e-ISSN: 2687-6698 **Research Article**

Turkish Journal of Analytical Chemistry
www.turkjac.org 2019
TurkJAC

Geochemical investigation of the potability of surface water in Çit Stream and related creeks in Avliyana Basin (Gümüşhane, NE Türkiye)

Alaaddin Vural[1*], Ali Gündoğdu[2], Fatih Saka[3], Volkan Numan Bulut[4], Mustafa Soylak[5]

[1] Gümüşhane University, Faculty of Natural Sciences and Engineering, Department of Geological Engineering, 29000, Gümüşhane, Türkiye,
[2] Karadeniz Technical University Maçka Vocational School, Department of Pharmacy Services, 61750, Trabzon, Türkiye
[3] Karabük University, Faculty of Engineering, Department of Civil Engineering, 78050, Karabük, Türkiye
[4] Karadeniz Technical University Maçka Vocational School, Department of Chemistry and Chemical Processing Technologies, 61750, Trabzon, Türkiye
[5] Erciyes University, Faculty of Science, Department of Chemistry, 38030, Kayseri, Türkiye

Abstract

In the study, physicochemical parameters of Çit Stream and related creeks in Avliyana Basin (Gümüşhane, NE Türkiye) were determined. In terms of water quality parameters, it has been observed that Çit Stream may have drinking water quality. According to the piper diagram, all of the samples except one have fallen into regions of a class of $CaCO_3$ and $MgCO_3$ waters. The different one is the mixed water class. It has been determined that the metal content that may pose a risk to water is below the permissible limits. It has been seen that there may be only one point of risk for lead. As a result, the physicochemical aspect of water quality of Çit Stream and related creeks in Avliyana Basin has been seen to be suitable for drinking water standards.

Keywords: Water quality, surface waters, trace element, piper diagram

1. Introduction

As throughout the world, Türkiye is a poor country in terms of freshwater resources [1]. According to data from the General Directorate of State Hydraulic Works of Türkiye (DSI), the total renewable water potential of Türkiye is estimated to be 234 billion m³ gross and the total surface water potential can be consumed for various purposes within the framework of today's technical and economic conditions is an average of 98 billion m³ per year. Therefore, it must be more rigorous in the context of the conservation and efficient use of water resources, and it should make water resources planning much more rigorous. Especially since the beginning of the 20th century, environmental problems brought about by rapid industrialization have been one of the most important issues that have given humanity a headache [2]. Human-induced heavy metal/trace element pollution has become a serious threat to terrestrial and aquatic systems [3–7]. The approach of utilizing natural resources in an environmentally friendly-sustainable development perspective continues with an increasing awareness after the 1980s [2,7]. Sustainable utilization of water, which is one of the most important natural resources, is among the priorities of societies in this context, and serious efforts are made for the protection and management of underground and surface water resources.

The study area in Gümüşhane is located in the northeastern Black Sea region, Türkiye (Fig. 1). The region has a typical continental climate. The average annual rainfall in the region is 470.1 mm (Turkish State Meteorological Service 2016) and lower than Türkiye's average annual rainfall (643 mm/year). Therefore, Gümüşhane's water resources, especially river resources should be evaluated in the most efficient way. The Büyük Çit Stream is one of the important rivers of Gümüşhane. The stream is fed groundwater and rains and after reaching 30–35 km, it connects to the Harşit River and then, flows to the Black Sea. There is no settlement in the vicinity of the source of the river and

Citation: A. Vural, A. Gündoğdu, F. Saka, V. N. Bulut, M. Soylak, Geochemical investigation of the potability of surface water in Çit Stream and related creeks in Avliyana Basin (Gümüşhane, NE Türkiye), Turk J Anal Chem, 4(1), 2022, 44–51.
https://doi.org/10.51435/turkjac.1102045

***Author of correspondence:** alaaddinvural@hotmail.com
Tel: + 90 (456) 233 17 13
Fax + 90 (456) 233 10 75
Received: April 12, 2022
Accepted: June 14, 2022

on the creek route except for the connection point to the Harşit river. The stream is used in the irrigation of gardens and a few trout production facilities, as well as in drinking water, especially the upstream. So, the stream is very important to the local people.

Surface waters suitable for drinking or recreational use, along with their feeding tributaries, should be monitored for a long time and frequently sampled and analyzed for water quality. For this purpose, water quality can be monitored in two stages: (*i*) First, pre-control samples are taken, and some basic parameters of the water are analyzed. Thus, the instantaneous status of the water is determined. (*ii*) In the light of the results obtained from the instantaneous control of the water, several samples are taken from the stations determined during certain periods of the year, and then a more comprehensive analysis is performed.

The main purpose of this study is to determine the instantaneous values of some physicochemical and heavy metal contents of the Büyük Çit Stream, one of the most important rivers in the region, to shed light on new studies to be carried out and to reveal whether it has potable water potential.

2. Sampling, Materials and Methods

Büyük Çit Stream (Torul, Gümüşhane, NE Türkiye) is located in the southern part of the eastern Black Sea region (Fig.1). The basement of rocks of the study region consists of granitoid of the Middle to Late Carboniferous Period [8]. These rocks are unconformably overlain by volcani-clastic unit Zimonköy formation [9], which passes upward conformably to the platform carbonate rocks called as “Berdiga formation” [10]. The Late Cretaceous clastic unit, conformably covers those carbonates. The Eocene volcanic and volcani-clastic unit called “Alibaba formation” overlies all of these rocks with an angular unconformity [11,12] and was intruded by calc-alkaline granitoids of a possible similar age (Avliyana granitoids, Fig. 1) [13,14].

“Büyük Çit Stream” passes through three settlements along the valley where it is located: Avliyana, Haviyana, and Altınpınar. A total of 17 water samples were collected in September 2016 from the stream along with these settlements and their tributaries. Twice sampling was done with 500 mL PP bottles from each sampling station. Since the first sampling was done for minor-trace element and heavy metal analysis, ultrapure concentrated HNO_3 was added to these bottles at a pH of approximately 2 (approximately 0.5 mL). No reagent was added to the other bottle. After the bottles were appropriately labeled, they were transported to the laboratory at the end of the day and stored in a refrigerator at +4 °C until the analysis.

As September is generally the dry season in the region, this month was preferred for sampling. Acidified and natural samples were analyzed for minor-trace elements and heavy metals at Gümüşhane University Labs (Türkiye), by microwave plasma atomic emission spectrometer (Agillent 4200 model MP-AES, Santa Clara, US) and inductively coupled plasma mass spectrometer (Agilent 7700e model ICP-MS, Santa Clara, US). Electrical conductivity (EC), temperature (T), total dissolved solids (TDS), dissolved oxygen (DO), Chloride (Cl^-), Nitrate (NO_3^-), ammonium (NH_4^+), and pH values were determined by electrochemical methods. Portable multiparameter devices, YSI Procomm II Portable meter (YSI Incorporated, Yellow Springs, OH, USA) and Hach-Lange HQD Series Portable Meter (Hach-Lange, Loveland, Colorado, US) with suitable electrode systems were used for this purpose.

Alkalinity and subsequent carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) analyzes were performed according to the titrimetric method reported by the American Public Health Association [15]. Hardness analysis was carried out according to the titrimetric method with EDTA (ethylenediaminetetraacetic acid) specified in [16]. Nitrite (NO_2^-) analyzes were performed according to the colorimetric method reported in [17]. The color intensity formed at the end of the reaction is in the spectrophotometer. Sulfate (SO_4^{2-}) contents were determined according to the turbidimetric method reported by [18]. The intensity of the turbidity formed at the end of the reaction was measured in a UV-Vis spectrophotometer (Hach-Lange DR3900) whose wavelength was adjusted to 420 nm, and sulfate concentrations were determined with the help of the standard calibration graphs [18].

3. Quality Control

Some statistical tests were applied to the results for the reliability and quality of the analysis results. Each sample was repeated at least 3 times and the mean values and standard deviations of the results were calculated. The LOQ, which is the lowest concentration that can be determined quantitatively, was calculated by taking 10 times the standard deviation of the data obtained as a result of the analysis of a series of blank solutions.

The presence of possible interferences was tested by applying spiked/recovery tests to the samples for all physicochemical parameters. The accuracy of the metal analysis was also tested with a standard reference material "CRM-TMDW-A Trace Metals in Drinking Water". Satisfactory results were obtained from the accuracy tests for all parameters.

A very effective accuracy parameter for water analysis is the charge-balance error (CBE) test. Surface waters contain mostly the following ions, which are almost 95% of the ions present in the water; HCO_3^-, CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, and K^+. In waters, the total ion charge must be zero, and the closer the result obtained from the CBE equation given in Formula 1 to zero, the less error there is in the analysis [19]. The CBE values of the water samples examined in this study were found to be between 0.7 and 7.9%.

$$CBE\ (\%) = \frac{\sum cations\ (meq/L) - \sum anions\ (meq/L)}{\sum cations\ (meq/L) + \sum anions\ (meq/L)} \times 100 \qquad (1)$$

CBE: Charge-balance error
meq: milliequivalent

4. Results and Discussion

The descriptive statistics of physicochemical parameters of the samples are listed in Table 1. Fig. 2 and Fig. 3 show the distribution of water quality parameters of the water samples taken from 17 points. The standard deviation values given in Table 1 are quite high for many parameters. This is due to widespread results. It can be seen more clearly from Fig. 3 that many parameters are heterogeneously distributed over a wide range.

Water temperature can cause changes in the physical and chemical properties of water by affecting many parameters dissolved in the water. In this context, the water temperature should also be considered when determining other parameters. In terms of health, the temperature value of drinkable water should be between 4 and 12. It is expected that the temperature values of the samples taken in September are generally higher than this range. What is important here is the temperature conditions under which other water quality parameters are present.

Perhaps the most critical parameter for water quality is pH. Perhaps the most critical parameter for water quality is pH. If the pH of the water is too high or too low, the aquatic organisms living in it will eventually die. pH also affects the water solubility and toxicity of chemicals and heavy metals. For health, the pH content of the waters should not be outside the range of 6.0–9.0. The pH values of the water samples examined in this study varied between 6.07 and 8.12 (mean of 7.53). Looking at the standard values in Table 2, according to TS 266, the pH value of drinking water should be between 6.5–9.0. According to WHO, this range is 6.5–8.5. Considering the pH results obtained from this study, only one sample was outside this range with a value of 6.07.

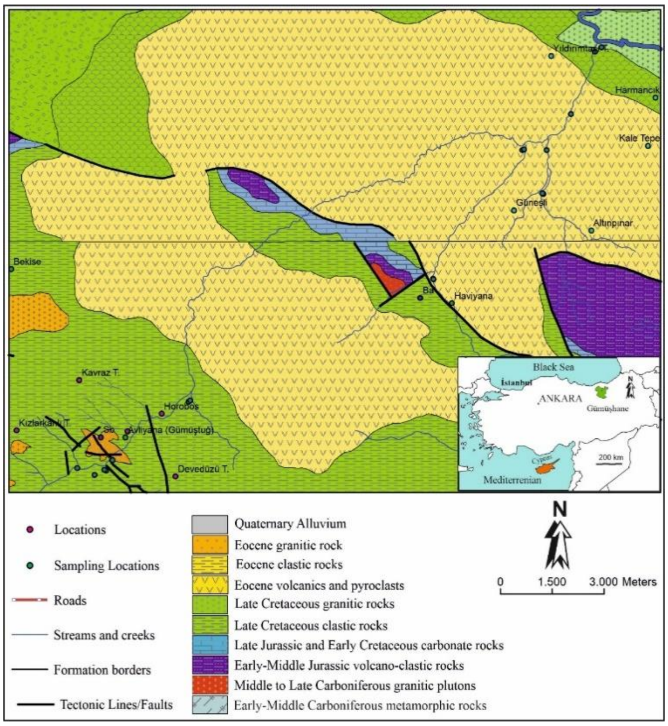

Figure 1. Geological map of the area and sample locations (modified from [13,20]).

According to WHO and EC, the electrical conductivity value in water should be < 2500 µS/cm. Although the electrical conductivity values in the examined waters are in accordance with the standards, it is seen that the values are distributed in a very wide range (31.6–379.3 µS/cm). Although the samples were taken from the same stream and its branches, the fact that the stream passes through different settlements and different geological geographies along the valley is reflected in the results.

In the directive published by the Turkish Ministry of Forestry and Water Affairs in the Official Gazette in 2016, in the table "Quality Criteria for General Chemical and Physicochemical Parameters of Inland Surface Water Resources by Class", it is reported that dissolved oxygen content should be > 8 mg/L for 1st class waters and between 6–8 mg/L for 2nd class waters. When the results are analyzed in terms of these criteria, the dissolved oxygen content in only one sample is critical (3.88 mg/L). The dissolved oxygen contents of the other samples are quite satisfactory.

TDS values of the samples are under permissible level. The scatter plot is similar to EC as the TDS values are calculated with a formula based on the results from the EC measurements. In other words, the comments made for EC values are also valid for TDS values.

The chloride contents of only two samples (w-14 and w-17) taken from the Altınpınar settlement were above the relevant LOQ value, and no chloride was detected in the other samples.

Table 1. Descriptive statistics of water quality parameters and trace elements concentration in water samples

Descripitive statistics	T (°C)	[1]pH	[2]EC (µS/cm)	DO (mg/L)	TDS (mg/L)	Hardness (°F)	NO_2^- (µg/L)	NO_3^- (mg/L)	Alkalinity (mg/L)	CO_3^{2-} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	NH_4^+ (mg/L)	Cl^- (mg/L)
Mean	16.8	7.53	190.5	7.74	151.1	12.6	4.4	0.90	79.1	16.8	79.1	15.2	0.05	2.7
Median	17.0	7.84	188.7	7.99	143.0	11.3	2.0	0.46	78.6	13.8	78.6	10.7	0.02	2.7
Std. deviation	2.0	0.63	120.5	1.02	96.1	8.3	9.7	0.84	31.5	14.0	31.5	10.1	0.05	0.1
Minimum	13.5	6.07	31.6	3.88	25.4	1.5	1.0	0.23	25.3	0.0	25.3	6.4	0.02	2.7
Maximum	21.4	8.12	379.3	8.36	289.9	24.3	40.0	3.04	157.1	46.0	157.1	42.8	0.13	2.8
LOQ (mg/L)	–	–	–	–	–	1.0	2.0	0.23	0.1	0.1	0.1	0.1	0.01	1.0

Descripitive statistics	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/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)
Mean	7.1	17.2	78.9	9.9	0.21	17.5	–	15.4	30.6	79.5	8.50	79.3	47.2	–
Median	5.6	17.5	78.7	9.5	0.13	13.79	–	15.4	30.6	74.7	8.50	83.6	13.9	–
Std. deviation	3.7	8.5	22.9	4.2	0.24	12.2	–	–	–	64.2	–	51.7	68.7	–
Minimum	3.4	5.6	28.0	3.0	0.05	8.3	–	15.4	30.6	15.1	8.50	21.8	10.8	–
Maximum	16.6	45.8	138.3	22.1	1.01	50.0	–	15.4	30.6	285.5	8.50	155.3	150.2	–
LOQ (µg/L)	10.7	7.3	7.3	4.7	10.3	8.3	10.0	10.3	10.3	9.0	6.7	11.7	10.0	10.0

* Respectively Class I and IV values
[1,2] The pH and electrical conductivity values are measured at 20 °C and 25 °C, respectively.
EC: Electrical conductivity, T: Temperature, DO: Dissolved oxygen, TDS: Total dissolved solids, °F: French unit of hardness
LOQ: Limit of quantification

There is no problem with chloride for either sample, as the reported guideline value (250 mg/L) for chloride is relatively high.

Hardness is an important water quality parameter. Water hardness is mainly caused by Ca^{2+} and Mg^{2+} ions.

Water containing these ions in large amounts becomes hard. The hardness values of the waters show a heterogeneous distribution in soft and medium hard classes between 1.5–24.3 °F. The WHO guideline value reported in 2017 is 20 °F. There are 5 samples that exceed this value, albeit slightly: However, according to TS266 records, water hardness is allowed up to 50 off. As a result, it can be said that the hardness values of the samples are within acceptable limits.

Alkalinity gives information about its ability to neutralize or buffer water against the ingress of any acidic substance. This function of water enables the living organisms it contains to continue their lives. The total alkalinity contents of the waters vary in a wide range between 27.6–133.4. Carbonate-rich rocks such as limestone increase the alkalinity of waters. Gümüşhane region has an important limestone reserve. It is quite possible for carbonate and bicarbonate ions to enter the waters not only with anthropogenic activities but also with geological formations. No limit value for alkalinity is given in the guide values.

Nitrite is a highly toxic substance that enters the waters as a result of microbiological contamination, and it is undesirable, especially in drinking water. Nitrite is an unstable substance and turns into nitrate, which is much less harmful after a while. The main sources of nitrite and nitrate compounds are fertilizer and sewage systems used especially in rural areas. Failure to control them can lead to serious problems. Guideline values for nitrite and nitrate are 0.5 mg/L and 50 mg/L, respectively, according to TS266. However, nitrite is allowed up to 3 mg/L in the WHO 2017 guideline. When the nitrite distributions of the analyzed water samples are examined, it is seen that the values are generally very low, but the w-13 coded sample does not exceed the limit value despite the relatively higher nitrite content (40 µg/L).

The presence of ammonia in water causes negative effects on human health, as in nitrate and nitrite. Ammonium enters the waters from domestic wastes, industrial wastes, and fertilizers. In short, due to anthropogenic effects, a significant amount of ammonium mixes into the waters and taste, and odor problems occur in the waters. The presence of NH_4^+ ions in the water indicates the possibility of mixing feces, ie sewage or animal wastes into the water. The ammonium ion is then converted to nitrite and then to nitrate by oxidation by bacteriological activities. Guideline values for ammonium are 0.5 mg/L according to TS266 and 1.5 mg/L according to WHO. Looking at the analyzed samples, ammonium was not observed in most samples. The results are in the range of 0.012–0.13 mg/L in ammonium detected samples. The presence of high sulfate in the water means high hardness, high sodium salt, and high acidity. For this reason, it is a pollutant whose analysis is routinely requested. Although the sulfate contents of the samples show a very heterogeneous distribution, it is seen that there is no problem based on the guide value.

One of the water quality parameters is undoubtedly the metal content of the waters and especially heavy metals are extremely important for health. Heavy metals can enter the waters through natural geological formations (especially from mining areas), as well as, of course, industrial, and anthropogenic activities. The metals given in Table 1 can be classified into 3 categories: minor elements, trace metals, and heavy metals. In this sense, Na, K, Ca, and Mg can be categorized as minor elements, Fe, Cu, Mn, and Zn as trace metals, and Al, Co, Ni, Pb, Cd, and Cr as heavy metals.

Na, K, Ca, and Mg, which are classified as minor elements, are also known as mineral elements and must be taken into the body regularly every day through a certain amount of water and other nutrients. However, excess of these minerals may not be healthy for the body. In drinking water, 200 mg/L Na is accepted as the upper limit. The water samples examined in this study show a Na distribution between 3.4–16.6 mg/L. Therefore, there is no danger for Na. No threshold values are specified in the guidelines for K, Ca, and Mg in waters. However, as the amount of Ca and Mg increases, the water becomes hard and undrinkable. While the K contents of the waters are homogeneously distributed between 5–25 mg/L, only the w-15 coded sample has a relatively high K of 48.8 mg/L. The Ca concentrations of the samples are distributed relatively homogeneously, like K. With a concentration of 138.3 mg/L, the sample w-15 has the highest Ca content.

Fe, Cu, and Zn, which are in the trace element class, are generally at normal levels in the samples examined. The upper limit of Fe is reported as 0.2 mg/L in the TS266 standard, and 0.3 mg/L in EPA and WHO. 1.01 mg/L Fe was detected in the w-2 coded sample and 0.51 mg/L Fe was detected in the w-12 coded sample. If 0.5 mg/L is taken as the threshold value, it would be appropriate to reanalyze these two samples. Zn values of 5 mg/L according to EPA and 4 mg/L according to WHO is reported as threshold values for waters. Among the samples, the w-1 coded sample has the highest Zn value with 0.29 mg/L. As a result, there is no problem for Zn. The standard values are given in Table 2 generally indicate 2 mg/L for Cu. While the Cu contents of the samples are generally between 0.008–0.023 mg/L, the w-12 coded sample contains 0.05 mg/L Cu (Fig. 2). However, no value exceeds the declared limit value.

WHO reports a 0.1 mg/L limit value for Al in drinking water. However, the limit value in other standards (Table 2) is 0.2 mg/L. When the samples are evaluated according to the WHO critical value, there are three samples exceeding 0.1 mg/L (Fig. 3).

While Co and Cr, which are classified as heavy metals in water, could not be detected in any sample, Mn, Ni, and Cd were detected in only one sample each. According to the WHO guideline values, Mn, Ni, and Cd in waters should be at maximum 0.5 mg/L, 0.07 mg/L, and 0.005 mg/L limit values, respectively. The w-15 coded sample contains 0.03 mg/L Mn, the w-12 coded sample contains 0.02 mg/L Ni, and the w-13 coded sample contains 0.008 mg/L Cd. Although the w-13 coded sample seems to be troublesome in terms of Cd, this sample needs to be analyzed again.

For Pb, WHO and other standards report a limit value of 0.01 mg/L. When the Pb distributions of the samples are examined in Fig. 2, it is seen that lead can be detected in only four samples, but these values are above the guide value. The w-13 coded sample exceeds the guide value by 15 times with a Pb content of 0.15 mg/L. It is interesting that Pb, which could not be detected in many samples, was detected above the guide value in 4 samples. Since these values are instantaneous values measured for a single time, a more detailed examination should be made by resampling.

Also, the chemical classification of the water samples from the study area was conducted using a Piper diagram (Fig. 4). All of the samples except one (w-186) have fallen into region 5 in the Piper diagram and these waters are in the class of $CaCO_3$ and $MgCO_3$ waters [21]. In the case of w-186 falls to region 9 in the Piper diagram and is in the class mixed water. This data shows compatibility with the geological structure of the region.

Table 2. Comparison of drinking water quality standards (mg/L)

Parameter	RWIHC (2005)	TS266 (2005)	WHO (2017)	EPA (2002)	EC (1998)
pH	6.5–9.5	6.5–9.5	6.5–8.5	6.5–8.5	6.5–9.5
EC	–	2500	2500	–	2500
NO_2^-	–	0.5	3	–	0.5
NO_3^-	50	50	50	45	50
SO_4^{2-}	250	250	250	250	250
NH_4^+	0.5	0.5	1.5	–	0.5
Hardness (°F)	–	50	20	–	–
TDS	–	–	600	500	–
Cl^-	250	250	250	250	250
Na	200	200	200	–	200
K	–	–	–	–	–
Ca	–	–	–	–	–
Mg	–	–	–	–	–
Fe	0.2	0.2	0.3	0.3	0.2
Cu	2	2	2	1	2
Mn	0.05	0.05	0.5	0.05	0.05
Zn	–	–	4	5	–
Cd	0.005	0.005	0.005	0.005	0.005
Al	0.2	0.2	0.1	0.2	0.2
Pb	0.01	0.01	0.01	0.015	0.01
Ni	–	–	0.07	–	–
Cr (Total)	0.05	0.05	0.05	1	0.05

RWIHC: Regulation on Water Intended for Human Consumption (Turkish Standard)
TS: Turkish Standards
WHO: World Health Organization
EPA: Environmental Protection Agency
EC: European Commission

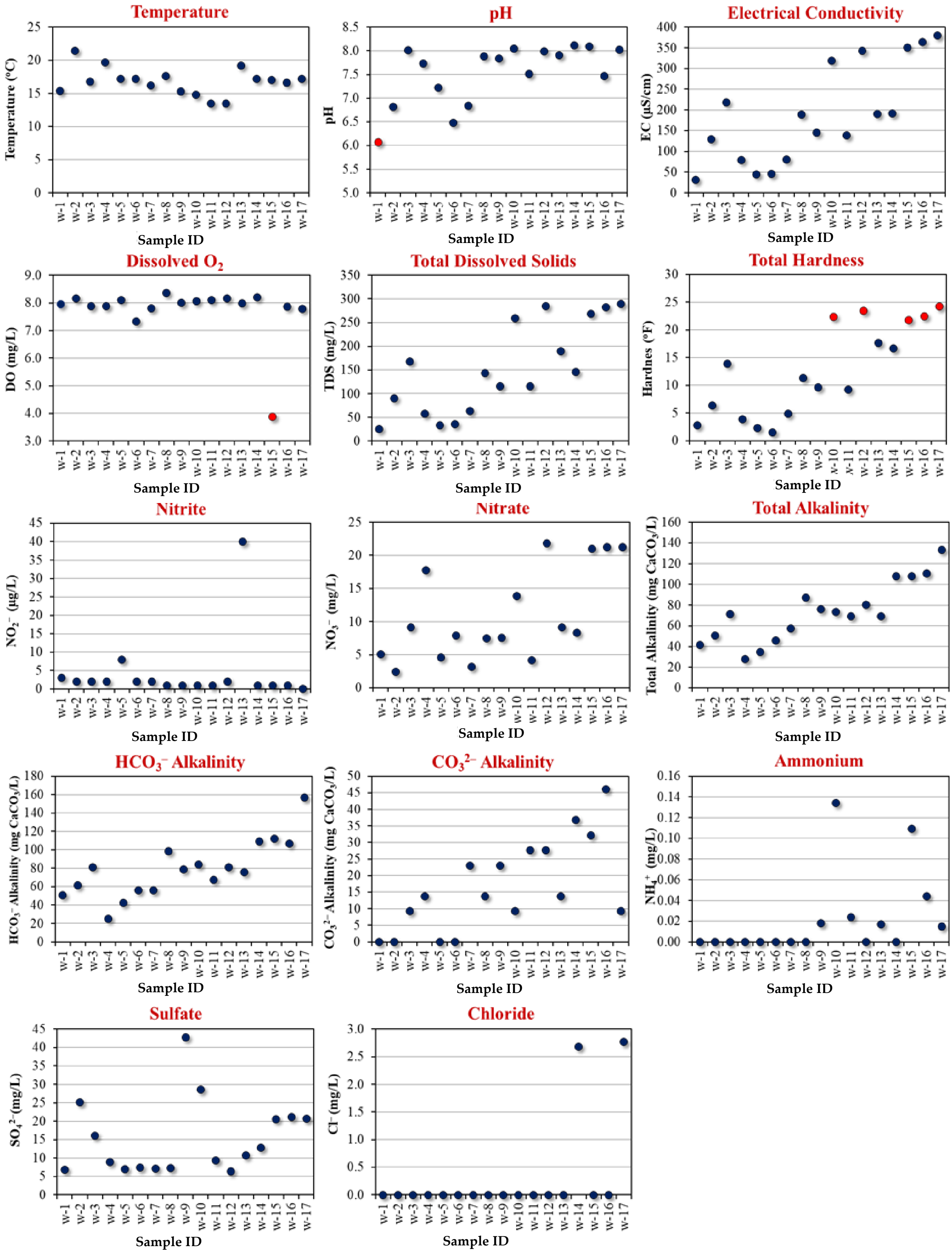

Figure 2. Distributions of some anions and physicochemical contents of the water samples for water quality

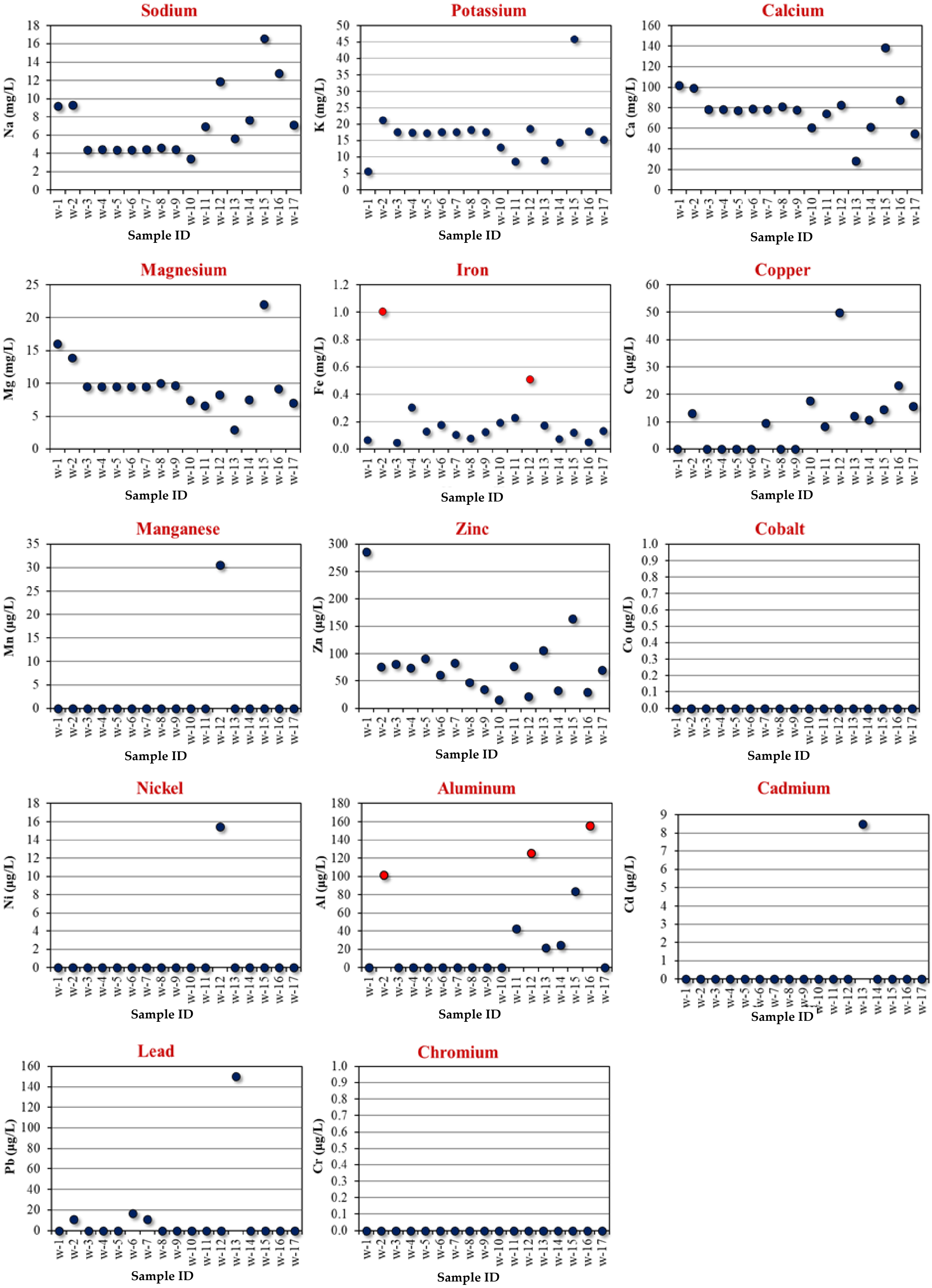

Figure 3. Some minor-trace element and heavy metal distributions in the water samples for water quality

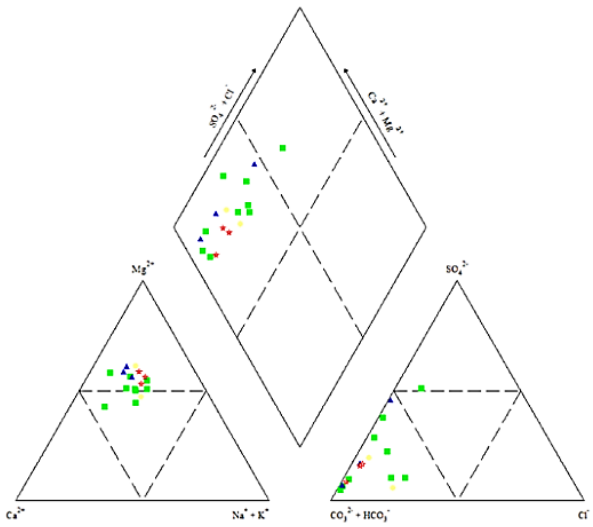

Figure 4. Piper diagram of the Büyük Çit Stream

5. Conclusion

In this study, analyses of some physicochemical water quality parameters were carried out by taking samples from the parts and branches of the Büyük Çit river, which is located within the borders of Gümüşhane province, along the valley. This study was designed to examine the effects of settlement areas in the valley, natural geological formations, and mining activities in the region on the water quality of the Büyük Çit river and to determine whether this river has a potable water potential in the future. In this study, only one sampling was made, revealing the instantaneous situation of the Büyük Çit river, and shedding light on new studies to be planned in the future.

Increasing pollution of clean drinking water sources points to a big problem in the future. For this reason, investigating the potential of uncontaminated surface waters as drinking water draws attention as an important study area.

As a result of the analyzes made, it was concluded that although some samples taken along the valley exceeded the guideline values in terms of some parameters, the Büyük Çit stream may have the potential to be used as drinking water in the future. It is thought that other additional studies to be made with these instantaneous values will gain more meaning. In addition, the microbiological evaluation of the examined waters, apart from the parameters applied in this study, will help to reach a healthier decision.

Acknowledgments:

This research was supported by Scientific Research Projects of TÜBİTAK under Grant Number:115Y146.

References

[1] B. Hölting and W. G. Coldewey, Hydrogeology, Springer, 2019.

[2] A. Vural and A. Çiftçi, An analysis of some concepts related to environmental issues and development by N-gram, Euroasia J Soc Sci Hum, 8, 2021, 18–28.

[3] A. Sungur, A. Vural, A. Gundogdu, and M. Soylak, Effect of antimonite mineralization area on heavy metal contents and geochemical fractions of agricultural soils in Gümüşhane Province, Türkiye, Catena, 184, 2020, 104255

[4] A. Sungur, A. Vural, A. Gündoğdu, and M. Soylak, Gümüştuğ Köyü (Torul-Gümüşhane) Tarım Topraklarında Manganın Jeokimyasal Karakterizasyonu, International Trace Analysis Congress (ITAC 2018/ES-AN 2018), 2018, 231.

[5] A. Vural, Trace/heavy metal accumulation in soil and in the shoots of acacia tree, Gümüşhane-Türkiye, Bull Miner Res Explor,148, 2014, 85–106.

[6] A. Vural and A. Gündoğdu, High-fluoride risk and toxicity in surface waters in Gümüşhane-Gökdere valley drainage network (NE Türkiye), J Eng Res Appl Sci, 9, 2020, 1323–1334.

[7] M. N. Ural, A. Vural, and A. Çiftçi, N-Gram Analysis of Nuclear and Alternative Energy Sources and Historical and Political Course, Euroasia Summit Congress on Scientific Researches and Recent Trend-6, 2020, 582–586.

[8] Y. Yılmaz, Petrology and structure of the Gümüşhane granite and surrounding rocks, NE Anatolia, 1972.

[9] Ü. Ağar, Geology of Demirözü (Bayburt) and Köse (Kelkit), KTU, Trabzon, 1977.

[10] S. Pelin, Alucra (Giresun) Güneydoğu yöresinin petrol olanaklan bakımından jeolojik incelemesi. Trabzon: Karadeniz Teknik Üniversitesi Yayını, 87, 1977.

[11] M. Arslan and I. Aliyazicioglu, Geochemical and petrological characteristics of the Kale (Gümüşhane) volcanic rocks: Implications for the Eocene evolution of eastern Pontide arc volcanism, northeast Türkiye, Int Geol Rev, 43, 2001, 595–610, 2001.

[12] S. Tokel, Stratigraphical and volcanic history of Gümüşhane region, 1972.

[13] A. Vural and A. Kaygusuz, Geochronology, petrogenesis and tectonic importance of Eocene I-type magmatism in the Eastern Pontides, NE Türkiye, Arab J Geosci, 14, 2021, 467.

[14] F. Sipahi, Ç. S. Eker, İ. Akpınar, M. A. Gücer, A. Vural, A. Kaygusuz, T. Aydurmuş, Eocene magmatism and associated Fe-Cu mineralization in northeastern Türkiye: a case study of the Karadağ skarn, Int Geol Rev, 2021, 1–26.

[15] APHA, Standard Methods For the Examination of Water and Wastewater, Part 2000 Physical & Aggregate Properties, Alkalinity 2320 B. Titration Method, (23. edition), 2017, USA, Washington.

[16] APHA, Standard Methods For the Examination of Water and Wastewater, Part 2000 Hardness 2340 C. EDTA Titrimetrik Method, (23. edition), Washington, 2017, USA.

[17] APHA, Standard Methods For the Examination of Water and Wastewater, Part 4000 Inorganic Nonmetallic Constituents, 4500-NO2- B. Colorimetric Method, (23. edition), 2017, USA, Washington.

[18] EPA, EPA Method 375.4, 1978, Methods for the Chemical Analysis of Water and Wastes (MCAWW), EPA/600/4–79/020), 1978.

[19] APHA, Standard Methods For the Examination of Water and Wastewater, Part 1000 Introduction, 1030 E Checking Analyses Correctess, 1. Anion-Cation Balance, (23. Edition), 2017, USA, Washington.

[20] İ. H. Güven, Doğu Pontidlerin 1/100.000 Ölçekli Kompilasyonu. Ankara: MTA Genel Müdürlüğü, 1993.

[21] A. M. Piper, A graphic procedure in the geochemical interpretation of water-analyses, Transactions, Amer Geophy Union, 25, 1944, 914, 1944.