before its use for consumption. Monitoring the quality of groundwater enables the knowledge of the current situation and proposes measures as well as actions for its exploitation and use in the future. The International Organization for Standardization (ISO) defines monitoring as "the planned process of sampling, measuring and subsequent recording or reporting, or both, of various characteristics of water, often with the aim of assessing conformity with specified objectives". WHO (2012) emphasizes that it is important for human health that all water intended for drinking-consumption is of good quality from the point of supply to the point of consumption. A valid method for assessing water quality is the water quality index (WQI) given by Horton (1965) and modified by Brown et al. (1972) which describes the suitability of water for human consumption, distinguishing five classes of water quality: excellent, good, poor, very poor and unusable. The water quality index has been widely applied in recent years by Kosovar/Albanian researchers. This research on the assessment of water quality in this study area is based on two main components: first, the lack of data regarding groundwater quality and second, the results achieved are valuable information for the community of the area that uses these waters for various purposes. The objective of the study was to assess the quality of groundwater and compare the findings with national as well as international guidelines for waters used for general public consumption. On the basis of field and laboratory research and the results achieved, this study not only assesses groundwater quality but also provides a basis for strategic planning and water management plan at the river basin level as outlined in the European Union's Water Framework Directive 2000/60 (WFD, 2000). In the specific case of the Toplluhë River basin, within which all water wells are open, water samples were taken for of this study.

Literature review

Today, there is a wide range of scientific literature and publications written globally, which is easily found on electronic platforms such as Web of Science, Scopus, Google Scholar, Research Gate, etc., in which groundwater quality is addressed. Authors and co-authors of these papers use physical, chemical, biological parameters, heavy metals, and indices relevant to the specific purpose to assess water quality, which they support with methodologies and standards accepted by the scientific community at a global level. On this basis, in this case study, a review of the current literature was conducted, which from different perspectives addresses the health status (quality) of the waters in the territory of the Municipality of Suhareka. Thus, a growing trend in recent decades nationwide, and in particular in the territory of the Municipality of Suhareka, is characterized by increased demand for water quantity, especially in urban areas. As Grimm et al. (2008) point out, urban developments have constantly been of interest to researchers, due to the fact that overpopulation of certain areas exerts pressures on the surrounding environment, continuously affecting it. On the other hand, urban transformations always bring about evident environmental changes, leading to concerns about sustainability (Seto et al., 2011). A close connection between urban population and environmental issues is also highlighted by (Torrey, 2004) in his paper. Urban consumption leads to pollution and degradation, which negatively affect public health and the use of natural resources on the one hand, while on the other hand, intensive rural activities in the agricultural sector, etc., where the use of nutrients (organic and chemical) and plant protection products have an increasing trend, affect environmental health, especially surface and groundwater, which is evident in this study area. A study conducted in (2013) by Halili et al. (2013) in the "Xhavit Syla" area of the Suhareka Municipality, reported that some of the analyzed physico-chemical and biological parameters in well water exceed the permitted values according to the EPA guidelines and Kosovo regulations. It was shown that 85% of the samples tested positive for E. coli, while 70% tested positive for Pseudomonas (Halili et al., 2023). Kryeziu et al. (2023) conducted a study to assess water quality in five locations (the samples are identified as water source (alb. Burimi), sample from urban area/tap, secondary school, primary school, and preschool institution), located mainly in the area of the city of Suhareka and concluded that the drinking water in that research area was within the standard of administrative instruction 16/2012 and the European Drinking Water Directive and is good, qualitative and safe for human consumption. In the Prizren region, near the current study area, Gashi et al. (2023) conducted a study on the assessment of drinking water quality from 10 artesian wells and concluded that four out of the 10 tested artesian wells showed poor drinking water quality. About 62 km from the current study area, the city of Prishtina is located in the urban area of which, Nuha et al. (2024) made an assessment of water quality from samples taken from four wells. According to (Nuha et al., 2024), it was found that manganese levels were within acceptable limits, while iron levels were shown to be higher than the permitted value. This study also highlighted the bacterial load in well waters and concerns regarding iron levels and electrical conductivity; however, it shows that most of the parameters tested were within acceptable limits for safe drinking water. Shehu (2019) assessed the water quality in the Toplluh River, which is the main river in the Suhareka Municipality, and derives as a result organic and inorganic pollution of the river water in the direction of its flow, also showing that the concentration of all heavy metals in sediment samples was significantly higher than average values, except for Cd. The findings reported from previous studies regarding the water quality in the territory of the Suhareka Municipality and other regions of the country indicate that there is a concern in terms of the quality of groundwater.

Study area

The study area is located in the southern part of the Republic of Kosovo (Figure 1). It extends between latitudes 42° 15’ 00” and 42° 30’ 00” north and longitudes 20° 45’ 00” and 21° 00’ 00” east.

It has an area of 361.78 km^2 (KCA, 2020) or constitutes 3.3% of the territory of Kosovo (KAS, 2013). According to the Development Plan of the Municipality of Suhareka, 41.7% of the area is covered by forests, 53.7% is agricultural land and 4.6% is other areas (MS, 2020). The data from the Directorate of Agriculture, Rural Development and Forestry of the Municipality of Suhareka, indicate that 4481 ha are planted with cereals, 949 ha with grape vines, 646 ha with vegetables and 279 ha with trees. The study area in the peripheral part is mainly surrounded by the elevated part of the terrain (mountainous part), while the plain part spreads in the southwest and west direction. The average altitude of the study area is 455 m, with the highest peak being Dera e Pasha (2029 m) and the peak Kryet e Ahishtës (1677 m) (KCA, 2020). This region is characterized by a continental-Mediterranean climate (Pllana, 2015; IWM, 1983). The average annual air temperature is 11 °C, while precipitation for the period 2016–2020 measured at two meteorological stations, Suhareka and Budakovë, showed an average value of 739.58 mm (Suhareka station) and 814.54 mm (Budakovë) (KEPA-KHI, 2019, 2020). The hydrographic network is relatively developed. The main river is the Toplluhë River, which has an average annual flow of 3.44 m^3/s and represents the main watershed of the study area with an area of 495 km^2 (MESPI, 2020). The geological structure of the study area includes rocks from the Paleozoic, Mesozoic, Neogene and Quaternary periods

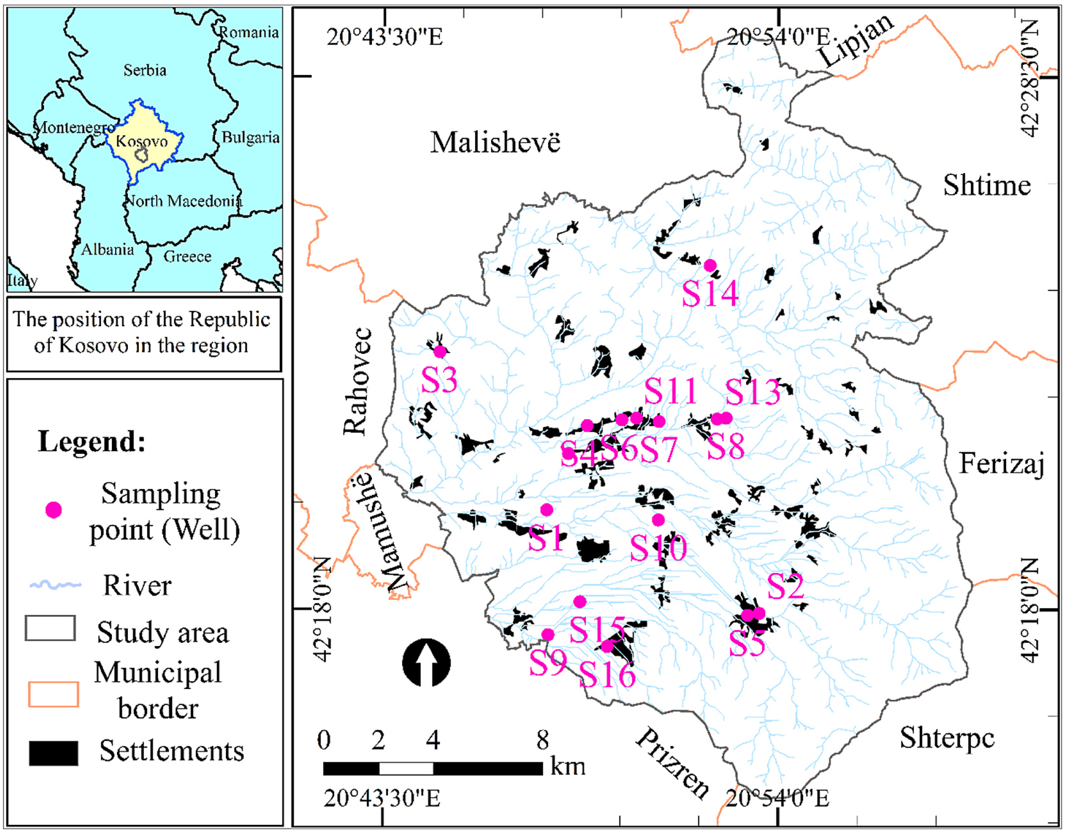

Figure 1. Study area

(ICMM, 2006a). The Paleozoic formations consist of chloritic-sericite shales and are mainly distributed in the southeastern and northeastern parts of the study area. The Jurassic consists of diabase, flint, and serpentinite formations represented by: clay, sandstone, siliceous, diabase, and serpentinite. The Triassic consists of metamorphosed sandstone and clay rocks. The Cretaceous consists of blocky and massive limestone, clays, and siliceous lenses. The Neogene consists of Plio-Quaternary gravels and sands and sandstones, sand, clays, tuffs and lignite. The Quaternary consists of alluvium, proluvium and deluvium represented by sand, gravel, clay, and silt (Figure 2a).

Hydrogeological Units, Aquifer (Figure 2b). Porous/intergranular porosity-Intergranular porosity aquifer with very high-medium permeability (e.g. sand, sand and gravel, sand, gravel and mud/silt) with $K_f > 10^{-5}$ m/s. Intergranular porosity aquifer with medium-low permeability (e.g. clay, sand and mud/silt) with $K_f = 10^{-5}–10^{-9}$ m/s. Fissured porosity aquifer with medium-low fracture permeability (e.g. limestone, limestone/marlstone, marble, metamorphic rock, sandstone, conglomerate, limestone/marlstone, plutonic rock) with $K_f = 10^{-5}–10^{-9}$ m/s. Fissured/karstified porosity aquifer with strongly alternating, local very high, fracture permeability (e.g. limestone, marble) with $K_f = 10^{-3}–10^{-9}$ m/s. Aquiclude without considerable intergranular or fissured porosity (e.g. sandstone, sandstone, mudstone/siltstone, conglomerate, metamorphic rock, volcanic rock, plutonic rock, pyroclastic rock) with $K_f < 10^{-9}$ m/s (ICMM, 2006b).

Methods and materials

To assess the quality of groundwater in the Municipality of Suhareka, 16 water samples were collected from dug and drilled wells (Figure 1). Of course, the more samples, the more representative the representation of what is being researched. Logistical and economic capacity allowed selecting only these 16 wells; however, the locations (wells) where water samples were taken were selected taking into account the geological structure, hydrogeological characteristics and other environmental factors so that the samples were as representative as possible for the purpose of the work. The construction of the well was mainly with prefabricated concrete blocks with a diameter of 800 mm opened with the help of machinery, while their depth was estimated at

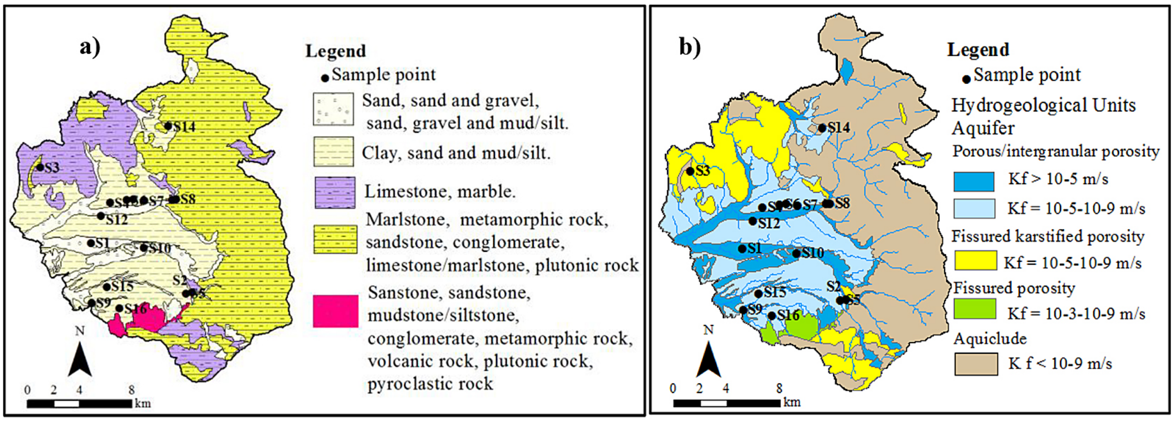

Figure 2. a) Geological map and b) Hydrogeological map

between 20–25 m. All wells are active and used by residents for drinking water, irrigation, in some cases the water from these wells is used for packaging water and liquids, as well as for other purposes in the industrial sector. The collection and storage of these water samples crucial because the quality of the result is greatly influenced by the method of collection, storage and analysis of the water sample (Madrid and Zayas, 2007). To avoid these weaknesses during water sampling, the water was placed in standard plastic (polyethylene) bottles with a volume of 1000 ml (sample bottles), the bottles were carefully closed with a stopper and each one was given an ID (S1, ..., Sn) (Figure 1). The water samples were stored in a hand-held refrigerator until they were sent to the laboratory for analysis of physicochemical parameters (sampling protocols: ISO 5667-3 (2003), ISO 5667-11 (2009). Some parameters, such as; water temperature, pH, EC, dissolved oxygen, as well as organoleptic and optical properties of water were measured directly during field work, while other parameters were analyzed in the laboratory by standard protocols and methodologies for such purposes (APHA, 1995). Table 1. shows the standards and techniques applied in the laboratory for the analysis of water samples-physical and chemical parameters.

The coordinates and elevation of the wells were determined using a Garmin 79C handheld GPS (Table 2). Results from field and laboratory research were statistically analyzed using standard methods. For statistical aspects, Excel and Past 4.03 programs were used, hydrochemical types were calculated with the Aquachem program, while for the cartographic part, the ArcMap v.10.5 program was used. To interpolate physical and chemical parameters to see their spatial distribution, the inverse distance weighted (IDW) method was employed using ArcMap 10.5 v. software. The World Health Organization standard (WHO, 2006, 2011) was used to compare the results of physical and chemical parameters. In total, 24 – mainly physical and chemical – parameters were analyzed, and the results for them are presented in (Table 3).

The data on the physical and chemical parameters analyzed for the groundwater of the study area are shown in Table 3. In the well with ID (S1), only NH_4^+ shows a value higher than the standard, in the well with ID (S2) NO_3^- and Mg^{2+} exhibit higher values than the standard, in the well with ID (S3) one of the analyzed parameters show values above the standard one, in the well with ID (S4) temperature, TOC, NO_3^- and Mg^{2+} show values higher than the standard. In the wells with ID (S5 and S6) all parameters show values within the standard. In the well (S7) the COD and TOC parameters show higher values, in the well with ID (S8) the parameters that have values above the standard ones are: EC, TDS, DR, in well (S9) the parameters such as: PO_4^{3-}, pH and Mg^{2+} show excess over the standard values. The well with ID (S10) does not exceed the standard values in any parameter. In the well with ID (S11), the parameters that show values higher than the standard (WHO, 2011) are: COD, TOC, EC, TDS, DR, Ca^{2+} and Mg^{2+}. In the wells with ID (S12, S13 and S14) all parameters are within standard values, in the well (S15), temperature, TCO, NO_3^- and Mg^{2+} exceed the limit values given in the standard, while in the well with ID (S16) the parameters: temperature, turbidity and Mg^{2+} exceed the standard value. Thus, of the 22 parameters that were compared with the World Health Organization standard

Table 1. Standards and techniques applied in the laboratory

Parameters	Unit	Standard method	Technique
Water temperature	C	DIN 38404-C4	Electrode (WTW 3210)
Turbidity	NTU	ISO7027:1999	Infra Red Spectroscopy (WTW430R)
Electro conductivity	μS/cm	ISO 7888:1985	Potentiometry (WTW 315i)
pH	0–14	ISO 10523:2008	Potentiometry (WTW 3210)
Dissolved oxygen	mg/L	ISO 5814:2012	Potentiometry (WTW Oxy 3210)
Chemical oxygen demand	mg/L	ISO 15705	Spectroscopy (WTW UV-VIS 6600)
Biochemical oxygen demand	mg/L	ISO 5815-2	Titration
Total suspended solids	mg/L	EN872	Gravimetry
Total organic carbon	mg/L	APHA 5310	Spectroscopy (WTW UV-VIS 6600)
Ammonium	mg/L	ISO7150-1	Spectroscopy (WTW UV-VIS 6600)
Nitrates	mg/L	ISO 7890/1:1986	Spectroscopy UV (WTW 7600)
Nitrites	mg/L	EN26777:1993	Spectroscopy UV (WTW 7600)
Phosphates	mg/L	ISO 15681-2:2018	Spectroscopy UV (WTW 7600)
Calcium	mg/L	ISO 6058:1984	Titrimetric
Magnesium	mg/L	ISO 6058:1984	Titrimetric
Sodium	mg/L	ISO 9964-3:1993	Flame emission spectrometry
Potassium	mg/L	ISO 9964-3:1993	Flame emission spectrometry
Chloride	mg/L	ISO9297	Spectroscopy (WTW UV-VIS 6600)
Sulfate	mg/L	APHA 4500	Spectroscopy (WTW UV-VIS 6600)
Bicarbonate	mg/L	ISO 9963:1984	Titrimetric
Carbon dioxide	mg/L	ISO 9963:1984	Titrimetric

Table 2. Data on the locations (wells) where water samples were taken for water quality assessment

ID	Water source	Coordinates		Amsl (m)	Geology/Lithology	Potential sources of water pollution in wells
S1	Well	42°20'00"N	20°51'22"E	458	Quaternary/Alluvial	Settlement, utilities contaminants
S2	Well	42°17'55"N	20°53'30"E	587	Quaternary/Alluvial, Proluvial	Agriculture land
S3	Well	42°23'51"N	20°44'59"E	543	Jurassic/Serpentinite	Settlement, wastewater, agriculture
S4	Well	42°21'47"N	20°48'25"E	382	Quaternary/Gravel, sand	Settlement, wastewater, agriculture
S5	Well	42°17'53"N	20°53'11"E	587	Quaternary/Proluvial	Settlement, wastewater, agriculture
S6	Well	42°21'37"N	20°48'55"E	388	Quaternary/Gravel, sand	Settlement, wastewater, utilities contaminants
S7	Well	42°21'45"N	20°49'50"E	402	Quaternary/Gravel, sand	Settlement, wastewater, utilities contaminants
S8	Well	42°21'43"N	20°50'50"E	412	Paleozoic - Chloritic, epidotic, sericitic, quartzite, metabasalt shales	Agriculture land
S9	Well	42°17'16"N	20°49'28"E	462	Quaternary/Proluvial	Agriculture land
S10	Well	42°19'46"N	20°50'50"E	467	Quaternary/Lake sediments	Agriculture land
S11	Well	42°21'46"N	20°50'14"E	409	Quaternary/Gravel, sand	Settlement, wastewater, utilities contaminants
S12	Well	42°22'09"N	20°52'36"E	449	Quaternary/Alluvial	Agriculture land
S13	Well	42°21'45"N	20°52'23"E	429	Quaternary/Alluvial	Agriculture land
S14	Well	42°24'45"N	20°52'13"E	656	Quaternary/Gravel, sand	Settlement, wastewater, agriculture
S15	Well	42°18'09"N	20°48'43"E	409	Quaternary/Proluvial	Settlement, wastewater, agriculture
S16	Well	42°17'32"N	20°47'54"E	383	Quaternary/Proluvial	Settlement, wastewater, agriculture

values (Table 3), the following results were obtained; in 7 water wells or 43.75% of them, not one of the 22 parameters exceeded the standard values, in two wells or 12.5% of them, four parameters exceeded the standard value, in three wells or 18.75% of them, only three parameters exceeded, in two wells or 12.50%, there were only two parameters exceeded, in one well, there was only one parameter exceeded, while in the well with ID (S11) it was shown that a number of seven parameters were above the standard values. Table 4 shows the values of parameters that are within the standard value limit and the values of parameters that are above the standard value (WHO, 2011).

RESULTS AND DISCUSION

Knowing the quality of water is of particular importance not only for drinking water supply, technical water supply, and irrigation, but also for the degree of its aggressiveness concerning construction materials, mainly concrete and iron. The quality of groundwater in this study area is addressed, based on physical and chemical parameters measured and analyzed in the laboratory. The organoleptic properties of groundwater in the study area showed (most of them) values within Administrative Instruction No. 10/2021 on the Use of Water for Public Consumption (OGRK, 2021). Thus, the

Table 3. Results of groundwater samples in the study area.

ID	Temp.	Aroma	Taste	Color	Tur	EC	TH	pH	TDS	DR	TSS	OD	COD
	°C	Sniff	Consumption	Pt/Co	NTU	μScm^{-1}	d°H	0-14	mg/L	mg/L	mg/L	mg/L	mg/L
S1	-				0.4	313	7.3	7.5	158	207	< 0.1	-	< 0.1
S2	-				0.3	681	21.3	7.37	344	449	0.1	5.8	0.1
S3	-				0.4	879	26.6	7.26	444	580	0.1	-	0.1
S4	17.9				5.4	720	24.6	7.5	364	475	0.1	5.7	8.5
S5	-				1	693	18.4	7.61	350	457	0.1	5.1	0.1
S6	13.5				1	693	18.4	7.61	350	457	0.1	5.1	0.1
S7	12				0.6	452	18.4	7.25	228	298	1.2	5.31	18.2
S8	-	Without	Without	Without	1.1	1026	26.1	7.16	518	677	0.1	-	0.1
S9	-				0.8	599	20.7	9.02	303	395	0.1	5.1	3.9
S10	-				2.6	431	11.9	7.33	218	284	0.1	7.3	7.8
S11	-				1	1180	34	7.59	596	779	5.4	6.8	26
S12	-				1	588	17.3	7.51	297	388	0.1	-	0.1
S13	-				1	848	21.6	7.61	428	560	0.1	-	0.1
S14	-				0.4	313	7.3	7.5	158	207	< 0.1	-	< 0.1
S15	17.9				5.4	720	24.6	7.8	364	475	0.1	5.7	8.5
S16	18.8				14.8	627	19.6	7.81	317	414	0.5	6.4	2.8
WHO	8-15		Without		10	1000	30	6.5–8.5	500	660	-	> 5	10
Min	12				0.3	313	7.3	7.16	158	207	0.1	5.1	0.1
Max	18.8				14.8	1180	34	9.02	596	779	5.4	7.3	26
Mean	16.02				2.33	672.69	19.88	7.59	339.81	443.88	0.59	5.83	5.46
Std. error	1.37				0.93	59.21	1.74	0.11	29.9	39.07	0.38	0.24	2.12
Variance	9.33				13.69	56094.76	48.46	0.18	14304.7	24429.45	2.01	0.59	62.98
Stand. dev	3.05				3.7	236.84	6.96	0.42	119.6	156.3	1.42	0.77	7.94
Median	17.9	Without	Without	Without	1	687	20.15	7.51	347	453	0.1	5.7	1.45
25 prcntil	12.75				0.45	486	17.58	7.34	245.25	320.5	0.1	5.1	0.1
75 prcntil	18.35				2.23	816	24.6	7.61	412	538.75	0.2	6.5	8.5
Skewness	-0.68				2.93	0.4	-0.21	2.77	0.4	0.41	3.48	0.9	1.74
Kurtosis	-2.45				9.3	0.22	0.47	9.44	0.22	0.22	12.42	-0.25	2.65
Geo. mean	15.77				1.16	631.82	18.46	7.58	319.17	416.94	0.18	5.79	0.92
Coeff. var	19.06				159.16	35.21	35.02	5.58	35.2	35.21	242.18	13.2	145.43

Table 3. Cont.

ID	BOD_5	TOC	NH_4^+	PO_4^{3-}	NO_2^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	CO_2
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
S1	< 0.1	< 0.1	0.72	0.0	0.07	22.6	39.7	7.5	4.77	0.72	9.23	8.6	146.4	23.2	6
S2	0.1	0.1	0.21	0.1	0	78.9	68.2	51	3.64	11.69	17.75	24.7	384.3	45.2	21.4
S3	0.1	0.1	0.21	0	0.02	34.5	111.9	47.6	6.04	8.92	11.36	28.6	542.9	49.5	38.9
S4	5.2	3.1	0.3	0.02	0.04	51	81.4	57.6	2.81	0.97	12.78	34.8	445	65.9	19.7
S5	0.1	0.1	0.02	0.12	0.08	49	80.2	31.1	23.7	1.77	32.4	45	305	62.3	10
S6	0.1	0.1	0.02	0.12	0.08	49	80.2	31.1	23.7	1.77	32.4	45	305	62.3	10
S7	4.7	7.3	0.01	0	0.03	15.28	53.3	47.6	7.26	0.74	17.75	13.7	384.3	34.3	28.1
S8	0.1	0.1	0.21	0	0.02	27.5	119.5	40.8	21.9	0.42	31.24	115	457.5	33.1	41.2
S9	0.2	1.2	0.3	0.27	0.01	10.4	36.1	68.1	1.66	0.35	7.1	0.9	439.2	23.05	0.5
S10	4.4	2.8	0.39	0.02	0.05	4.92	58.5	16.3	3.88	0.93	16.33	8.8	232	26.1	14.9
S11	8.1	7.1	0.1	< 0.002	< 0.07	7.3	152.8	54.9	30.17	1.27	48.28	127	585.6	114.2	19.6
S12	0.1	0.1	0.08	0	0.07	1.1	88.6	21.4	4.51	1.68	11.36	28.6	353.8	57.4	14.2
S13	0.1	0.1	0.1	0	0.07	3.2	73.4	49.1	39	3.27	23.43	62.6	469.7	95.9	15
S14	< 0.1	< 0.1	0.07	0	0.07	22.6	39.7	7.5	4.77	0.72	9.23	8.6	146.4	23.2	6
S15	5.2	3.1	0.3	0.02	0.04	51	81.4	57.6	2.81	0.97	12.78	34.8	445	65.9	19.7
S16	0.1	0.8	0.44	0.03	0.03	9.84	46.9	56.6	2.88	0.73	4.97	8.8	439.2	142.1	8.9
WHO	10	3	0.5	0.2	0.5	50	120	50	120	12	250	250	650	-	-
Min	0.1	0.1	0.01	0.002	0.001	1.1	36.1	7.5	1.66	0.35	4.97	0.9	146.4	23.05	0.5
Max	8.1	7.3	0.72	0.27	0.08	78.9	152.8	68.1	39	11.69	48.28	127	585.6	142.1	41.2
Mean	2.04	1.86	0.22	0.05	0.05	27.38	75.74	40.36	11.47	2.31	18.65	37.22	380.08	57.73	17.13
Std. error	0.75	0.68	0.05	0.02	0.01	5.67	7.98	4.74	2.99	0.81	2.97	9.2	31.71	8.64	2.83
Variance	7.91	6.48	0.04	0.01	0	515.11	1019.59	360.21	142.66	10.51	141.18	1354.56	16088.97	1193.84	128.2
Stand. dev	2.81	2.55	0.19	0.07	0.03	22.7	31.93	18.98	11.94	3.24	11.88	36.8	126.84	34.55	11.32
Median	0.1	0.45	0.21	0.02	0.04	22.6	76.8	47.6	4.77	0.97	14.56	28.6	411.75	53.45	14.95
25 prcntil	0.1	0.1	0.07	0	0.02	7.94	48.5	23.83	3.07	0.72	9.76	8.8	305	27.85	9.18
75 prcntil	4.83	3.1	0.3	0.1	0.07	49	86.8	56.18	23.25	1.77	29.29	45	454.38	65.9	20.98
Skewness	1.02	1.46	1.24	2.18	-0.13	0.78	0.92	-0.58	1.22	2.41	1.2	1.61	-0.54	1.2	0.89
Kurtosis	-0.42	1.11	1.89	5.07	-1.32	-0.13	0.85	-0.85	0.18	5.07	1.01	2.09	-0.18	1.11	0.49
Geo. mean	0.44	0.53	0.13	0.01	0.03	16.97	69.85	33.93	7.02	1.32	15.58	22.08	354.81	49.35	12.54
Coeff. var	137.68	136.55	87.37	158.45	59.71	82.88	42.16	47.02	104.14	140.5	63.71	98.89	33.37	59.85	66.09

groundwater of the study area was shown to be odorless, tasteless, and colorless.

Water temperature

Water temperature as one of the main properties of water – greatly affects the development of chemical processes in water, the amount of gas and salts dissolved in it. It is noted here that groundwater has a slightly higher temperature and causes low solubility of gases. On the other hand, the concentration of sodium and potassium increases along with temperature, indicating that the sodium and potassium waters are saturated. The high temperature of groundwater indicates that these waters are close to the Earth's surface and are affected by air temperature fluctuations in the study area. A classification given by Dakoli (2007) shows that drinking waters to the average annual temperature of the country are divided into;:very cold waters $T < 4$ °C, cold $T = 4–16$ ° C and warm $T > 16$ °C. The groundwater temperature in the study area measured in five water samples showed the following values: $T_{min} = 12$ °C (S7), $T_{max} = 18.8$ °C (S16), and $T_{averg}. = 5.72$ °C ± 8.14 (Table 3). The groundwater temperature values were compared with the classification (Dakoli, 2007) and it resulted that 3 water samples or 60% classify the groundwater of the study area as warm water, while 2 water samples

Table 4. Values of parameters that are within the standard value limit and the values of parameters that are above the standard value

ID	Number of parameters				ID	Number of parameters			
	Within standard values	%	Above standard values	%		Within standard values	%	Above standard values	%
S1	21	95.45	1	4.55	S9	19	86.36	3	13.64
S2	20	90.91	2	9.09	S10	22	100	0	0
S3	22	100	0	0	S11	15	68.18	7	31.82
S4	18	81.82	4	18.2	S12	22	100	0	0
S5	22	100	0	0	S13	22	100	0	0
S6	22	100	0	0	S14	22	100	0	0
S7	20	90.91	2	9.09	S15	18	81.82	4	18.18
S8	19	86.36	3	13.6	S16	19	86.36	3	13.64

or 40% classify the groundwater as cold water. Also, a comparison of the groundwater temperature of the study area was made with the standard value (T = 8–12 °C) of Administrative Instruction No. 10/2021 (OGRK, 2021) and the World Health Organization (WHO) and resulted in that 83.33% of the water samples in the study area showed a value above the standard, while only 16.67% showed that they are within the standard value.

Turbidity

Turbidity is primarily caused by organic matter, bacteria, clay molecules, silica, carbonates, iron hydroxide, and colloidal sulfur. Groundwater turbidity in the study area showed values ranging from 0.30 NTU (S2) to 14.80 NTU (S16), with an average value of 2.33 NTU ± 3.7 (Table 3). The values of this parameter were compared with the standard value according to AI No. 10/2021 (OGRK, 2021) and WHO (Tru = 10 NTU) and it resulted in that 15 water samples or 93.75% are within the standard value, while only one water sample (S16) or 6.25% are above the standard value.

The electrical conductivity

The electrical conductivity Of the groundwater of the study area showed a value from 313.00 μScm^{-1} (S1) to 1180 μScm^{-1} (S11) and an average value of 627.56 μScm^{-1} ± 236.84 (Table 3 and Figure 3a). The measured values for EC in groundwater in the study area showed that they are within the standard value of AI No. 10/2021 (OGRK, 2021) (EC = 2500 μScm^{-1}) and (EC = 2000 μScm^{-1}) according to WHO (2011). The EC values of the study area were compared with the classification given by Handa (1969) as follows: EC = 0-250 μScm^{-1} (Class salinity is Low), 251–750 μScm^{-1} (Medium), 751–2250 μScm^{-1} (High), 2251–6000 μScm^{-1} (Very High), which is used for irrigation of agricultural crops. According to this classification, it resulted that the groundwater in 13 water samples or 81.25% was at the limit (EC = 251–750) classifying these waters in the medium salinity class which can be used for irrigation with moderate measures (can be used with moderate leaching), while 3 water samples or 18.75% was at the limit (EC = 751–2250) classifying the water in the high salinity class and description: can be used for irrigation purposes with some management practices.

Total dissolved solids

The amount and character of TDS depends on the solubility and type of rocks with which the water has been in contact and indicates the total concentration of dissolved salt ions from soils and rocks, including any organic matter and some water of crystallization in the water. Generally, low TDS is caused by the influence of rock-water interaction about recharge water at topographic highs, and high TDS is due to the impact of anthropogenic origin concerning discharge water at topographic lows (WHO, 2003; Subba Rao, 2016). The TDS of the study area showed values from 158 mg/l (S1) to 596 mg/l (S11) with an average value of 339.81 mg/l ± 119.60 (Table 3 and Figure 3b). The TDS values in the groundwater of the study area were shown to be within the WHO (2011) reference value for drinking water (Table 3).

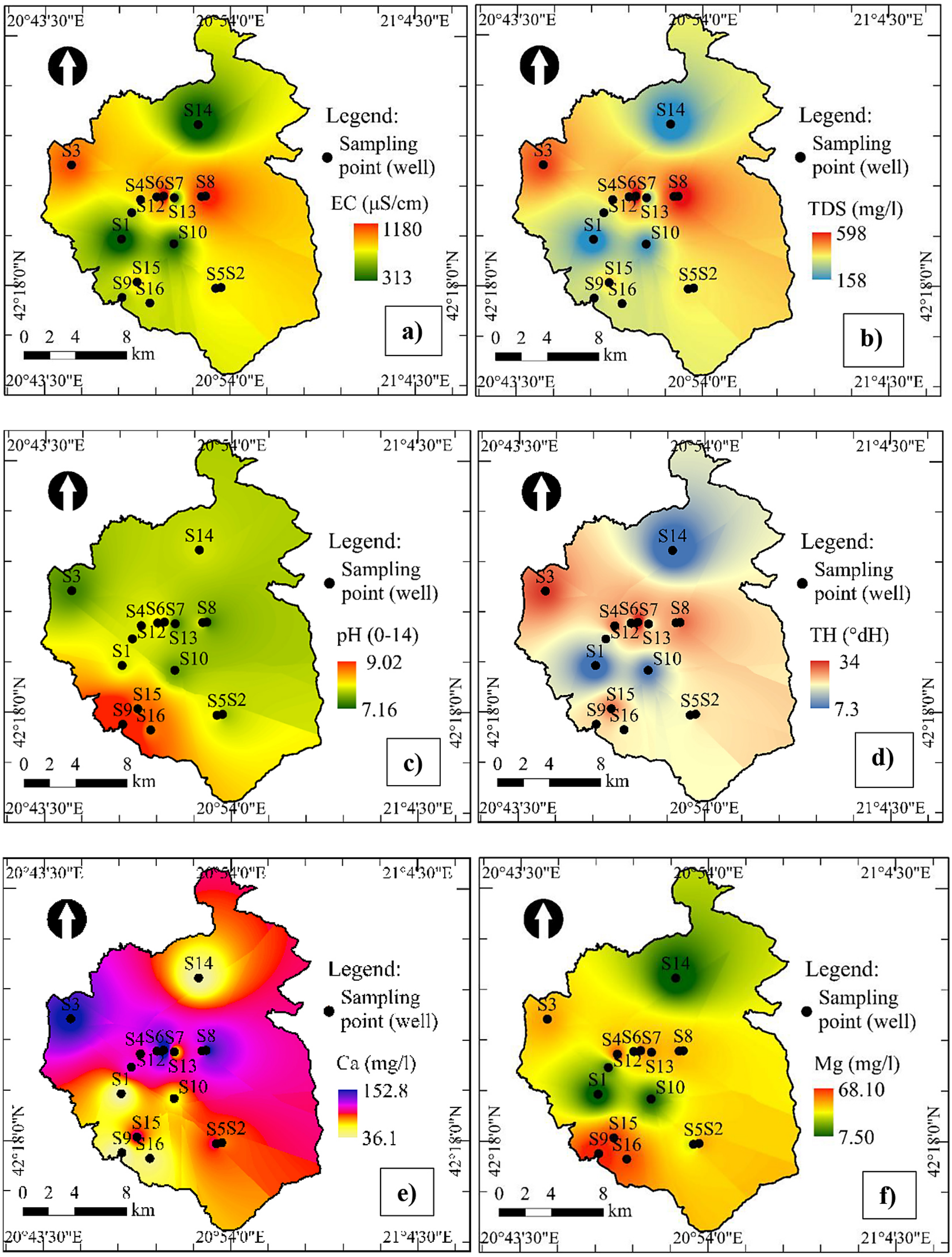

Figure 3. Spatial distribution of a) EC, b) TDS, c) pH, d) TH, e) Ca and f) Mg

Dry residue

The size of the dry residue classifies groundwater into three main groups: Freshwater with dry residue < 1.000 mg/l, Saline water with dry residue 1.000 to 35,000 mg/l and very Saline water with dry residue > 35,000 mg/l (Konomi, 2001). The dry residue (after evaporation) in the groundwater of the study area ranges from 207.00 mg/l to 779.00 mg/l with an average value of 443.88 mg/l ± 156.30 (Table 3), classifying these waters as freshwaters with dry residue below 1.000 mg/l. The use of groundwater in industry depends on the technological process;

however, according to some authors, the water used for boilers should not have a dry residue above 300 mg/l. Groundwater in 13 water samples or 81.25% showed dry residue values above the limit allowed for its use in boilers, while 3 water samples (S1, S10, S14) or 18.75% showed values within the limit value.

The pH

The pH is a key indicator of water quality. The pH of water is a measure of acid-base balance and, in most natural waters, is controlled by the carbon dioxide-bicarbonate-carbonate equilibrium system (WHO, 2007). According to Prasanth et.al. (2012) pH indicates the acidity or alkalinity of a solution. The pH values in the groundwater of the study area showed values from 7.16 to 9.02 with an average value of 7.59 ± 0.42 (Table 3 and Figure 3c). Thus, in 15 water samples or 93.75% of them, according to this parameter, the water is classified as weakly alkaline water (pH limit = 7–9), while only one water sample (S9) or 6.25% of them classifies the water as alkaline water (pH limit > 9). The pH values of the study area were compared with the values of AI No. 10/2021 (pH = 6.5–9.5) and the WHO standard (pH = 6.5–8.5) and it resulted that this parameter is within the standard values, the exception being the water sample (S9) which showed a value above the WHO standard. Also, the pH values of groundwater were compared with the FAO standard (2011) which sets the pH limit = 6.5–8.4, for water used for irrigation and resulted that 15 water samples or 93.75% are within this standard and only one water sample (S9) or 6.25% is above the standard value. Groundwater with low pH (generally acidic) is considered aggressive and can affect iron as well as concrete structures. According to the Concrete Guideline (European Concrete Standard EN 206-1:2000) the limit values for the classes of exposure to aggressive chemicals from natural soil and groundwater are classified as: pH ≤ 6.5 and ≥ 5.5 slightly aggressive, pH < 5.5 and ≥ 4.5 moderately aggressive and pH < 4.5 and ≥ 4.0 very aggressive. On the basis of the limits for pH values indicated in the EN 206-1:2000 standard, it results that the pH values in the groundwater of the study area are not aggressive, they do not present corrosive effects (corrosion) for civil engineering structures.

Dissolved oxygen

Dissolved oxygen content is a very important qualitative parameter that determines the health status of waters (Bode, 2012). Its presence in groundwater leads to the development of processes of self-purification from pollution, while its absence in shallow waters indicates water pollution. Its presence in large quantities has a negative impact; water with a lot of oxygen becomes aggressive with high corrosive properties for metal parts of water pipes, concrete, etc. In the groundwater of the study area, dissolved oxygen was measured in 10 water samples and showed values ranging from 5.10 mg/l (S5, S6, S9) to 7.30mg/l (S10) with an average value of 5.83 mg/l ± 2.98 (Table 3). The WHO standard values (WHO, 2007, 2011, 2012, 2017) for drinking water provide a limit (> 5) for dissolved oxygen, while according to AI No. 10/2021 (OGRK, 2021) no limit values are set for this parameter. A comparison of dissolved oxygen values for groundwater in the study area with the WHO standard value (> 5) showed that all water samples analyzed were within the WHO standards.

Total suspended matter

Total suspended matter showed values from 0.10 mg/l to 5.40 mg/l with an average value of 0.59 mg/l ± 1.34 (Table 3).

Chemical oxygen demand

Chemical oxygen demand in two samples it showed values below 0.1 mg/l (S1, S14), while in 14 other samples the COD value showed values from 0.10 mg/l to 26 mg/l (S11) with an average value of 5.46 mg/l ± 7.62 (Table 3). The values of this parameter were compared with the standard value according to WHO and it resulted that: 14 water samples or 87.5% are within the standard value, while 2 water samples or 12.5% are above the standard value (WHO, 2011).

Biochemical oxygen demand

Biochemical oxygen demand represents the amount of oxygen needed for the biological decomposition of organic substances in water by the action of microorganisms at 20 °C for five days. High BOD_5 values in water are a sign of organic pollution, which affects water quality and the aquatic environment. In the groundwater of the study area, BOD_5 showed values from 0.10 mg/l to 8.10 mg/l (S11) with an average value of 2.04 mg/l ± 2.71 (Table 3). The standard value for this parameter according to WHO (2011) is 1 mg/l, so 11 water samples or 68.78% are within the standard value, while 5 water samples or 31.25% are above the standard value in the groundwater of the study area (Table 5).

Total organic carbon

Total organic carbon showed values from 0.10 mg/l to 7.30 mg/l (S7) with an average value of 1.86 mg/l ± 2.45 (Table 3). In total, 12 water samples or 75% of them showed TOC values within the WHO standard value (3 mg/l) and 4 water samples or 25% are above the WHO standard.

Phosphate ions

Phosphate ions in the groundwater of the study area showed values from 0.002 mg/l to 0.27 mg/l (S9) with an average value of 0.047 mg/l ± 0.073 (Table 3). 15 samples or 93.75% are within the WHO standard value, while 6.25% or one water sample is above the WHO standard value which is (0.2 mg/l).

Ammonium ions

Ammonium ions showed values from 0.01 mg/l (S11) to 0.72 mg/l (S1) with an average value of 0.22 mg/l ± 0.19 (Table 3).

Nitrites

Nitrites showed values from 0.001 mg/l (S9) to 0.083 mg/l (S6) with an average value of 0.046mg/l ± 0.029 (Table 3). In 16 water samples or 100% of them, it turns out that they are within the standard value of WHO and AI No. 10/2021 (OGRK, 2021).

Nitrates showed values from 1.10 mg/l (S12) to 78.90 mg/l (S2) and an average value of 27.38 mg/l ± 22.70 (Table 3). These values were compared with the standard value according to WHO (2011) and AI No. 10/2021 (OGRK, 2021) and resulted that 13 water samples or 81.25% are within the standard value, while 3 water samples or 18.75% are above the standard value.

Chlorine

Chlorine is widely found in waters, often in predominant concentrations. The Cl^- content under natural conditions ranges from 2 mg/l to 10 mg/l (Dakoli, 2007), while the pollution of groundwater with chlorine leads to the phenomenon of inversion of water salinization, especially in urban and rural areas where the Cl^- content increases from tens to hundreds of milligrams per liter. In shallow groundwater, the chlorine ion is associated with the sodium and potassium ions, while in deep waters it is also associated with the Ca^{2+} ion. This ion in the groundwater of the study area showed values ranging from 4.97 mg/l (S16) to 48.28 mg/l (S11) and an average value of 18.65 mg/l ± 11.88 (Table 3). The chlorine ion values in the 16 water samples analyzed in the groundwater of this area showed that they are within the standard values according to AI No. 10/2021(OGRK, 2021) and WHO (2011). Referring to the natural values of the presence of Cl^- (from 2 to 10 mg/l), it results that 4 water samples or 25% remain within the limit of natural values, while 12 water samples or 75% are above the limit of natural values. Therefore, in the groundwater of the study area, it is observed that the increase in Cl^- may have come from atmospheric precipitation, and the alteration of minerals such as apatite, rock salt, etc. However, the main indicators of the increased presence of Cl^- in the study area are anthropogenic impurities, such as wastewater

Table 5. BOD level, water quality and sample in study area

BOD level (mg/l)	Water quality	Study area	
		No. sample	%
1–2	Very good (there will not be much organic waste present in the water supply	2	10
3–5	Fair: moderately clean	-	-
6–9	Poor: usually indicates organic matter is present and bacteria are decomposing this waste	-	-
100 or greater	Very poor: very polluted, contains organic waste	-	-

streams, industrial wastewater, and urban and rural waste dumps. This claim is based on the release of wastewater (urban, industrial, etc.) without treatment into receiving environments, as well as the uncontrolled storage of urban and rural waste in the environment. The Cl^- values in the groundwater of the study area do not make them aggressive towards construction materials, such as concrete and iron. A Cl^- content of waters > 100 mg/l makes them aggressive towards concrete and iron. According to Hanson et al. (1994) and Hassan (1998) the Cl^- values for water quality for micro-irrigation systems are given in the limits: Cl^- < 142 mg/l (Low), Cl^- = 142–355 mg/l (moderate) and Cl^- > 355 mg/l (high). Therefore, even according to the division given by (Hanson et al., 1994; Hassan., 1998) it results that the Cl^- values in the groundwater of the study area are within this division and can be used for such a purpose. Another classification given by Mass (1990) for the Cl^- content in water shows that the water with Cl^- below (<) 70 mg/l (effect on crops; generally safe for all plants), Cl^- 70–140 mg/l (effect on crops; sensitive plants show injury), Cl^- above (>) 350 mg/l (effect on crops; can cause severe problems). The Cl^- values in groundwater were also compared with the classification given according to Mass (1990) and it resulted that the groundwater in the study area has no effect and is generally safe for use for all plants.

Sulfate

Sulfate is always associated with Ca^{2+} and less often with Mg^{2+} and is characteristic of groundwater (Dakoli, 2007). From a natural point of view, the main source of SO_4^{2-} in groundwater is from the dissolution of gypsum and anhydrite, as well as the oxidation of sulfide minerals (Çadraku, 2021; Çadraku et al., 2016). SO_4^{2-} can also enter shallow groundwater from the decomposition of sulfur-containing plant and animal substances, and then from atmospheric precipitation. In the groundwater of the study area, SO_4^{2-} in significant quantities entered from wastewater (polluted), from the process of washing urban and rural waste, industrial wastewater, etc. The values of SO_4^{2-} in the groundwater of the study area were found to be from 0.90 mg/l (S9) to 127 mg/l (S11) with an average value of 37.22 mg/l ± 36.80 (Table 3). Sanitary hygiene standards set the maximum SO_4^{2-} content in drinking water at up to 250 mg/l (WHO, 2011; OGRK, 2021), which indicates that the groundwater of this study area is within the standard values about the SO_4^{2-} parameter. On the other hand, the high concentration of SO_4^{2-} in water, above 150 mg/l, gives it aggressive properties towards concrete and cement structures, while in food industrial branches, water should not contain SO_4^{2-}. The concrete guide (Hirschi et al. Series #93-05) gives a breakdown of SO_4^{2-} content in groundwater as follows: SO_4^{2-} ≥ 200 and ≤ 600 mg/l (slightly aggressive), SO_4^{2-} > 600 and ≤ 3000 mg/l (moderately aggressive) and SO_4^{2-} > 3000 and ≤ 6000 mg/l (very aggressive). Even according to this grouping given by (Hirschi et al. Series #93-05) it results that the groundwater in the study area does not exhibit the aggressive element. The water in the sample (S11) shows a value with an increasing trend with other values but remains within the SO_4^{2-} limit values of ≥ 200 and ≤ 600 mg/l (slightly aggressive).

Total hardness

Total hardness determines the total content of Ca^{2+} and Mg^{2+} salts dissolved in water. Water hardness refers to its ability to foam with soap. The water with high hardness does not wash and cook food well (Konomi, 2001). The sum of carbonate and non-carbonate hardness determines the overall hardness. According to (WHO, 2011) the total water hardness value is 30 d°H. This parameter in the groundwater of the study area showed values from 7.30 d°H (S1) to 34.00 d°H (S11) with an average value of 19.88 d°H ± 6.96 (Table 3 and Figure 3d). According to the overall hardness, groundwater is divided into: soft (TH = 4 to 8 d°H), moderately hard (TH = 8 to 16 d°H), hard (TH = 16 to 28 d°H) and very hard (TH > 28 d°H) (Dakoli, 2007; Konomi; 2001) Table 6. Two water samples or 12.5% of them classify the groundwater of the study area as soft water, 1 water sample or 6.25% belongs to the water with average overall hardness, 12 water samples or 75% show that the groundwater in the study area is hard and 1 water sample or 6.25% belongs to the water with very high hardness. Therefore, the groundwater in the study area is generally hard. These waters are of concern for their use in the food industry, as during the boiling process in vessels (kettles) they form the so-called kettle scale, thus affecting the reduction of thermal conductivity, burning and corrosion of the vessels (kettles).

According to the U.S. EPA (1986) the overall hardness is divided into: not soft (0–60 mg/l),

Table 6. Total hardness in study area

Groundwater, TH (ºdH)				Reference
Soft	Moderately hard	Hard	Very hard	
4 to 8	8 to 16	16 to 28	> 28	Dakoli, 2007
< 6	6 to 12	12 to 30	> 30	Konomi, 2001

Groundwater, TH (meq/l)*				Reference
Soft	Moderately hard	Hard	Very hard	
1.5 to 3	3 to 6	6 to 10	> 10	Dakoli, 2007
< 4	4 to 8	8 to 12	> 12	Konomi, 2001

Note: * 1 milligram equivalent/l = 2.8 german degrees.

moderately hard (60–120 mg/l), hard (120–180 mg/l) and very hard (> 180 mg/l). On the basis of on the calcification (U.S. EPA, 1986), results show that 14 water samples or 87.5% classify the groundwater of the study area as very hard, while 2 or 12.5% belong to hard waters. Values for TH were also calculated according to the equation: $TH = 2.5 \times Ca^{2+} + 4.1 \times Mg^{2+}$ which were then compared with the classification given by Sawyer and McCarty (2003). According to the classification given by Sawyer and McCarty (2003), the overall hardness is grouped into: soft class (0–75 mg/l), moderately hard (75–150 mg/l), hard (150–300 mg/l), and very hard (over 300 mg/l). According to the classification (Sawyer and McCarty, 2003), it results that 13 water samples or 81.25% classify the groundwater of the study area as very hard, 1 or 6.25% belong to hard waters, while 2 water samples or 12.5% belong to the moderately hard class.

Calcium

Calcium represents one of the main inorganic cations in water. It enters the water from the dissolution of Ca^{2+} chloride and sulfate salts. The groundwater of the study area showed values ranging from 36.10 mg/l (S9) to 152.80 mg/l (S11) with an average value of 75.74 mg/l ± 31.91 (Table 3 and Figure 3e). In principle, Ca^{2+} in freshwater ranges from 4 mg/l to 100 mg/l (Enviro SCI Inquiry, 2000–2011). According to this principle, it results that 13 water samples or 81.25% showed that they were within the limit (Ca^{2+} = 4–100 mg/l), while 3 water samples or 18.75% showed that they were above the value (Ca^{2+} = 4 mg/l -100 mg/l). The Ca^{2+} values of the study area were compared with the WHO standard values (WHO, 2011) which allows a maximum allowed value in water for Ca^{2+} of 120 mg/l, and resulted that 13 water samples or 81.25% are within the WHO standard value, while 3 water samples or 18.75% are above the standard values.

Magnesium

Magnesium values showed fluctuations from 7.50 mg/l (S1) to 68.10 mg/l (S9) with an average value of 40.36 mg/l ± 18.98 (Table 3 and Figure 3f). Compared to the maximum allowed value in water for Mg^{2+} which is 50 mg/l (WHO, 2011), it results that 10 water samples in the study area or 62.50% are within the standard value, while 6 water samples or 37.50% are above the standard values. According to the Concrete Guide (European Concrete Standard EN 206-1:2000) the limit values for the classes of exposure to aggressive chemicals from natural soil and groundwater indicate that values of $Mg^{2+} \geq 300$ and ≤ 1000 mg/l water are slightly aggressive, $Mg^{2+} > 1000$ and ≤ 3000 mg/l water is moderately aggressive and $Mg^{2+} > 3000$ and Saturation water is very aggressive. On the basis of the European Standard for Concrete EN 206-1:2000 (Hirschi et al. Series #93-05) it results that the Mg^{2+} values in groundwater in the study area are not or are considered slightly aggressive. According to Biezok (1972), the limiting values for assessing the aggressiveness of water and soil towards concrete are: $Mg^{2+} < 100$ mg/l (none to slight); Mg^{2+} from 100 to 300 mg/l (mild); Mg^{2+} from 300 to1500 mg/l (strong) and $Mg^{2+} > 3000$ mg/l (very strong). On the basis of the classification according to (Biezok, 1972), it results that 16 water samples or 100% are within the $Mg^{2+} < 100$ mg/l limit, indicating that the groundwater of this study area is slightly aggressive (none to slight). According to (Australian Water Resources Council, 1969) suggested limits for magnesium in drinking water for livestock range from < 250 mg/l to 500 mg/l (for poultry and livestock). Even according to these values given by (Australian Water Resources Council, 1969) the groundwater of the study area is permitted for use as drinking water for poultry and livestock.

Sodium

Sodium is very widespread in groundwater. It enters groundwater from urban and industrial pollution, especially from industrial wastewater discharges that contain large amounts of Na^+. Groundwater is also enriched with Na^+ through ion exchange processes. Some authors emphasize that in shallow infiltration waters with low mineralization Na^+ is < 1 mg/l, while in mineralized waters Na^+ reaches values > 100 gr/l. The Na^+ values in the groundwater of the study area were found to range from 1.66 mg/l (S9) to 39.00 mg/l (S13) with an average value of 11.47 mg/l ± 11.94 (Table 3). All water samples analyzed for Na^+ showed that they were within the standard values of AI No. 10/2021 (OGRK, 2021) (Na^+ = 200 mg/l) and WHO (2011) (Na^+ = 120 mg/l). Therefore, according to many suggestions in the literature, it turns out that the content above 200 mg/l is considered harmful to the body.

Potassium

Potassium predominates in non-saline waters. In the waters, it comes from the decomposition of organic matter. K^+ values in groundwater of the study area range from 0.35 mg/l (S9) to 11.69 mg/l (S2) with an average value of 2.31 mg/l ± 3.24 (Table 3). The K^+ values of the study area were compared with the standard value (maximum allowed value, K^+ = 12) according to (WHO, 2011) and it was found that this parameter is within the standard value.

Bicarbonate

Bicarbonate is dominant in shallow groundwater, with low mineralization. The amount of HCO_3^- in groundwater is affected by the pH of the water. The fgoundwater associated with limestone is mainly hydrocarbonate water (Dakoli, 2007). In the groundwater of the study area, the HCO_3^- values were found to be from 146.40 mg/l (S1) to 585.60 mg/l (S11) and a value of 380.08 mg/l ± 126.84 (Table 3). According to the standard (WHO, 2011), the maximum allowed value for drinking water for HCO_3^- is 650 mg/l, so it turned out that the groundwater of the study area in all analyzed water samples showed HCO_3^- values within the standard value. The HCO_3^- content from 24.4 mg/l to 128.1 mg/l (Konomi, 2001) in water indicates aggressiveness. This allows the water to act on the calcium carbonate of the concrete and form an aqueous solution of calcium bicarbonate. The values for HCO_3^- in the presented limits (from 146.40 mg/l to 585.60 mg/l) indicate that the water is aggressive towards clay and metals.

Carbonate

Carbonate the values in the groundwater of the study area range from 23.05 mg/l (S9) to 142.10 mg/l (S16) and average value 57.72 mg/l ± 34.55 (Table 3). It is predominant in shallow groundwater, with low mineralization. AI No. 10/2021 (OGRK, 2021) and WHO, (2011), do not define limit values for the content of CO_3^{2-} in drinking water.

Carbon dioxide

Carbon dioxide is found in water as free CO_2. When water has an excess amount of CO_2, it is called aggressive CO_2 and has aggressive properties for concrete and iron. According to various authors, the CO_2 content in waters of atmospheric origin fluctuates from tens of mg/l, while in waters of juvenile origin it fluctuates from 2000 to 3000 mg/l. The groundwater of the study area, shows values from 0.50 mg/l (S9) to 41.20 mg/l (S8) with an average value of 17.13 mg/l ± 11.32 (Table 3).

Water quality index

Water quality index to calculate the WQI in this case, the Weight Arithmetic Water Quality Index (WA-WQI) method was used (Brown et al. 1972; Ansari et al. 2013; Paun et al. 2016; Çadraku and Beqiraj, 2022; Çadraku et al., 2023). WQI is considered a water quality index that can be used effectively to improve water quality programs. The also represents an effective tool for monitoring surface water as well as groundwater pollution (Saleem et al., 2016). The Weighted Arithmetic Water Quality Index (WAWQI)-WQI for groundwater of the study area was calculated according to the steps shown below (Brown et al., 1972) and referring to the

WHO standard limit values (Table 3). Weighting: according to the Central Pollution Control Board (CPCB, 2007–2008), the word weight means the relative importance of each factor in the overall water quality and depends on the level allowed in drinking water. Rating scale: each chemical factor has been assigned a water quality rating to calculate WQI. To calculate the WQI, the following steps are followed:

Step 1: Calculate the unit weight factors for each parameters by using the Equation 1:

$$W_n = {}^{K}/_{S_n} \tag{1}$$

where: K – is the constant of proportionality (Kalavathy et al., 2011) which is found by Equation 2:

$$K = \frac{1}{\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3} + \dots + \frac{1}{S_n}} \tag{2}$$

On summation of all selected parameters unit weight factor ($W_n = 1$)

Step 2: Calculate sub-index (Q_n) value using the Equation 3:

$$Q_n = \frac{[(V_n - V_0)]}{[(S_n - V_0)]} \times 100 \tag{3}$$

where: Q_n – is sub-index; V_n – is the estimated value; S_n – is the standard desirable value of the n^{th} parameters; V_0 – is ideal value for pure water (0 for all parametres except pH and DO) which is found by Equation 4 and 5;

$$Q_{pH} = \frac{(V_{pH} - 7)}{(8.5 - 7)} \times 100 \tag{4}$$

$$Q_{DO} = \frac{(V_{DO} - 14.6)}{(6 - 14.6)} \times 100 \tag{5}$$

Step 3. Combining step 1 and step 3, the WA-WQI is calculated by using the equation (5):

$$WQI = \frac{\sum W_n \times Q_n}{\sum W_n} \tag{6}$$

where: $\Sigma W_n \times Q_n$ - $W_n(\text{pH}) \times Q_n(\text{pH}) + W_n(\text{DO}) \times Q_n(DO) + ... + W_n(Y_n) \times Q_n(Y_n)$

According to the Brown et al. (1972) method, the groundwater in this study area was classified from very poor to excellent (Table 7).

Table 8 shows the number of water samples and their percentage participation based on the water quality index limits and water quality status in the study area.

From the WQI in Table 8, it results that 7 water samples or 50.00% show a value of WQI = 0–25, classifying the groundwater as having excellent quality, 3 water samples or 21.43% with a WQI value of 26–50 with good quality, 4 water samples or 28.57% with a WQI = 51–75 with

Table 7. WQI value and water quality status in the study area

Water source	ID	No. of parameters	WQI	Water quality status
Well 1	S1	14	122.53	Unfit for consumption
Well 2	S2	14	43.00	Good
Well 3	S3	14	41.67	Good
Well 4	S4	14	57.32	Poor
Well 5	S5	14	9.40	Exellent
Well 6	S6	14	9.40	Exellent
Well 7	S7	14	5.13	Exellent
Well 8	S8	14	39.07	Good
Well 9	S9	14	59.78	Poor
Well 10	S10	14	68.18	Poor
Well 11	S11	14	22.81	Exellent
Well 12	S12	14	17.46	Exellent
Well 13	S13	14	22.40	Exellent
Well 14	S14	14	14.85	Exellent
Well 15	S15	14	59.08	Poor
Well 16	S16	14	83.86	Very poor

Table 8. Number of water samples and percentage participation

WQI	Water quality status	Study area	
		No. of sample	%
0–25	Excellent	7	50.00
26–50	Good	3	21.43
51–75	Poor	4	28.57
76–100	Very poor	1	7.14
> 100	Unfit for consumption	1	7.14

poor quality, one water sample or 7.14% is in the range of WQI = 75–100 and shows the very poor quality and also one water sample or 7.14% is in the range > 100, indicating that the water is unusable. An example of the WQI calculation is shown in Table 9. SoThus in general, it results that the groundwater of this study area, according to the quality index values, has a generally excellent to good quality state with a tendency for water quality deterioration in a certain (small) number of wells. Figure 4a shows the spatial distribution of WQI in study area.

Hydrochemical types of water

Hydrochemical types of water the hydrochemical composition of groundwater in the study area appears complex and varies widely (Table 3). These hydrochemical features of groundwater are determined by a series of factors of geological and hydrogeological character such as: the wide area of their distribution, lithological heterogeneity, the degree of communication with lateral basins, the different structural construction of specific sub-basins, etc. The complexity and wide variation of the hydrochemical composition of groundwater in the study area are expressed by the diversity of its hydrochemical types. Thus, in the study area, these hydrochemical types of water were distinguished (Table 10). The chemical types with the highest participation are: the hydrochemical type of water Ca-Mg-HCO_3-CO_3 and Mg-Ca-HCO_3-CO_3 (Figure 4b).

Piper diagram (Piper, 1944) are powerful because they are used for both the classification of water quality data and the identification of processes impacting the data, such as end-member mixing of waters, ion exchange, and mineral precipitation and dissolution (Shelton et al., 2018). The Piper diagram (Figure 5) shows the hydrochemical types of water in the study area, where the connection between carbonate-limestone rocks and the alluvium of the Toplluhë River valley is evident.

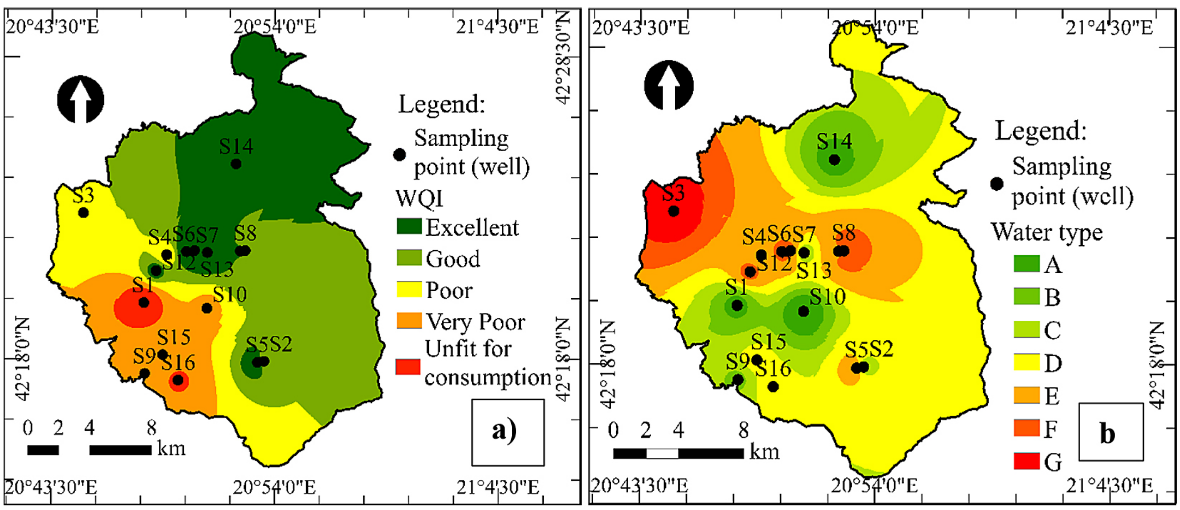

Figure 4. Spatial distribution of a) WQI and b) Hydrochemical types of water in study area
A) Ca-Mg-HCO_3; B) Ca-HCO_3-CO_3; C) Mg-Ca-HCO_3; D) Mg-Ca-HCO_3-CO_3; E) Ca-Mg-HCO_3-CO_3; F) Ca-Mg-HCO_3-SO_4; G) Mg-HCO_3-CO_3

Table 9. Example of WQI calculation

Parameter	WHO (2011), Sn	1/Sn	∑1/Sn	K=1/ (∑1/Sn)	Wn = K/ Sn	Ideale value, (Vo)	Estimated value (Vn)	Vn/Sn	Vn/Sn*100 = Qn	Wn*Qn
pH	8.5	0.1176	2.4035	0.4161	0.0489	7	7.16	0.107	10.667	0.5221
Tur	10	0.1000	2.4035	0.4161	0.0416	0	1.1	0.1100	11.000	0.4577
EC	1000	0.0010	2.4035	0.4161	0.0004	0	1026	1.0260	102.600	0.0427
TDS	500					0				
NH_4^+	0.5					0				
NO_3^-	50					0				
Cl^-	250					0				
SO_4^{2-}	250					0				
TH	30					0				
Ca^{2+}	120					0				
Mg^{2+}	50					0				
Na^+	120					0				
K^+	12					0				
HCO_3^-	650	0.0015	2.4035	0.4161	0.0006	0	457.5	0.7038	70.385	0.0451
		2.4035			1					39.07

Table 10. Hydrochemical types of water by percentage

Hydrochemical types	Water source ID	Number of water samples	%
$Ca\text{-}Mg\text{-}HCO_3$	S10	1	6.25
$Ca\text{-}Mg\text{-}HCO_3\text{-}CO_3$	S5, S6, S11, S12	4	25
$Mg\text{-}Ca\text{-}HCO_3\text{-}CO_3$	S4, S13, S15, S16	4	25
$Ca\text{-}HCO_3\text{-}CO_3$	S1, S14	2	12.5
$Mg\text{-}Ca\text{-}HCO_3$	S2, S7, S9	3	18.75
$Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$	S8	1	6.25
$Mg\text{-}HCO_3\text{-}CO_3$	S3	1	6.25

Correlation

Correlation the study of correlation often aims to show the statistical independence of two variables (Selenica, 2009), that is, to prove that two random variables are related (correlated), or are not related to each other. Depending on the values of the correlation coefficient, there are the following types of relationships: r =1 positive linear functional relationship, r ≈ 1 strong positive linear relationship, r > 0 positive linear relationship, r = 0 no linear relationship, independent variables, r < 0 negative linear relationship, r = -1 negative linear functional relationship. The correlation coefficient always ranges from -1 to + 1. The correlation relationship for the physical and chemical parameters of the study area are shown in Figure 6., where it is clearly observed that some of the parameters show strong positive relationships.

Hierarchical clustering (dendograms) presents an alternative approach to grouping objects based on their similarities. In Figure 7, the hierarchical clustering of parameters in the study area is shown.

Principal components analysis

Principal components analysis a principal component analysis plot shows similarities between groups of samples in a data set (Holland, 2019; Shlens, 2014). Each point on a principal component analysis plot represents a correlation between an initial variable and the first and second principal components. Principal component analysis, or PCA, reduces the number of dimensions in large data sets to principal components that retain most of the original information. This is done by transforming the potentially correlated variables into a smaller set of variables, called

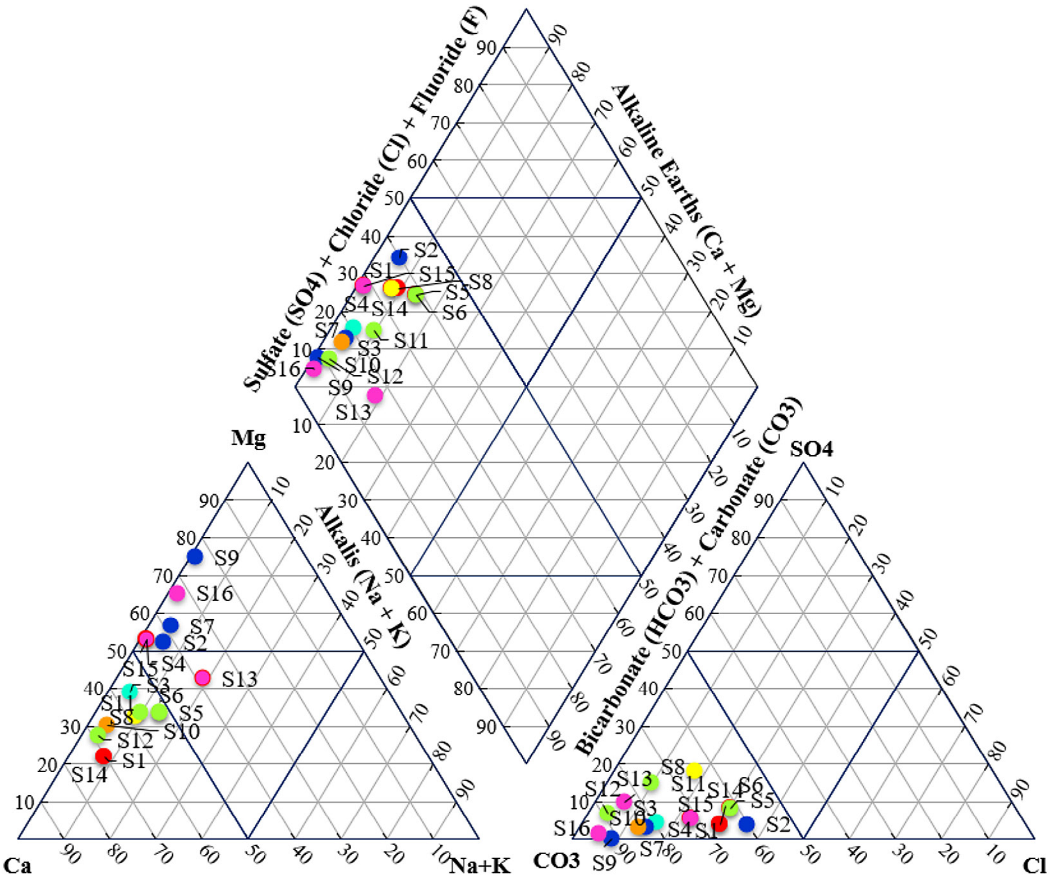

Figure 5. Piper diagram of the chemical composition of groundwater in the study area

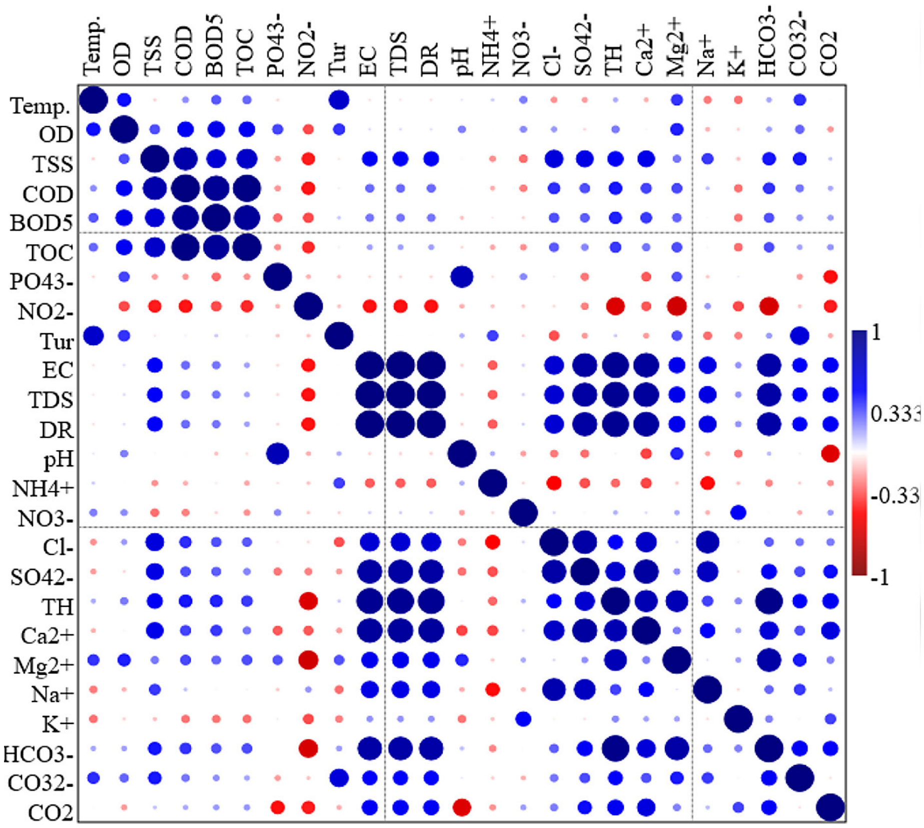

Figure 6. Correlation plot

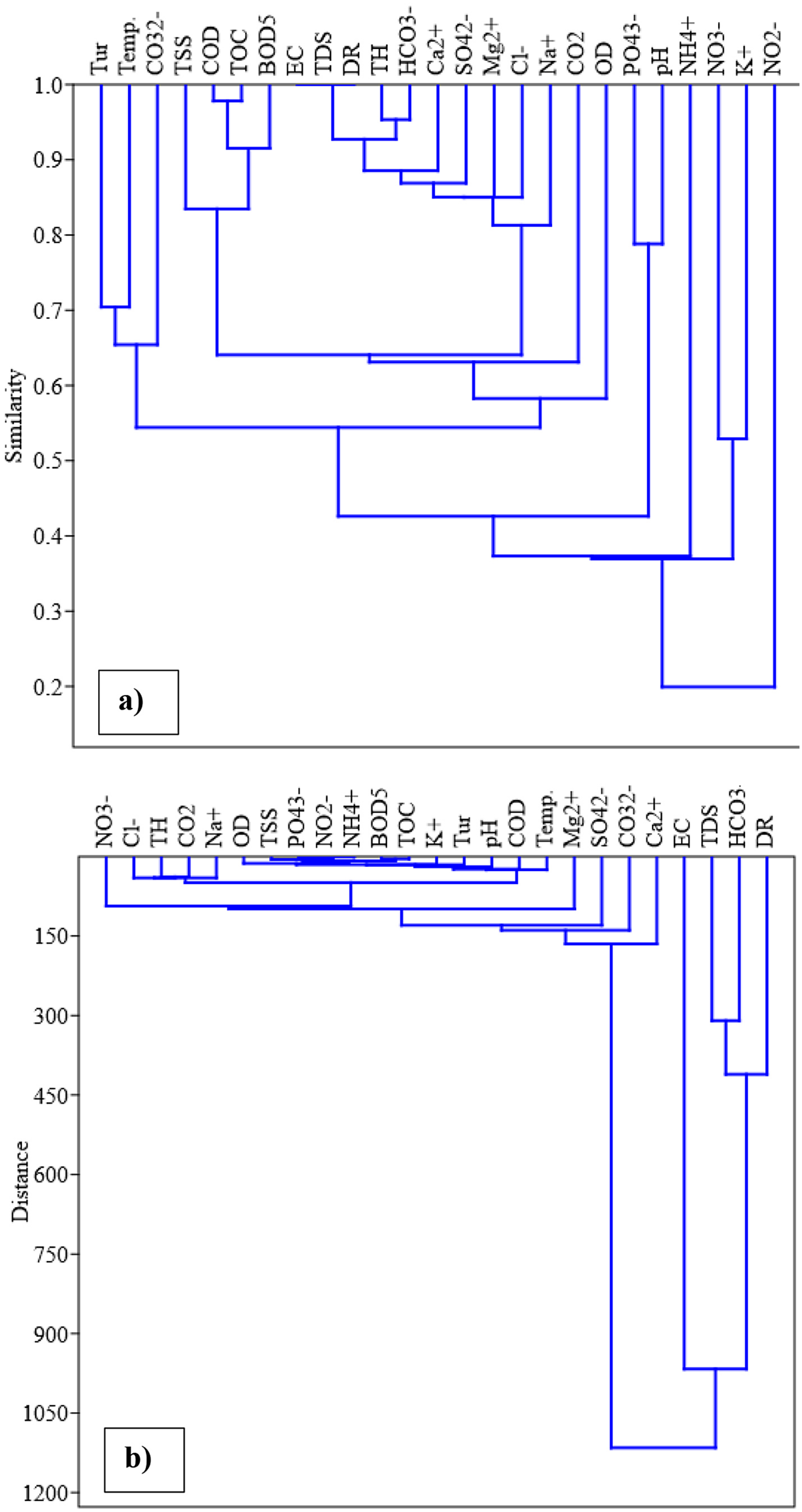

Figure 7. Herarchical clustering, algorithm single linkage, similarity index (a) correlation and (b) euclidean

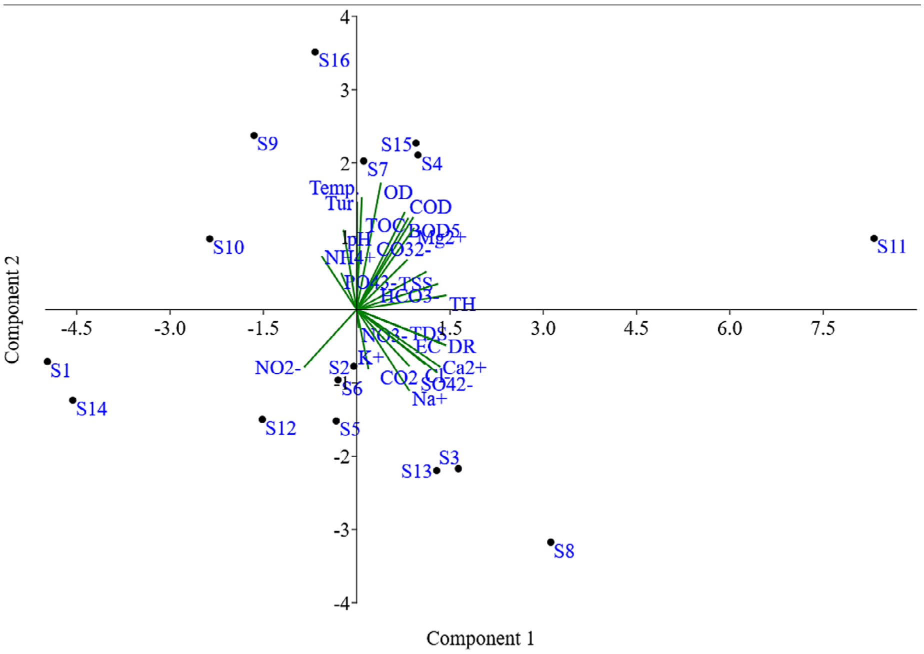

Figure 8. Principal components analysis in study area

principal components. The principal component analysis (PCA) for the parameters analyzed in the study area is shown in Figure 8.

CONCLUSIONS

In general terms, it can be concluded that the literature researched and reviewed for the needs of this study shows that current studies published on electronic platforms such as: Web of Science, Scopus, Google Scholar, Researchgate, etc., from the largest number of countries in the world in which groundwater is treated from a qualitative point of view for their use for drinking water, irrigation, industry, and other purposes, results in concern and differs from country to country. Groundwater quality is reported to be better in the countries that have now consolidated the legal framework, policies and strategic documents for planning and good governance of water resources (based on the concept of integrated water resources management), while a more pronounced trend of groundwater pollution is reported in developing countries, where the legal framework, policies and strategies are not yet consolidated and implemented to the necessary extent (prevention level). For example; a data from Earth in the Future (accessed 18.05.2025) reports that approximately 100 million people globally are exposed to high levels of arsenic in groundwater. It also reports that nowhere is the problem more devastating than in large areas of Bangladesh and the West Bengal region of India, where millions have been poisoned by arsenic. This area is intensively irrigated, which has changed the flow of groundwater over a large region. As a result, a shallow aquifer is the source of groundwater for 35–77 million inhabitants who obtain their water from shallow tube wells.

In the study area, wells are open in rural settlements, urban and agricultural areas. The position where the wells are opened has different geological structures, hydrogeological and pedological characteristics, which is related to their chemical composition and the possibility or impossibility of their contamination by pollution coming from above (surface). The wells have a diameter of 800 mm and a depth ranging from 20–25 m with a partial hygienic-sanitary construction, which easily allows the penetration of pollutants to the groundwater table. The water from wells is used for various purposes: drinking, irrigation, partially for water bottle and juices, in the extractive and processing industry, etc. The potential pollutants of well water are residential areas with accompanying infrastructure, wastewater (in the absence of factories for its treatment), urban waste (in the absence of recycling), agricultural pollution (exceeding the norms for the use of fertilizers, pesticides, etc.), industry (lack of treatment of industrial waters after the process), etc.

However, the study highlights that: the majority of physical and chemical parameters measured and analyzed in groundwater samples of the study area fall (are) within (the limits) set by the World Health Organization and Administrative Instruction No. 10/2021 of the National Institute of Public Health of Kosovo. However, it was also noted that some wells showed the values that exceeded these parametric limits. These exceedances are mainly related to urban development, overexploitation of water resources, and the growth of the agricultural and industrial sectors, particularly in processing industries. Thus, chemical oxygen demand shows values above the standard value in two water samples, namely in the well (S7 and S11), total organic carbon shows value higher than the reference value in the wells (S4, S7, S11 and S15), phosphates shows value above the standard value only in the well (S9), turbidity shows a value higher than the reference value only in the well (S16), electrical conductivity, dry residue and TDS show a value higher than the reference value in the well (S8 and S11), pH shows a value higher than the reference value only in the well (S9), ammonia shows a value higher than the reference value in the well (S1), nitrates showed a value higher than the reference value only in the well (S2), calcium shows value higher than the reference value in the well (S11) and magnesium in the well (S9,S11, S15 and S16). The WQI categorizes the water the quality excellent to good with the exception of well S1, which is deemed unsuitable for drinking water. Wells: S16, S4, S9 and S10, are classified as having very poor to poor water quality. The application of the water quality index in this study proved useful, because it provides an overall assessment of water quality and is easily understandable to the public and also represents a useful mechanism-tool in many ways in the field of water quality management. The most common hydrochemical types identified were Ca-Mg-HCO_3-CO_3 and Mg-Ca-HCO_3-CO_3. The scientific community, institutions involved in policy and legislation drafting, the community using these waters, etc., will benefit from the results presented in this paper. The scientific community, and in particular the local and regional one, will have available data and information from recent years regarding water quality for this territory. All stakeholders will have the data and information that increase their level of safety when using groundwater for drinking water and other purposes from this study area. These results presented in this paper will facilitate the work of local and central institutions when drafting policies and legislation related to water use for their use for drinking water, etc. Thus, in general, the groundwater of the study area shows parametric values within the acceptable limits given by the World Health Organization and Administrative Instruction No. 10/2021, however, a preliminary treatment is recommended before consumption for drinking. Under these conditions, the paper recommends that institutions develop a monitoring system based on local or European Union standards for such purposes. Management and monitoring for environmental protection (air, soil and water) in the study area would guarantee public health and ensure sustainable development in the territory of the Suhareka municipality.

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