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ORIGINAL PAPER

Investigation of the quality and physical-geochemical characteristics of the drinking water in Gümüşhane (Turkey) city central

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Abstract The physical (turbidity, color, smell, taste, pH, and conductivity) and geochemical properties (Ca, Mg, Na, Fe, Mn, Al, K, Cl^-, HCO_3^-, SO_4^{2-}, Fe, Cu, Co, Ni, Zn, Cd, Pb, and Cr) of the drinking water in Gümüşhane city center were determined. This city center constitutes the study area. The pH levels of the water samples ranged from 6.3 to 8.2, and their conductivities ranged between 240 and 900 μS. These findings were concordant with the drinking water standards of the Turkey Standard Institute and the World Health Organization. The hardness of the water samples in the study area was between 18.1 and 115.1 °Fr. These samples were classified as extremely hard, hard, and quite hard. In addition, an assessment using the criteria for Inland Surface Water Classification indicated that considering certain parameters (pH levels, amount of Na, SO_4^{2-}, Fe, Mn, Al, Co, Ni, Cu, and Cr), the samples belonged to class I (high quality) water. When Cl^- amount and conductivity were considered, the samples belonged to the first and second classes (less polluted) of water. The water in the study area was generally classified as carbonated and sulfated (Ca + Mg > Na + K) water classes. This water contained more weak acids than strong acids ($HCO_3^- + CO_3^{2-} > Cl^- + SO_4^{2-}$). The pH levels (6.3–8.2) of the water in the study area were unrelated to the varying concentrations of metals in the water. Elements such as Fe, Ni, Cd, Pb, Zn, and Cu increase in the water through the water–rock interaction in the area in which water rises or through the mixture of water with either mine or industrial wastes. In addition, several water samples belonged to an acceptable water class for drinking and usage.

Keywords Quality · Geochemical · Drinking water · Gümüşhane · Turkey

Introduction

Water is the basis of life and is essential to vital bodily functions. Essential functional elements in biological systems (including H, Na, and K) are the main nutrients that sustain life revealed through water dissolution. This phenomenon highlights the significance of the amount of elements dissolved in water. Water is non-compressible, non-odorous, and colorless. Furthermore, it is dispersed in all parts of the body and is present in human tissue. More water is also found in the blood than in the bones. Therefore, given its necessity to human life, clean water, without harmful chemicals such as As, Cu, Pb, and pathogenic microorganisms should be provided. Considering such significance, the substances in water directly affect living organisms. Metals such as As, Cd, Cr, Ni, and Pb are highly toxic, and they have carcinogenic, mutagenic, and teratogenic effects. Therefore, these elements must be analyzed to determine the effects of metals on life quality. The amount of metal in drinking water should be specifically identified for health purposes.

Thus far, the geochemical characteristics of Gümüşhane drinking water have not been studied. Gültekin (1998) alone investigated the tectonic relationships, physicochemical properties, isotopic composition, trace elements, dissolved gas content, radioactivity, and suitability of mineral drinking water resources in Gümüşhane and Bayburt. The current study is the first geochemical study on the drinking water in the Gümüşhane (Turkey) city central. This research particularly determines the physical and geochemical properties of the

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water here and evaluates it by studying the water quality relative to the chemical properties of the rocks located close to the water.

Study area and geology

Gümüşhane is located in the southern part of the eastern Black Sea region. The study area covers the city center, which mainly includes granitoid, sedimentary, and volcanic rocks (Fig. 1). The study area is based on the Paleozoic-aged Gümüşhane granitoid (Yılmaz 1972). The Jurassic-aged Zimonköy Formation (Eren 1983) is a volcano-sedimentary series that exhibits erosional unconformity through a thin base conglomerate on granitoid rocks. Volcano-sedimentary series is often generated by limestone that contained chert nodules and bands. The Berdiga Formation (Pelin 1977) conforms to the Zimonköy Malm–Lower Cretaceous Formation. The former presumably cannot conform to the Kermutdere Formation (Tokel 1972). The Eocene-aged Alibaba Formation (Tokel 1972) displays angular unconformity on this formation.

Material and methods

A total of 32 water samples were collected from selected drinking water source points (water tanks and fountains). These samples were physically and geochemically analyzed

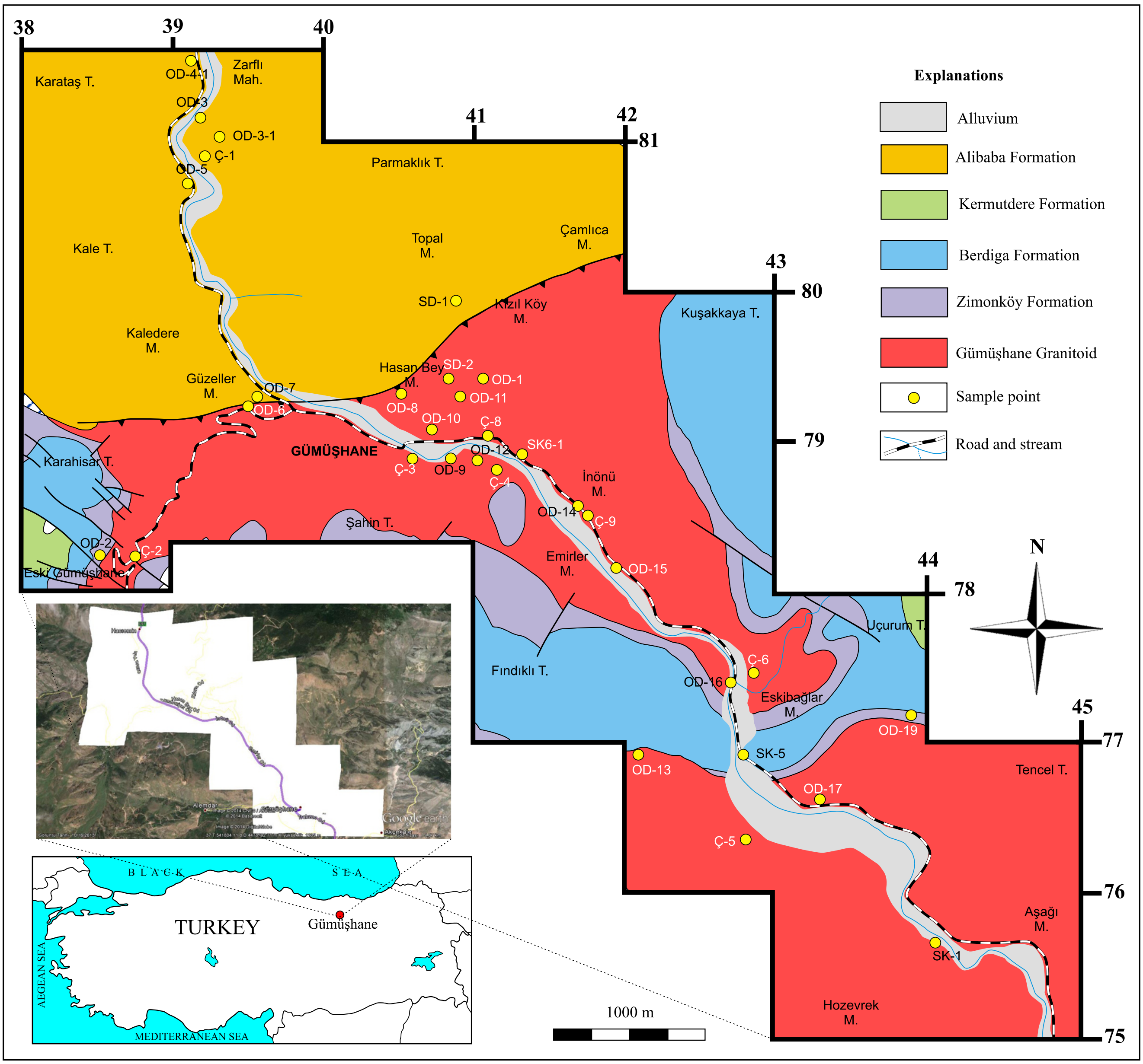

Fig. 1 The geological and sampling map of the study area (Güven 1993)

(various anions and cations were specifically studied) using different techniques at the Laboratory of the Department of Food Engineering of the Faculty of Engineering and Natural Sciences in Gümüşhane University. The analyses were performed with sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), and chloride (Cl^-) as the anionic species. The metals Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Na, K, Ca, and Mg were examined for the cationic species as well. Sulfate analysis was conducted according to the Turkish Standard (TS) 5095 (1987) using turbidimetric method, carbonate analysis according to TS 3790 (1988) with the titration method, and chloride analysis according to TS 4161 ISO 9297 (1998) using the titrimetric method. The metals were investigated with a microwave plasma-atomic emission spectrometry instrument (Agilent Technologies 4100) according to the emission spectrometer method (Balaram et al. 2013; Vysetti et al. 2014). Sulfate concentration was determined with a device that measured Lovibond Turbicheck brand turbidity. The detection limit of the device was 0.05 ppm (mg/L). Turbidimetry and nephelometry determination methods were used to measure water turbidity in milligrams per liter SiO_2 nephelometric turbidity units (NTU) (Bilgin 2003; Yılmaz 2004). The conductivity and pH levels of the water samples were obtained from the Gümüşhane Public Health Laboratory. Information on the operating conditions and the device performance are summarized in Table 1 (Agilent Technology 2011; Jankowski et al. 2005).

Results and discussions

Physical parameters of the drinking water

As mentioned previously, the water samples were obtained from Gümüşhane city center areas. The coordinates, rock types, and physical characteristics (color, smell, taste, turbidity, pH level, and conductivity) are listed in Table 2. The samples were cold, clear, colorless, tasteless, and odorless. Drinking water turbidity consists of clay, silt, organic matter, microorganisms suspended in the water, large observable sediments, and precipitated $CaCO_3$, $Al(OH)_3$, $Fe(OH)_3$, or similar materials. This turbidity negatively affects water quality. Pure water turbidity may be greater than 1000 and less than 1 NTU. Water turbidity must be low to be used in all areas; drinking water turbidity should be less than 5 NTU (TS 266 2005). The turbidity values of the studied water samples ranged from 1 to 346 NTU (Table 2). According to TS 266 (2005), the turbidity values of the samples OD-2, C-9, and OD-8 were within the proper limits; however, those of the other water samples exceeded this limit. The pH level of the water for drinking and usage in the study area ranged from 6.3 to 8.2; these levels should be within the drinking water standards of TS 266 (pH 6.5–9.5) and of the World Health Organization (WHO 2014;

Table 1 Operating conditions and analytical characteristics of the MP-AES device

Elements	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Na	K	Ca	Mg
Wavelength, nm	396.152	228.802	340.512	425.433	324.754	371.993	403.076	352.454	405.781	213.857	588.995	766.491	393.366	285.213
Nebulizer pressure, kPa	240	140	240	240	240	120	240	240	240	140	240	240	120	240
Stability and sampling time, s	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Peristaltic pump speed, rpm	15	15	15	15	15	15	15	15	15	15	15	15	15	15
The detection limit (LOD), µg/L	1.4	0.3	0.1	0.2	0.3	1.6	0.4	1.0	0.4	1.2	2.3	3.4	3.2	3.2
Limit of quantification (LOQ), µg/L	4.7	1.0	0.3	0.6	1.0	5.3	1.3	3.0	1.3	4.0	7.8	11.4	10.6	6.4
Relative standard deviation (BSS), %	4.9	0.4	0.7	1.3	0.6	1.2	0.7	0.9	1.5	1.0	1.2	0.7	4.7	6.4

Table 2 Location, coordinate, physical properties, and rock types of the water samples taken from the study area

Sample no.	Location	Coordinate	Turbidity (NTU)	Color	Smell	Taste	pH	Conductivity (μS)	Rock type
SD-1	Karaer M. up water reservoir	540,850–4,479,910	346	Colorless	Odorless	Normal	7.5	550	Granitoid
SK5	Alemdar yellow bridge water well	542,729–4,476,898	28.5	Colorless	Odorless	Normal	7.4	628	Alluvium
OD-2	Süleymaniye M. imam house	538,567–4,478,196	2.82	Colorless	Odorless	Normal	7.5	–	Granitoid
OD-1	Çamlıca M. water reservoir	541,050–4,479,414	21	Colorless	Odorless	Normal	7.6	260	Granitoid
SK6-1	Gümüşhane Anadolu high school housing.	541,339–4,478,916	26	Colorless	Odorless	Normal	7.5	500	Alluvium
OD-15	Yeni M. religious office building	541,955–4,478,123	33.7	Colorless	Odorless	Normal	7.5	600	Alluvium
OD-13	İnönü M. training tools building	542,086–4,477,923	27.9	Colorless	Odorless	Normal	7.6	550	Granitoid
OD-19	Bağlarbaşı M. water reservoir	543,964–4,476,215	28.5	Colorless	Odorless	Normal	7.4	900	Granitoid
Ç-2	Süleymaniye M. fountain	538,751–4,478,184	93.5	Colorless	Odorless	Normal	8.2	–	Granitoid
SD-2	Karaer M. water reservoir	540,832–4,479,418	29.5	Colorless	Odorless	Normal	7.5	680	Granitoid
OD-7	Gümüşhane State Hospital	539,615–4,479,309	30.3	Colorless	Odorless	Normal	7.4	587	Alluvium
OD-5	Özcan M. slaughterhouse	539,069–4,480,703	24.8	Colorless	Odorless	Normal	6.8	350	Andesite–basalt
OD-3	Hacı Emin M. Bahri Aydın house	539,169–4,481,145	29.3	Colorless	Odorless	Normal	–	–	Andesite–basalt
SK-1	Sema Doğan Park water well	544,023–4,475,675	29.5	Colorless	Odorless	Normal	7.0	550	Granitoid
Ç-9	İnönü M. Mordut fountain	541,753–4,478,463	2	Colorless	Odorless	Normal	7.7	560	Alluvium
OD-14	İnönü Mah. Mordut tea hearth	541,752–4,478,476	26.5	Colorless	Odorless	Normal	7.5	700	Granitoid
OD-17	Bağlarbaşı M. Toki	543,264–4,476,584	27.8	Colorless	Odorless	Normal	7.3	730	Granitoid
Ç-4	Karşıyaka Özdenoğlu fountain	541,123–4,478,809	23.5	Colorless	Odorless	Normal	8.2	240	Alluvium
OD-16	Köprülüler oil	542,737–4,477,370	14	Colorless	Odorless	Normal	7.7	640	Granitoid
OD-6	Güzeller M. girls' dormitory	539,610–4,479,300	23.5	Colorless	Odorless	Normal	7.5	550	Alluvium
Ç-6	Eski Bağlar fountain	542,761–4,477,427	24	Colorless	Odorless	Normal	7.4	500	Granitoid
OD-12	Karşıyaka M. lower of the mosque tea hearth	541,017–4,478,869	24.5	Colorless	Odorless	Normal	7.5	660	Alluvium
OD-8	Hasanbey M. Bilali Habeşi Mosque housing	540,527–4,479,308	1.45	Colorless	Odorless	Normal	7.5	630	Andesite–basalt
Ç-8	Karaer Mah. Atatürk Park fountain	541,108–4,479,002	31	Colorless	Odorless	Normal	6.3	560	Granitoid
OD-4-1	Canca M. Sadirvan	539,090–4,481,600	27	Colorless	Odorless	Normal	8.0	550	Andesite–basalt
OD-3-1	Hacı Emin M. stop fountain	539,330–4,481,036	8.5	Colorless	Odorless	Normal	7.6	–	Andesite–basalt
Ç-1	Özcan Mah. fountain	539,196–4,479,874	14.5	Colorless	Odorless	Normal	7.7	430	Andesite–basalt
OD-9	Gümüşhane male dormitory	540,873–4,478,891	25.8	Colorless	Odorless	Normal	7.0	260	Alluvium
Ç-5	Bağlarbaşı M. Hacı Kasım fountain	542,861–4,476,332	30.3	Colorless	Odorless	Normal	7.6	700	Granitoid
Ç-3	Karşıyaka Çilenkler fountain	540,601–4,478,893	24	Colorless	Odorless	Normal	8.0	600	Granitoid
OD-11	Karaer M. Health Directorate	540,871–4,479,271	24.8	Colorless	Odorless	Normal	7.5	268	Granitoid
OD-10	Karaer M. Zafer tea hearth	540,725–4,479,057	21	Colorless	Odorless	Normal	7.5	550	Alluvium

pH 6.5–9.2). Thus, the pH level of the water in the study area fell within the given limits, except for the C-8 sample (pH = 6.3, Table 2), and it can be classified as "class I" according to the 2012 Inland Surface Water Classification of the Ministry of Forestry and Water Works (MFW). The pH values of the Galyan stream water from Trabzon (Bulut et al. 2010), the drinking water from Yozgat (Soylak et al. 2002), and the Fırtına stream water from Rize (Gedik et al. 2010) were 7.5–8.3, 6.90–8.13, and 6.88–7.761, respectively, which can be classified as class I. Therefore, the pH values of the Galyan stream water from Trabzon, the drinking water from Yozgat, the Fırtına stream water from Rize, and the drinking water in this study were compatible with the values and guidelines proposed by TS 266 and WHO.

The water conductivity in the study area ranged between 240 and 900 μS, which satisfied the TS 266 and WHO standards. These standards suggest that water conductivity should be <2500 μS. Based on the TS 266 water conductivity, the C-9 sample (240 μS) was very good, the OD-19 sample (900 μS) was usable, and the other samples (260–730 μS) were classified as good water (Table 3). Therefore, 3 % of the samples were regarded as very good, and 94 % were considered good. However, the connections between the conductivity and pH levels of these samples were not established. Despite an increase in the conductivity of the water samples, the water pH level remained constant.

Chemical parameters of the drinking water

The water from the study area was analyzed in terms of its major cations, anions, and trace elements, as well as its geochemical properties (Table 4). The analysis results on the metal concentrations in these samples were compared with the TS 266 and WHO drinking water standards (acceptable maximum values). The water in this area was acceptable by the drinking water standards of the WHO, except for the SD-1 and OD-3-1 samples. Moreover, the Cd and Pb contents in some water samples were unacceptable (Table 4). When the elements in the samples were analyzed separately according to TS 266, the Fe content in the samples generally adhered to these standards, except for sample SD-1 (Fe = 243.2 μg/L). The Pb content in a number of water samples exceeded the 10 μg/L indicated in the TS 266 and WHO standards (Table 4). The Cd contents in the water samples were acceptable based on the drinking water standards in Turkey (<5 μg/L), except for those in the following 12 samples: C-6, OD-12, OD-8, C-8, OD-4-1, OD-3-1, C-1, OD-9, C-5, C-3, OD-11, and OD-10. The Cd values of the 10 samples ranged from 5.2 to 8.0 μg/L, which exceeded both TS 266 (Cd < 5 μg/L) and WHO (Cd < 3 μg/L) standards. The calcium and magnesium values in the drinking water from Yozgat ranged from 15 to 120 and from 3 to 47 mg/L, respectively (Soylak et al. 2002). The Ca content of the water samples (39.9–239.7 mg/L) in this study was typically above the TS 266 standards as well, except for the four samples, C-1, C-3, OD-11, and OD-10. Furthermore, these concentrations fulfilled the WHO standards, except for sample OD-3-1. The Mg content of the five water samples (SD-1, C-9, C-4, OD-3-1, and C-3; 61.9–161.4 mg/L) exceeded the TS 266 but adhered to the WHO standards. The Na content of sample SD-1 was excessively high (239.4 mg/L), whereas that in the other samples met the TS 266 and WHO standards. The K content in the nine samples exceeded the TS 266 standards.

According to the 2012 Inland Surface Water Classification of the MFW, the water samples were considered first-class (high quality) water based on the pH level and the amount of Na, SO_4^{2-}, Fe, Mn, Al, Co, Ni, Cu, and Cr. The samples were also regarded as first- and second-class (less contaminated) water according to the conductivity and the amounts of Cl^-, Pb (except for samples SK-5, SD-1, OD-1, and OD-19), Zn (except for samples OD-10, OD-11, C-3, C-5, OD-9, OD-3-1, and SK6-1s), and Cd (except for samples C-6, OD-12, OD-8, C-8, OD-4-1, OD-3-1, C-1, OD-9, C-5, C-3, OD-11, and OD-10).

The water hardness in the study area ranged from 18 to 115.1 °Fr (Lenntech 2014; Table 5). The samples were classified as quite hard (28.4–31.7 °Fr), hard (33–53 °Fr), and extremely hard (55.1–115.1 °Fr), except for one sample (O-1 at 18 °Fr; Table 5).

The alkalinity in almost all natural water is attributed to carbonate (CO_3^{2-}) and hydroxide (OH^-) ions and rarely exceeds 500 mg/L $CaCO_3$ (Doğan 1981). The HCO_3^- (mg/L) values in the samples ranged from 87 to 283 mg/L, except for one sample (SD-1, HCO_3^- = 1963 mg/L). However, TS 266 does not provide a limit value for alkalinity.

Table 3 Classification according to the conductivity of the water (Erguvanlı and Yüzer 1987)

Conductivity	Classification	Conductivity of water samples in the study area (μS)
Less than 250	Very good	240 (a sample)
250–750	Good	260–730 (30 samples)
750–2000	Usable	900 (a sample)
2000–3000	Suspect	–
More than 3000	Unusable	–

Table 4 The important some element analysis results of the water samples in the study area

Element Sample/unit	Fe µg/L	Cu µg/L	Co µg/L	Ni µg/L	Mn µg/L	Zn µg/L	Cd µg/L	Al µg/L	Pb µg/L	Cr µg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	$(SO_4)^{2-}$ mg/L	Cl^- mg/L	HCO_3^- mg/L	French water hardness	Conductivity µS	Symbol in the graphic
SD-1	243.2	22.3	<0.3	7.5	60.2	<4.0	<1.0	<4.7	43.9	<0.6	195.9	161.4	239.4	4.2	502	50.6	1963	115	550	●
SK-5	<5.3	15.8	<0.3	16.1	<1.3	<4.0	<1.0	<4.7	23.7	<0.6	161.8	45.0	24.0	5.4	12.9	14.4	261	59	628	▲
OD-2	<5.3	4.0	<0.3	9.7	<1.3	<4.0	<1.0	<4.7	<1.3	<0.6	80.8	35.8	5.9	2.1	3.0	7.2	109	35	–	■
OD-1	<5.3	8.5	<0.3	61.2	<1.3	<4.0	<1.0	<4.7	43.7	<0.6	147.9	39.1	25.4	5.9	17.6	7.2	218	53	260	Δ
SK6-1	<5.3	7.4	<0.3	11.2	<1.3	624.0	<1.0	<4.7	17.5	<0.6	151.1	42.2	26.9	5.9	16.0	72.2	218	55	500	□
OD-15	<5.3	< 1.0	<0.3	12.3	<1.3	<4.0	<1.0	<4.7	19.1	<0.6	91.6	64.8	28.4	7.3	18.7	21.6	174	49	600	□
OD-13	<5.3	5.9	<0.3	11.7	6.0	48.0	<1.0	<4.7	18.3	<0.6	157.5	40.4	22.4	4.8	15.0	7.2	218	56	550	□
OD-19	<5.3	5.4	<0.3	15.4	6.9	<4.0	<1.0	<4.7	20.1	<0.6	162.6	36.3	24.3	5.4	22.5	28.9	196	56	900	▲
Ç-2	11.0	<1.0	<0.3	7.8	<1.3	36.0	<1.0	<4.7	14.6	<0.6	125.5	68.3	16.8	15.9	124.0	10.8	163	59	–	■
SD-2	<5.3	<1.0	<0.3	9.8	<1.3	<4.0	<1.0	<4.7	16.3	<0.6	130.6	41.5	27.3	4.5	21.3	14.0	218	50	680	●
OD-7	<5.3	<1.0	<0.3	8.4	<1.3	<4.0	<1.0	<4.7	14.3	<0.6	89.9	38.4	24.2	6.3	17.3	50.0	185	38	587	■
OD-5	<5.3	<1.0	<0.3	9.3	<1.3	<4.0	<1.0	<4.7	15.1	<0.6	104.2	40.7	25.0	3.9	25.5	18.0	229	43	350	■
OD-3	<5.3	<1.0	<0.3	7.8	<1.3	<4.0	<1.0	<4.7	<1.3	<0.6	122.2	41.6	28.0	8.2	27.2	14.0	207	48	–	×
SK-1	<5.3	<1.0	<0.3	12.4	<1.3	<4.0	<1.0	<4.7	15.4	<0.6	112.1	34.0	21.6	5.5	26.5	14.0	196	42	550	▲
Ç-9	<5.3	<1.0	<0.3	9.8	<1.3	12.0	<1.0	<4.7	13.7	<0.6	84.4	67.3	6.8	5.0	30.5	7.2	196	49	560	□
OD-14	5.7	<1.0	<0.3	7.7	<1.3	<4.0	<1.0	<4.7	<1.3	<0.6	77.8	33.1	21.2	6.5	26.2	25.0	229	33	700	□
OD-17	<5.3	<1.0	<0.3	9.1	<1.3	<4.0	<1.0	<4.7	<1.3	<0.6	110.2	35.1	22.8	6.5	25.1	21.6	207	42	730	▲
Ç-4	7.3	<1.0	<0.3	8.3	<1.3	<4.0	4.2	<4.7	<1.3	<0.6	88.7	82.7	20.7	6.3	21.2	21.6	250	56	240	+
OD-16	<5.3	<1.0	<0.3	8.5	<1.3	<4.0	4.7	<4.7	<1.3	<0.6	90.7	31.2	16.7	8.3	9.27	10.8	174	35	640	▲
OD-6	15.4	<1.0	<0.3	7.5	<1.3	<4.0	5.0	<4.7	<1.3	<0.6	121.3	41.5	23.9	7.4	25.2	18.0	229	47	550	Δ
Ç-6	<5.3	<1.0	<0.3	7.6	<1.3	<4.0	5.2	<4.7	<1.3	<0.6	97.7	50.0	15.7	9.3	32.6	10.8	218	45	500	▲
OD-12	9.9	<1.0	<0.3	8.4	<1.3	<4.0	5.9	13.3	15.1	<0.6	128.5	38.7	25.3	18.3	26.1	14.4	218	48	660	+
OD-8	23.2	6.5	<0.3	8.5	<1.3	216	6.1	13.2	<1.3	<0.6	162.0	39.0	24.4	18.6	23.8	18.0	218	56	630	Δ
Ç-8	12.5	<1.0	<0.3	7.2	<1.3	24.0	6.3	< 4.7	<1.3	<0.6	95.0	36.8	24.7	19.0	27.8	94.0	163	39	560	•
OD 4-1	11.0	<1.0	<0.3	7.5	<1.3	<4.0	6.6	21.5	<1.3	<0.6	117.4	38.3	25.5	9.0	28.5	21.6	229	45	550	■
OD-3-1	53.3	5.5	<0.3	7.3	<1.3	1848	6.8	19.6	17.5	<0.6	239.7	61.9	57.8	5.8	347	18.0	229	85	–	×
Ç-1	<5.3	<1.0	<0.3	8.2	<1.3	12.0	7.1	22.7	<1.3	<0.6	56.5	9.7	13.2	14.3	20.0	10.8	87	18	430	■
OD-9	<5.3	<1.0	<0.3	6.8	<1.3	2760	7.3	22.2	<1.3	<0.6	102.0	34.5	21.1	7.9	29.5	25.0	207	40	260	+
Ç-5	16.3	<1.0	<0.3	6.7	<1.3	2772	7.4	23.0	<1.3	<0.6	98.8	16.9	17.2	18.2	34.7	21.6	174	32	700	▲
Ç-3	35.2	<1.0	<0.3	4.3	<1.3	2772	7.5	21.0	<1.3	<0.6	39.9	100.8	21.7	19.3	31.7	18.0	283	51	600	+
OD-11	34.9	<1.0	<0.3	4.9	<1.3	2736	7.7	21.9	<1.3	<0.6	63.8	30.3	19.0	18.5	23.6	14.4	218	28	268	●
OD-10	36.4	<1.0	<0.3	4.8	<1.3	2724	8.0	23.8	<1.3	<0.6	72.0	32.3	17.5	18.6	20.1	14.4	196	31	550	●
TSE[a]	<200	<2000	–	<20	<50	<5000	<5	<200	<10	<50	<75	<50	<200	<12	<250	<250				
WHO[b]	<300	<2000	–	<20	<100	<15,000	<3	<200	<10	<50	<200	–	<200	–	<250	<250				

[a] TSE: Turkey drinking water standard

[b] WHO: World Health Organization drinking water standard

Table 5 The classification of the waters in the study area according to the hardness degrees (Tuncay 1994)

Water classification	Hardness degree		Hardness values of the water samples in the study area (mg/L $CaCO_3$)
	mg/L or ppm $CaCO_3$	Fr (French water hardness)	
Very soft	0–72	0–7.2	–
Soft	72–145	7.2–14.5	–
Medium hard	145–215	14.5–21.5	181 (a sample)
Quite hard	215–325	21.5–32.5	284–317 (3 samples)
Hard	325–540	32.5–54	330–530 (19 samples)
Extremly hard	>540	>54	551–1151 (9 samples)

A high Cl concentration in water is a sign of contamination; thus, it is an important parameter of water quality. According to TS 266, the Cl content in drinking water should be lower than 250 mg/L. The Cl contents in the water samples from the study area ranged from 7.2 to 94 mg/L (Table 4). Thus, the concentration was acceptable.

The sulfate generated through the oxidation of gypsum, anhydride, and pyrite is an important ion to mix natural water. Sulfate concentration varies in all natural water; in fact, the sulfate in industrial wastewater increases the amount of sulfate in natural water. Water with a high sulfate concentration is bitter-tasting with high hardness, sodium, and acidity. Human muscles are affected by 1–2 g sulfate (Güler and Çobanoğlu 1994). Furthermore, the SO_4^{2-} concentration in the water samples was appropriate (3–124 mg/L) as per TS 266, except for two samples (SD-1 and OD-3-1). This concentration was also below the maximum limit (250 mg/L) for drinking water (Table 4).

Contamination by metal elements

The contents of metal elements (Fe, Mn, Cu, Co, Ni, Zn, Cd, Al, Pb, and Cr) in the water samples were determined separately with reference to TS 266 (Table 4). The Fe and Mn concentrations were high in surface water during certain months of the year and were almost always high in groundwater. Thus, water for drinking and usage was adversely affected as these elements generate undesirable colors and turbidity in drinking water; they also lead to cross-sectional narrowing and clogging when they accumulate in the inner walls of the pipes. The total amount of dissolved Fe compounds was more than 200 μg/L in drinking water. This high concentration can cause serious illnesses in humans, such as stomach problems in children (Kaya and Akar 1998). Fe also occasionally releases rust into water. The Fe concentrations ranged from 5.7 to 53.3 μg/L in 14 water samples and below 5.3 μg/L in the remaining samples. These values were in line with TS 266 (Table 4). In contrast, the concentration in sample SD-1 failed to meet these standards. The Mn contents of two samples were between 6.0 and 6.9 μg/L, whereas those of the other samples were below 1.3 μg/L (Table 4). These values were acceptable according to the TS 266 standards, which prescribed a maximum limit of <50 μg/L) (Table 4). However, the concentration in sample (SD-1) failed to meet this standard.

Cu is not naturally found in water. This element is typically used as a disinfectant and is mixed into water through sulfate solutions or copper pipe corrosions. Cu is absorbed by the human body as an essential element; Cu deficiency causes anemia and bone structure disorders. However, excessive Cu causes mucosal inflammation, vascular disease, liver and kidney diseases, and depression through central nervous system disorders (Güler and Çobanoğlu 1994; Baysal 1999; Soylak and Doğan 2000). According to TS 266, the recommended limit for Cu intake is 100 μg/L and the maximum acceptable limit is 2000 μg/L. Cu concentration ranged from 4 to 22.3 μg/L in eight water samples, whereas the Cu contents in other samples were under 1.0 μg/L (Table 4). Thus, these values do not exceed the recommended maximum limit by TS 266.

Co is found in volcanic rocks and causes ailments such as cancer, lung and heart damage and dysfunction, and increased cholesterol, fat levels, and blood sugar (Atabey 2005). The Co contents in the water samples were below 0.3 μg/L (Table 4).

Readily available Ni compounds are deposited into rivers and other bodies of water along with industrial wastes. Ni in food and water does not contribute to serious health problems because this element is not toxic (Güler and Çobanoğlu, 1994). According to TS 266, Ni concentration must not exceed 20 μg/L. The Ni concentration in all water samples ranged between 4.3 and 16.1 μg/L (Table 4), except for sample OD-1 (Ni = 61.2 μg/L). Therefore, the Ni content in the water in this area was mainly below the acceptable maximum limit.

Zn is not often detected in water. This element can pass from installation components or copper containers to water when they are melted by acidic water. Excess Zn, which can harm humans, changes the taste and appearance of water (Baysal 1999). According to TS 266, the recommended Zn limit is 100 μg/L and the highest acceptable limit is 5000 μg/L. The

Zn contents of 13 water samples were between 12 and 2772 μg/L, whereas those of the other samples were <4 μ/L.

Cd is a highly toxic element that aggravates the degradation of galvanized tubes. This element is used as a stabilizing agent in the plastic industry and is mixed into water through industrial wastes (Tüzen et al. 2005). Cd can be absorbed into the body through drinking water, food, air, and industrial methods. This element and its compounds are carcinogenic; they induce many ailments, such as headaches, thirst, throat dryness, irritation, heavy coughs, bronchitis, emphysema, anemia, and kidney stones (Güler and Çobanoğlu 1994). The Cd concentrations in 15 water samples ranged from 4.2 to 8.0 μg/L, whereas those in the other samples were below 1.0 μg/L (Table 4). The CD contents 10 samples (C-6, OD-12, OD-8, C-8, OD-4-1, OD-3-1, C-1, OD-9, C-5, C-3, OD-11, and OD-12) ranged from 5.2 to 8.0 μg/L. According to TS 266, the recommended maximum limit for Cd is <5 μg/L; therefore, these samples indicate that the water in the area is hazardous to humans.

Pb is a natural component of the earth's crust; however, it is not found in natural water such as drinking water, stream water, and groundwater. This element enters these bodies of water because of environmental pollution (including industrial waste, lead pipes deformation, and leaded gasoline combustion). Pb is a highly toxic element to the human body, which when taken in high doses causes loss of appetite, abdominal pain, fatigue, lead paralysis, sensory organ disorders, and brain disorders caused by stress (Güler and Çobanoğlu 1994). The Pb concentrations in several of the samples were below 1.3 μg/L and were acceptable based on TS 266 (Table 4). However, the Pb contents were high and varied from 13.7 to 43.9 μg/L in samples SD-1, SK-5, OD-1, SK-6-1, OD-15, OD-13, OD-19, C-2, SD-2, OD-7, OD-5, SK-1, C-9, OD-12, and OD-3-1.

Cr is detected in the form of Cr^{+3} and Cr^{+6} ions in water. The 3-valent Cr is rarely observed because it is insoluble, and the 6-valent Cr is carcinogenic. Therefore, drinking water must be protected from Cr contamination. This element is mixed with water through industrial wastes (such as metallic coating, as well as wastes from paint factories, paint, explosives, ceramics, and paper). The 6-valent Cr causes ulcers and bronchitis, as well as lung and kidney diseases (Güler and Çobanoğlu 1994). According to TS 266, the maximum limit for Cr is 50 μg/L. The Cr concentrations in the water samples were lower than 0.6 μg/L (Table 4) and were acceptable for drinking water.

Al, among the most abundant element in the earth's crust, is detected in natural water in miniscule amounts. This element is mixed into water through soil and rocks, as well as municipal and industrial wastes. According to WHO, the daily Al consumption requirement for humans is 88 mg. A small percentage of this value is consumed through drinking water. Al does not exert a specific toxic effect; however, if taken in excess, this element can cause neurological diseases such as Alzheimer's (Aksoy 2000). According to TS 266, the maximum limit value for Al is 200 μg/L. The Al concentrations of 10 water samples were between 13.2 and 23.8 μg/L, whereas those of the other samples were below 4.7 μg/L (Table 4), which were acceptable based on TS 266.

Piper diagram

The chemical classification of the water samples from the study area was conducted using a Piper diagram (Fig. 2). Mg^{+2} and HCO_3^- ions comprised the majority of cations and anions, respectively. The samples located in the I-, II-, and IV-numbered areas are depicted in the Piper triangle diagrams (Fig. 2). Accordingly, the water samples in the study area were labeled as Ca^-, Mg^-, mixed composition, and bicarbonate water. The water samples located in the 1-, 2-, and 5-numbered areas are presented in the Piper rhombus diagram (Fig. 2). These samples were generally classified as carbonate and sulfate (Ca + Mg > Na + K) water and are composed of more strong than weak acid radicals (HCO_3 + CO_3 > Cl + SO_4). In addition, the carbonate hardness of the water was greater than its non-carbonate hardness. This water belonged to the water class of $CaCO_3^-$ and $MgCO_3^-$, where carbonate hardness exceeded 50 % (Canik 1998).

Water quality

Drinking water quality is an important parameter in defining the quality of life. Water quality is determined based on the

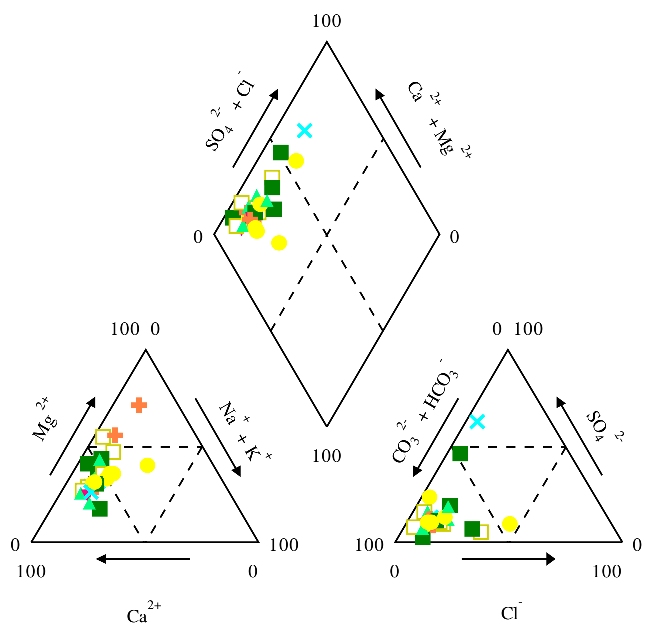

Fig. 2 The classification in the Piper diagram of the water samples in the study area. *Symbols* are in the Table 4

Table 6 The water classification and pollution parameters of the water samples in the study area

Sample no.	Location	Pollution parameter	Water class	Rock type
SD-1	Karaer M. up water reservoir	Fe, Co, Cr, Ni, Mn, Zn, Cd, Al	I	Granitoid
		Cu, Na, Cl	II	
		Pb	III	
		SO_4	IV	
SK5	Alemdar yellow bridge water well	Fe, Cu, Co, Cr, Ni, Mn, Zn, Cd, Na, Al, Cl, SO_4	I	Alluvium
		Pb	III	
OD-2	Süleymaniye M. imam house	Fe, Cu, Co, Cr, Ni, Mn, Zn, Cd, Na, Pb, Al, Cl, SO_4	I	Granitoid
OD-1	Çamlıca M. water reservoir	Fe, Cu, Co, Cr, Mn, Zn, Cd, Na, Al, Cl, SO_4	I	Granitoid
		Pb, Ni	III	
SK6–1	Gümüşhane Anadolu high school housing	Fe, Cu, Co, Cr, Mn, Cd, Na, Al, SO_4	I	Alluvium
		Pb	II	
		Zn	III	
OD-15	Yeni M. religious office building	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, Cl, SO_4	I	Alluvium
		Pb	II	
OD-13	İnönü M. training tools building	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, Cl, SO_4	I	Granitoid
		Pb	II	
OD-19	Bağlarbaşı M. water reservoir	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, SO_4	I	Granitoid
		Pb, Cl	II	
Ç-2	Süleymaniye M. fountain	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, Cl, SO_4	I	Granitoid
		Pb	II	
SD-2	Karaer M. water reservoir	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, Cl, SO_4	I	Granitoid
		Pb	II	
OD-7	Gümüşhane State Hospital	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, SO_4	I	Alluvium
		Pb, Cl	II	
OD-5	Özcan M. slaughterhouse	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, Cl, SO_4	I	Andesite–basalt
		Pb	II	
OD-3	Hacı Emin M. Bahri Aydın house	Fe, Cu, Co, Cr, Mn, Cd, Pb, Zn, Na, Al, Cl, SO_4	I	Andesite–basalt
SK-1	Sema Doğan Park water well	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, Cl, SO_4	I	Granitoid
		Pb	II	
Ç-9	İnönü M. Mordut fountain	Fe, Cu, Co, Cr, Mn, Cd, Zn, Na, Al, Cl, SO_4	I	Alluvium
		Pb	II	
OD-14	İnönü Mah. Mordut tea hearth	Fe, Cu, Co, Cr, Mn, Cd, Pb, Zn, Na, Al, Cl, SO_4	I	Granitoid
OD-17	Bağlarbaşı M. Toki	Fe, Cu, Co, Cr, Mn, Cd, Pb, Zn, Na, Al, Cl, SO_4	I	Granitoid
Ç-4	Karşıyaka Özdenoğlu fountain	Fe, Cu, Co, Cr, Mn, Pb, Zn, Na, Al, Cl, SO_4	I	Alluvium
		Cd	II	
OD-16	Köprülüler oil	Fe, Cu, Co, Cr, Mn, Pb, Zn, Na, Al, Cl, SO_4	I	Granitoid
		Cd	II	
OD-6	Güzeller M. girls' dormitory	Fe, Cu, Co, Cr, Mn, Pb, Zn, Na, Al, Cl, SO_4	I	Alluvium
		Cd	II	
Ç-6	Eski Bağlar fountain	Fe, Cu, Co, Cr, Mn, Pb, Zn, Na, Al, Cl, SO_4	I	Granitoid
		Cd	III	
OD-12	Karşıyaka M. lower of the mosque tea hearth	Fe, Cu, Co, Cr, Mn, Zn, Na, Al, Cl, SO_4	I	Alluvium
		Pb	II	
		Cd	III	
OD-8	Hasanbey M. Bilali Habeşi Mosque housing	Fe, Cu, Co, Cr, Mn, Na, Pb, Al, Cl, SO_4	I	Andesite–basalt
		Zn	II	
		Cd	III	
Ç-8	Karaer Mah. Atatürk Park fountain	Fe, Cu, Co, Cr, Mn, Na, Pb, Al, Zn, SO_4	I	Granitoid
		Cl	II	
		Cd	III	
OD-4-1	Canca M. Sadirvan	Fe, Cu, Co, Cr, Mn, Pb, Zn, Na, Al, Cl, SO_4	I	Andesite–basalt
		Cd	III	
OD-3-1	Hacı Emin M. stop fountain	Fe, Cu, Co, Cr, Mn, Na, Cl, Al, Cd	I	Andesite–basalt
		Pb	II	
		Zn, SO_4	III	
Ç-1	Özcan Mah. fountain	Fe, Cu, Co, Cr, Mn, Pb, Zn, Na, Al, Cl, SO_4	I	Andesite–basalt
		Cd	IV	
OD-9	Gümüşhane male dormitory	Fe, Cu, Co, Cr, Mn, Pb, Na, Al, Cl, SO_4	I	Alluvium
		Zn, Cd	IV	
Ç-5	Bağlarbaşı M. Hacı Kasım fountain	Fe, Cu, Co, Cr, Mn, Pb, Na, Al, Cl, SO_4	I	Granitoid
		Zn, Cd	IV	
Ç-3	Karşıyaka Çilenkler fountain	Fe, Cu, Co, Cr, Mn, Pb, Na, Al, Cl, SO_4	I	Granitoid
		Zn, Cd	IV	
OD-11	Karaer M. Health Directorate	Fe, Cu, Co, Cr, Mn, Pb, Na, Al, Cl, SO_4	I	Granitoid
		Zn, Cd	IV	
OD-10	Karaer M. Zafer tea hearth	Fe, Cu, Co, Cr, Mn, Pb, Na, Al, Cl, SO_4	I	Alluvium
		Zn, Cd	IV	

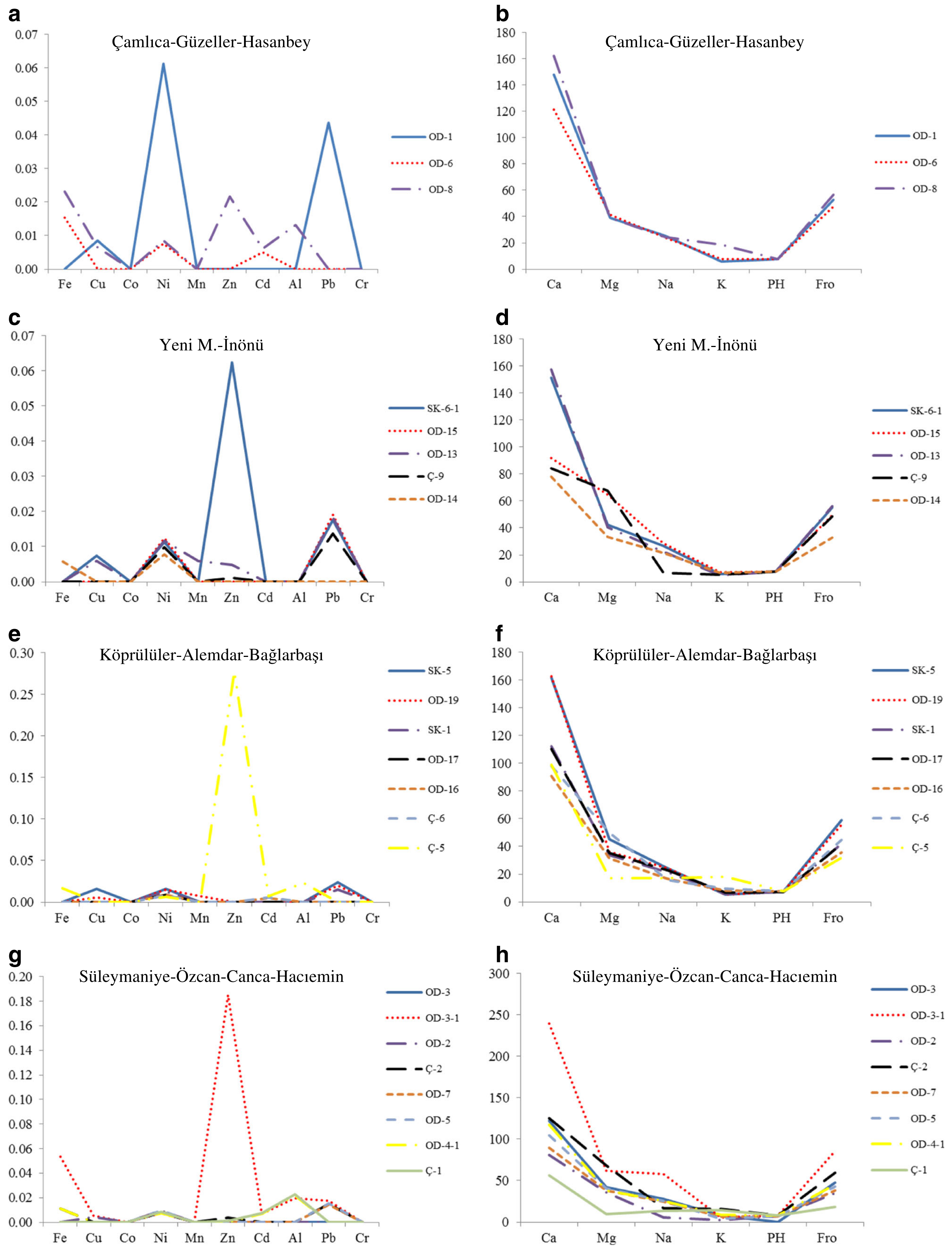

Fig. 3 The element (µg/L and mg/L) group distribution diagrams of the water samples in the study area (Zn values were divided 10) and the element (ppm and %) distribution diagrams of the wall rocks

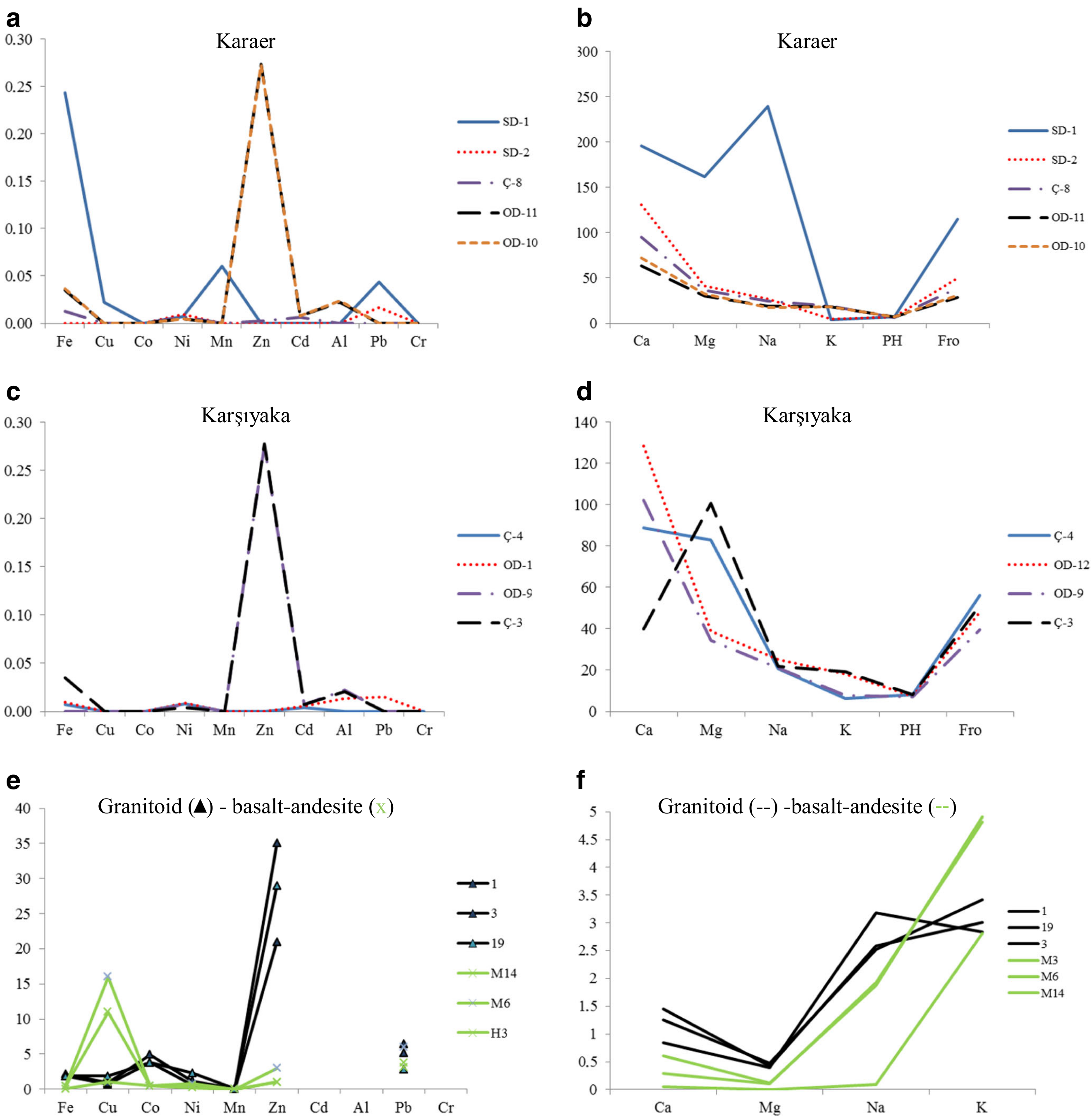

Fig. 3 (continued)

physical and chemical properties of water. With reference to the Inland Surface Water Classification (MFW, 2012), the water samples in the study area were classified as first-class [according to quality, pH level, and Na, $(SO_4)^{2-}$, Fe, Mn, Al, Co, Ni, Cu, and Cr contents]. These samples were also classified as first- and second-class according to pollution level and conductivity, as well as the amounts of Cl^-, Pb (except for samples SK-5, SD-1, OD-1, and OD-19), Zn (except for samples OD-10, OD-11, C-3, Ç-5, OD-9, OD-3-1, and SK6-1), and Cd (except for samples C-6, OD-12, OD-8, C-8, OD-4-1, OD-3-1, C-1, OD-9, C-5, C-3, OD-11, and OD-10), as shown in Table 6.

The presence of the pollutants Pb, Cd, Zn, Ni, Cl, and SO_4 in the water samples may indicate that metal and industrial wastes were mixed into the surrounding drinking water through the corrosion of lead pipes and exhaust fumes. A sudden increase in the Cl^- concentration in water suggests that water can be contaminated by industries. In this study, water quality is measured against the acceptable maximum limits provided by the TS 266 and the WHO rather than according

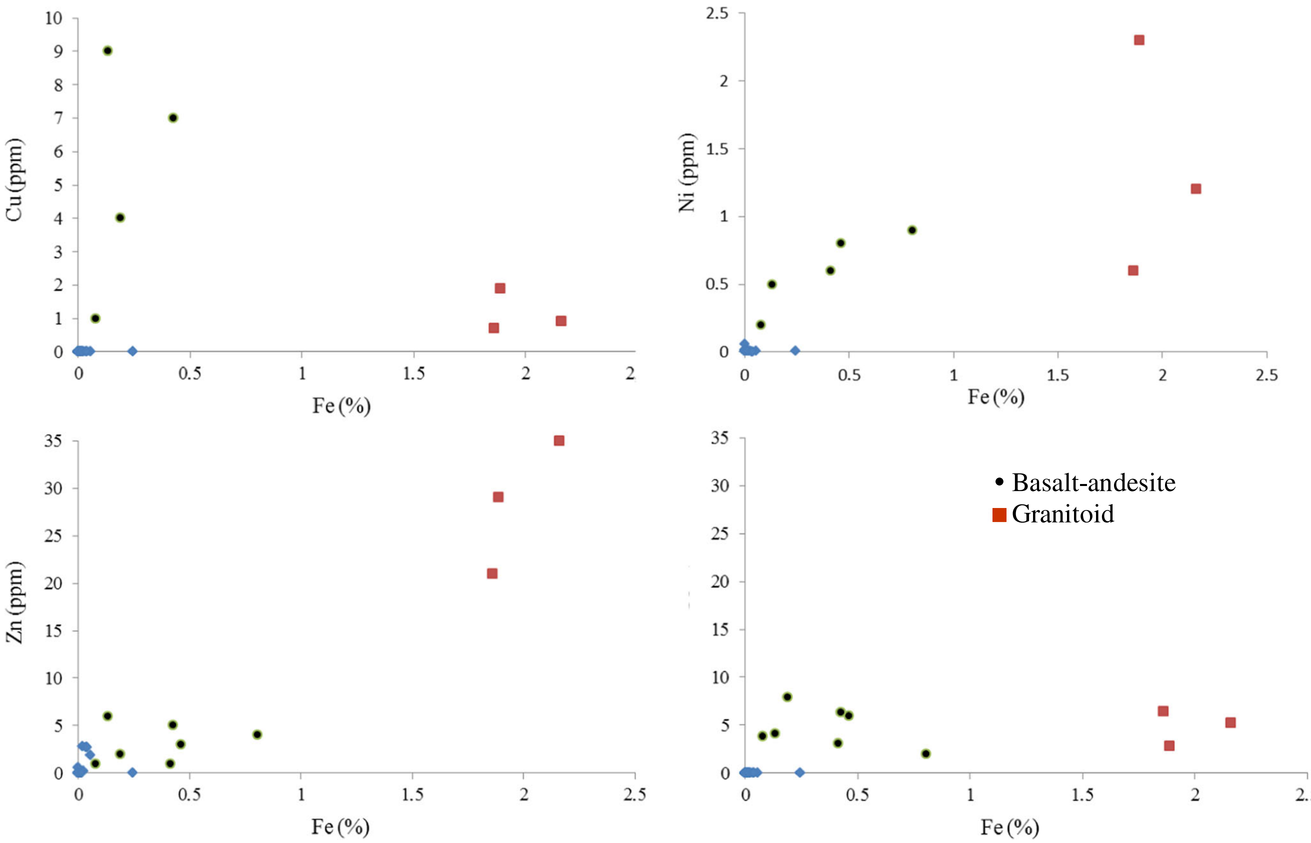

Fig. 4 The Cu (ppm), Ni (ppm), Zn (ppm), and Pb (ppm) exchanges with Fe (%) between wall rock and water samples from the study area (basalt–andesite values from Aslan 2010; granitoid values from Topuz et al. 2010 and Sipahi 2011)

to the Inland Surface Water Classification (MFW, 2012). The results confirm that the TS 266 and WHO standards can be applied to classify usable water. The Fe, Ni, Cd, Pb, and SO_4 concentrations in a number of the water samples exceeded the acceptable maximum limits provided by these standards, although the samples were within the limits in terms of other parameters. Therefore, several water sources were usable, whereas others were risky because of their Cd and Pb contents (samples C-6, OD-12, OD-8, C-8, OD-4-1, OD-3-1, C-1, OD-9, C-5, C-3, OD-11, and OD-12 for Cd; SD-1, SK-5, OD-1, SK-6-1, OD-15, OD-13, OD-19, C-2, SD-2, OD-7, OD-5, SK-1, C-9, OD-12, and OD-3-1 for Pb; Table 4).

Natural sources of groundwater are typically surrounded by sand, gravel, limestone, marl, granite, and sandstone. Thus, geological units positively affect water chemistry. Elements such as Al, Fe, As, Ag, Hg, Co, Cd, Cr, Pb, Ni, Ba, Mn, Zn, Cu, Se, and Sb can be enriched in water through the interaction of rocks with natural and underground water sources. Certain pipes used in water distribution can also increase the Pb, Ni, and SO_4 concentrations in water. Furthermore, the combustion of leaded petrol is a major source of environmental Pb, particularly in urban areas. Lead is discharged by vehicles into the air and is subsequently adsorbed by environmental samples such as soil and plants (Asubiojo et al. 1997, Soylak and Elçi 2000). Pb then enters the waterways from the soil, which affects lead levels in natural waters. The ppm values of the elements in the water samples were similar when examined collectively in a single diagram (Fig. 3). The water samples were grouped based on sources to indicate a parallel distribution, thus accounting for the parallel increases in the contents of several elements. This finding indicates that aside from mining or industrial waste, the elements originated from wall rocks and mix with water. The parallel distributions of the elements in the water suggest that the water originates from one source or from similar sources. In this study, the chemical composition of the water was generally similar to granitoid and basalt–andesite compositions. The Ca, Na, and K contents of the water were lower than the granitoid (chemical values derived from Topuz et al. 2010) and basalt–andesite values (chemical values derived from Aslan 2010; Fig. 3). The Fe, Pb, Zn, and Cu contents in the water were high, but they were lower than the granitoid and basalt–andesite values and typically remained acceptable based on TS 266. The sole exception was Pb content.

Furthermore, the turbidity derived from the physical properties of water is important. Precipitated $CaCO_3$ is presumably caused by high Ca and Mg concentrations; as a result, the turbidity of the water samples (1–346 NTU) exceeded the limit (<5 NTU; TS 266; Table 4).

Varying concentrations of metals such as Fe, Al, Cu, and Mn were investigated in relation to ions such as Ca, Mg, Na, K, and HCO_3^-, and no significant relationships were observed. In contrast, the Fe, Al, Cu, Mn, Ca, Mg, Na, Zn, Pb, and Ni contents in the water samples were significantly related to those in the wall rocks (values derived from Aslan 2010; Fig. 4). Exchanges of Cu, Ni, Zn, and Pb concentrations with Fe concentrations in the water samples were compatible with and close to those of the basalt–andesite.

The collective evaluation of the studied metals (Fe, Cu, Pb, Zn, Ni, Na, and K) and the pH levels of the water samples yielded no significant associations. The pH levels of 7–8 were ineffective given the element concentrations in the water of the study area. The hardness (273–1010 mg/L $CaCO_3$) in the springs from Kayseri–Yozgat was indicative of limestone (Soylak and Doğan 1996). The water samples in the study were generally classified as hard and very hard. In addition, the types of rock (granitoid, basalt–andesite, limestone, and alluvium) from which water samples were obtained, especially limestone, can be related to water hardness. No relationship was established among pH levels, metals (Fe, Pb, Ni, Na, and K), and water hardness. The Na^+ ions in the water samples were presumably enriched because of plagioclase weathering. Moreover, Mg^{2+} ions increased because of the amphibole, biotite, and augite weathering in granitoid and basalt–andesite rocks. Ca^{2+} ions were detected in the water because of the plagioclase, amphibole, and calcite weathering. K^+ ions were identified in the water through the feldspar and biotite weathering in the rocks.

Conclusions

The main findings of this paper are summarized as follows:

1. The pH levels of the water samples ranged from 6.3 to 8.2, and their conductivities were between 240 and 900 µS. These findings satisfied the TS 266 and WHO standards.
2. The hardness of the water samples in the study area was between 18.1 and 115.1 °Fr. These samples were classified as extremely hard, hard, and quite hard.
3. The water in the study area generally belonged to carbonated and sulfated (Ca + Mg > Na + K) water classes. This water contained more weak than strong acids (HCO_3^- + CO_3^{2-} > Cl^- + SO_4^{2-}).
4. The water samples in the study area were classified as first-class according to the quality and pH level, as well as the Na, $(SO_4)^{2-}$, Fe, Mn, Al, Co, Ni, Cu, and Cr contents. Moreover, samples were classified as first- and second-class according to the pollution level and conductivity, as well as the amounts of Cl^-, Pb (except for samples SK-5, SD-1, OD-1, and OD-19), Zn (except for samples OD-10, OD-11, C-3, Ç-5, OD-9, OD-3-1, and SK6-1), and Cd (except for samples C-6, OD-12, OD-8, C-8, OD-4-1, OD-3-1, C-1, OD-9, C-5, C-3, OD-11, and OD-10).
5. The pH levels (6.3–8.2) of the water in the study area were unrelated to the varying concentrations of metals in the water.
6. No correlation was observed among the metal concentrations in the drinking water samples of the study area.
7. The types of rock (especially limestone) can be related to water hardness.
8. Several water sources are usable, whereas others are risky because of their Cd (samples C-6, OD-12, OD-8, C-8, OD-4-1, OD-3-1, C-1, OD-9, C-5, C-3, OD-11, and OD-12), Pb (samples SD-1, SK-5, OD-1, SK-6-1, OD-15, OD-13, OD-19, C-2, SD-2, OD-7, OD-5, SK-1, C-9, OD-12, and OD-3-1), and Fe contents (sample SD-1).

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