



## The Heavy Metals and Minor Elements Effects of Mineralization and Alteration Areas with Buried Ore Deposits Potential on the Surface Waters

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(Alınış / Received: 07.04.2022, Kabul / Accepted: 19.06.2022, Online Yayınlanma / Published Online: 30.06.2022)

### Keywords

Heavy metal contamination,  
Alteration area,  
Surface water,  
Gümüşhane

**Abstract:** This paper aims to elucidate the potential environmental risks associated with ore deposits and alteration areas related to these mineralizations by quantifying contamination in stream waters. For this purposes, 23 surface water samples were collected from the streams and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for heavy metals and minor elements. Concentrations of heavy metals in surface waters reached 160 µg/L for Al, 288.6 µg/L for Mn, 13.2 mg/L for Fe, 58.2 µg/L for Co, 164.4 µg/L for Zn, 100.2 µg/L for Cu, 2.4 mg/L for Sr, 77.0 µg/L for Ba, 96.7 µg/L for Pb, 115.4 µg/L for V, 101.5 mg/L for Ca, 15.0 mg/L for Mg, 24.4 µg/L for Ni, and 16.0 mg/L for Na. In addition, high arsenic, cadmium values (137.9 µg/L for As, 6.7 µg/L for Cd), were detected in some locations. Some other heavy metals are below the limit of quantification (LOQ). At the end of the study, a heavy metal pollution risk has been reached in the surface waters examined from the instant data obtained, caused by various anthropogenic, agricultural and industrial activities, as well as alteration areas with buried ore deposit potential and ore deposit areas. More detailed studies should be carried out by increasing the number and period of sampling in such areas and precautions should be taken against possible heavy metal contamination risks.

### 1. Introduction

It is estimated that the water in the world water cycle is  $1.380000 \cdot 10^{12} m^3$  and 3/4 of the earth's surface is covered with water. Despite the abundance of water, most of it is salty and only 2.5% is freshwater [1]. A very small portion of freshwater is drinkable. 68.7% of these waters are in the form of ice and snow. 1.2% is in lakes, rivers, wetlands and polar regions and only 30.1% is in the form of fresh groundwater [1]. Especially with the rapid population growth and industrialization of the world, water resources (especially freshwater resources), today, are one of the

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most vital natural resources for all countries. Water management policies are now at the top of the priorities of all countries. In the past, uncontrolled/unconscious industrialization moves have caused human-induced pollution of water resources over time. Now, nowadays water contamination/pollution is a major problem for all countries related to the economic/industrial growth of any country. Water pollution is not only caused by anthropogenic factors, but also by mixing trace elements released into the environment through natural processes, water pollution can occur depending on natural processes [2].

Contrary to popular misconception, Türkiye is not a water-rich country, on the contrary, it is among the countries in the middle risk group suffering from water stress [3]. Considering the amount of usable water per capita per year (1400 m<sup>3</sup> according to 2017 data), Türkiye is in the class of countries facing water scarcity [4]. It is predicted that Türkiye's population will reach 100 million in 2040, and the annual amount of usable water per person will decrease to 1120m<sup>3</sup>. Therefore, the sustainable management of Türkiye's water resources is a national issue that is the responsibility of all sectors, both on the basis of society, the public and the individual. Based on the strategic importance of water for Türkiye, a Climate Change Strategy document has been prepared by the Government of Türkiye. In addition, the National Climate Change Adaptation Strategy and Action Plan were prepared by the Ministry of Environment and Urbanization and the targets in water resources management were set. In addition, the name of the ministry was changed to the Minister of Environment, Urbanization and Climate Change on October 29, 2021.

When evaluated in terms of water resources, Gümüşhane has a potential above Türkiye's average. In addition to large rivers and streams (Harşit River, Çitderesi River etc.) there are lakes, albeit on a small scale. Although it has decreased in recent years, the amount of precipitation it receives in the form of snow is at a significant level, and snow can remain until the end of June and July in the high areas. This ensures that the creeks of Gümüşhane are flowing in almost every season. The region is also in an important metallogenic belt and is home to many mineral deposits such as copper, lead, silver, gold etc. [5,6]. Although mineral deposits are important raw materials in the development of countries, they also bring some environmental problems. Such environmental problems bring the risk of pollution to the soil, plants and especially the waters of the region [7,8].

The Arzular-Kabaköy, Kaletaş, Dölek and its surrounding areas are situated at the east of the Gümüşhane city (NE Blacksea Region) and these areas host either mineral deposits (Arzular-Kabaköy gold deposit, Kaletaş gold mineralization) or hydrothermal alteration areas with buried mineralization potential. There are many large (Arzular Stream, Kabaköy Stream, etc.) and small streams (Yoncalık creek, Kalyaz creek, Yetirmez Creek, etc.) in the area. City, town and especially village residents mostly get their drinking water from these streams. These streams are also used by the local people for irrigation activities for agricultural purposes. Considering the litho-chemical, geological and metallogenic characteristics of the region, the surface waters in the area have the risk of heavy metal pollution/contamination. The aim of the study is to investigate the heavy metal pollution risk of the streams and creeks in Arzular-Kabaköy, Kaletaş, Dölek and their surroundings and to determine the water quality of the surface waters.

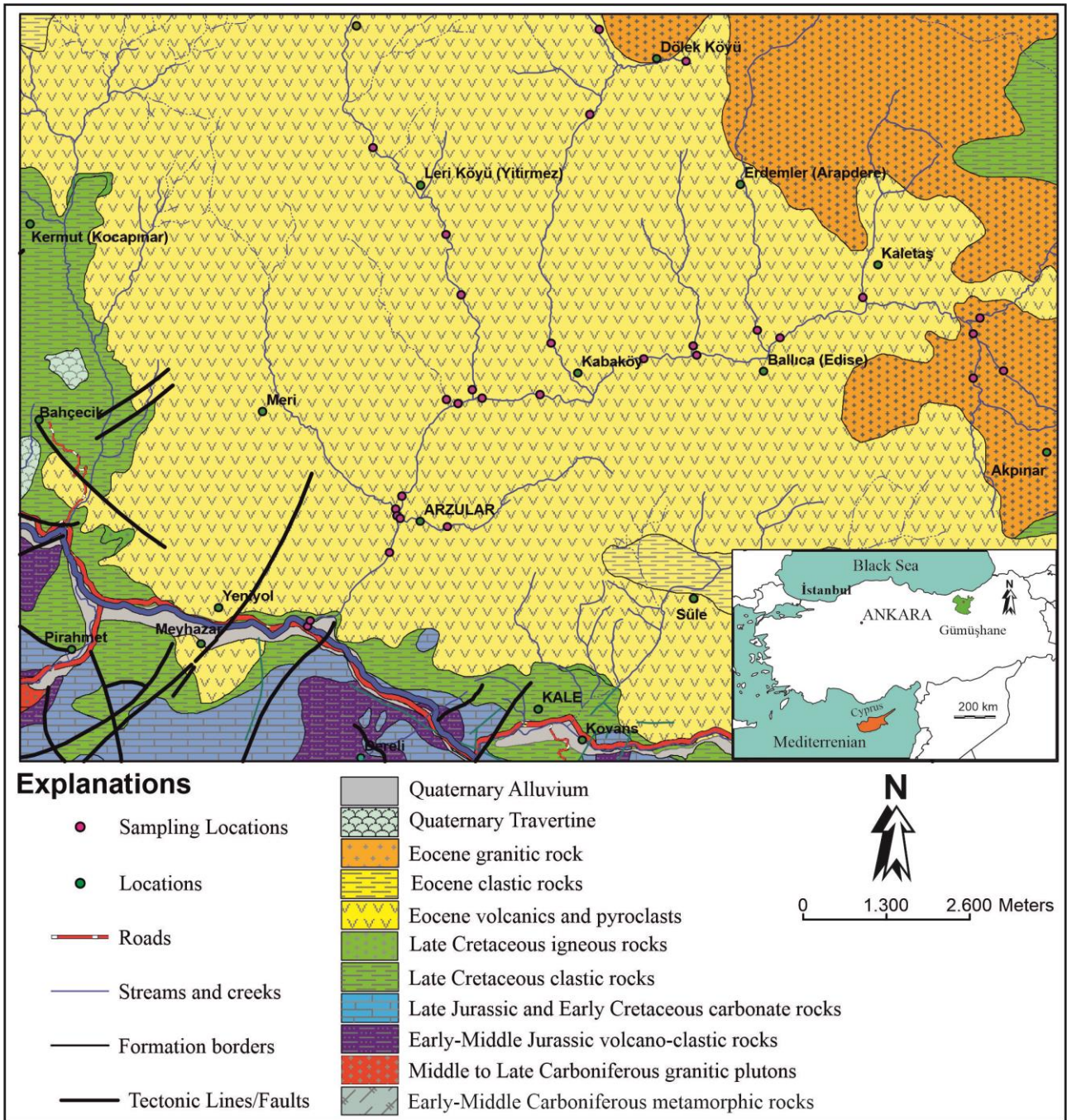


Figure 1. Geological and location map of the study area (After [9])

## 2. Material and Method

### 2.1. Geological and Hydrological/Hydrogeological Features of The Study Area

The study area covering Arzular-Kabaköy, Kaletaş, Dölek and its vicinity is located in the southern zone of the Black Sea Tectonic Unit (Fig. 1). In the Gümüşhane province, it can be observed all stratigraphic units of the region. If the general geology of the site is mentioned, the basement geological unit of the region consists of pre-Jurassic (Early-Middle Carboniferous) metamorphic rocks [10] and middle-late Carboniferous unmetamorphosed granitoids [11,12]. These basement units are unconformably overlain by an early to middle Jurassic volcani-clastic unit which passes upward to the late Jurassic and early Cretaceous carbonate rocks. In the area, late Cretaceous clastic unit begins with sandy limestones at the bottom and grades upward to red pelagic limestone and then to a turbiditic series which conformably overlies late Jurassic and early Cretaceous carbonates. All these units -outside of the study area, in Torul/Gümüşhane and its near vicinity- were cross cut by late Cretaceous intrusions [13] and were cut and cover by late Cretaceous volcanic rocks [14]. The Eocene volcanic and volcani-clastic rocks overlie the late Cretaceous volcanic and/or sedimentary rocks with an angular unconformity [15], and intruded by calc-

alkaline granitoids of same age [16]. The youngest units in the region are actual travertine occurrences [17], talus and alluvium.

All lithological units belonging to the geology of the region are observed in the area that is the subject of this study on the risks of heavy metal and/or minor elements on surface waters (Fig. 1). Pre-Jurassic metamorphic rocks are observed in the southern parts of the study area, while unmetamorphosed granitoids crop out in the southwestern part of the study area. The Early to middle Jurassic volcani-clastic unit, late Jurassic and early Cretaceous carbonate rocks, and late Cretaceous clastic crop out to the west and southwest of the study area.

In the study area, dominantly Eocene volcani-clastic rocks outcrop in the vast majority of the area and these rocks undergone intense hydrothermal alteration and weathering and host some epithermal ore deposits such as Arzular gold deposits, Kaletaş gold mineralizations. Actual travertine occurrences are also observed around Bahçecik and Tekke villages in the area [17], and there are alluviums in the stream banks.

## 2.2. Sampling, Reagents-Solutions and Analysis

For elucidating the potential environmental risks associated with mineralization and alteration areas with buried ore deposits potential by quantifying the heavy metal contamination in stream waters in the areas, 23 surface water samples were collected from the streams (Fig. 1) in September 2016, and analyzed for some heavy metals and minor elements by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Agilent 7700e model ICP-MS, Santa Clara, US) at Gümüşhane University Central Research Laboratory, Gümüşhane, Turkey. Water pH measurements were also performed in the area during sampling.

Surface water samples were taken with 500 mL PP bottles. Prior to sampling, the bottles were thoroughly rinsed with tap water, washed with 1:10 dilute nitric acid, then again well washed with tap water, then ultrapure water, and finally labeled. As soon as water samples were taken for metal analysis, they were acidified with 0.5 mL of ultrapure concentrated HNO<sub>3</sub>. After the water samples were brought to the laboratory during the day, they were filtered through a vacuum filtration device with a 0.45 µm nitrocellulose membrane. The clear water samples were then analyzed in terms of some heavy metal/minor element contents using the ICP-MS.

## 2.3. Quality Assurance

Both accuracy tests were made with some parameters of the measurements made in ICP-MS and the performance of the system was tested. First, the calibration method used for measurements on the device was the internal standard method to eliminate possible interference [18]. <sup>45</sup>Sc, <sup>89</sup>Y, <sup>185</sup>Re, <sup>209</sup>Bi isotopes were used as the internal standards.

Table 1 reflects some analytical performance criteria (RSD, LOD and LOQ) of the ICP-MS instrument used in metal measurements. The limit of detection (LOD), expressed as the smallest signal (or concentration) that the relevant method/device can detect for each metal, was calculated by taking 3 times the standard deviation of the results obtained from the measurement of a series of blank solutions (approximately 20). Similarly, the limit of quantification (LOQ), which is the lowest signal or concentration quantitatively sensed by the instrument/method, is 10 times the standard deviation of the results from blank solutions. Relative standard deviation (RSD), the most common indicator of the repeatability, was determined by dividing the standard deviation of the results obtained from 20 repeated measurements of a series of multi-element standard solutions at very low concentration by the mean value. This ratio was multiplied by 100 and the results were converted to the percent relative standard deviation (RSD%). The accuracy of the method has been proven in two ways. The first is the spiked/recovery tests, and the other is the certified reference material (CRM-TMDW-A Trace Metals in Drinking Water) analysis. As a result of both tests, very satisfactory results were obtained with recovery values between 95–105% [19,20].

**Table 1. Analytical performance of the device, Agilent 7700x ICP-MS**

	1	2	3	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Parameter	pH	Ca	Mg	Na	K	Sr	Fe	Ba	Zn	Cu	Al	Mn	Cd	Co	Ni	Pb	Cr	V	As	Rb
RSD (%)	0.02	3.1	2.8	3.0	3.6	1.2	3.4	2.6	2.0	2.6	4.1	2.2	3.0	3.4	2.3	3.3	3.8	4.2	3.8	2.8
LOD (µg/L)	-	2.2	1.4	3.2	2.2	2.9	3.1	2.5	2.7	2.5	3.5	3.1	2.0	3.0	3.1	3.0	3.0	2.7	2.1	2.7
LOQ (µg/L)	-	7.3	4.7	10.7	7.3	9.7	10.3	8.3	9.0	8.3	11.7	10.3	6.7	10.0	10.3	10.0	10.0	9.0	7.0	9.0

## 3. Result and Discussion



Descriptive statistics parameters for pH values and some minor-trace elements and heavy metals contents of the streams in the study area are given in Table 2. Figure 2 and Figure 3 also reflect the distributions of these contents of a total of 23 water samples. In addition, dot distribution maps plotted for the same parameters can be seen in Figure 4. Since some elements are detected only in limited locations above the detection limit (such as, Cr, Co, Cd), and some (Na, Mg etc.) are abundant in nature under normal conditions, their point distribution maps have also been created (Figure 4).

Interestingly, the Ca, Mg and Na contents of five samples between w-28 and w-32 coded samples are at very low levels (Figures 2 and 4). These samples were taken from the small branches of the main stream and were probably fed by rain water. Therefore, their effects on distribution are also great. Since the levels of some metals were below the LOQ value, these metals could be detected in a limited number of samples. In this respect, when Table 2 is examined, Cr could be determined in only two samples, and Cd and Co in three samples. The fact that domestic wastes (batteries, parts of some household appliances and electronic devices, etc.) were occasionally encountered at the points where these samples were taken indicate anthropogenic pollution at these points.

It has been found that the pH values of the waters vary between 7.02 to 8.68 (Table 1 and Figures 2 and 4). According to these values, waters are between slightly neutral and generally basic but some of them are near neutral to acidic in especially intense altered areas such as Leriköy, northwest of Kabaköy, northwest of Akpınar etc. (Figure 1). It has been observed that pH values are more alkaline, especially in areas exposed to anthropogenic effects. Probably due to detergent-based household waste.

It has been observed that Mn and Fe concentrations are high especially in two samples coded w-34 and w-35 in the areas close to granitic intrusions in the northeast of the field (Figure 2). Considering that the mobilities of Mn and Fe are close to each other, the observed results met the expectations (Figure 4). Cu concentrations were observed at high values around Dölek village, around Arzular village and northwest of Akpınar village, where intense alteration development occurs. Zn values also show a similar pattern with Cu because they have similar physicochemical properties. While the Al values of the samples are generally below 40 µg/L, the three samples coded w-35, w-36 and w-36 have high contents with values of 109.4 µg/L, 160.0 µg/L and 117.4 µg/L, respectively. Vanadium (V) could be determined quantitatively in 14 samples. While the results were below 20 mg in most samples, 115.4 mg V was detected in the w-44 coded sample, 63.4 in the w-50 coded sample, and 47.5 mg V in the w-45 coded sample. Although there is no remarkable situation in other metal contents, the results show a very heterogeneous distribution. It is expected that the clarification of the origins of these anomalies will be clarified with the completion of the other parts of the study (periodical water results, stream sediment and soil data)

The metal contents of the studied water samples were compared with the EPA's guidelines for surface waters. Table 3 summarizes these guideline values. The red dots on the graphs represent samples that exceed the EPA-reported limit values (Figures 2 and 3). The surface water's pH values are within the standards but some HMTEs were above the EPA's standards. Mn values were found to be higher than EPA standards, especially at Dölek village alteration zone. In addition to the two samples with high Mn content, w-34 and w-35, the other two samples, w-25 and w-36, are slightly above the guideline value. As to Fe, those values are generally high in whole area. In terms of Fe content, while many samples are outside of the A1 class surface water quality, two samples coded w-34 and w-35 have extremely high Fe content with 13.15 mg/L and 13.14 mg/L contents, respectively. High Mn and Fe values are associated with the intense hydrothermal alteration of the region, and since Mn and Fe are mobile elements, they can easily pass into water at surface conditions and at appropriate pH values. The stream from which these samples were taken should be monitored especially in terms of Mn and Fe.

w-34 and w-35 coded samples have high values for Co metal, which can be detected only in three samples. While Ni can be detected at four sample points similar to Co, the w-34 and w-35 coded samples have the highest value here too. These values slightly exceed the EPA's guidelines for drinking water. The fact that household wastes (battery, electronic device fragments and small household appliances, etc.) are encountered at sampling points suggest that high Ni and Co values are probably anthropogenic. EPA reports the limit value for Ba content of A1 class surface waters as 0.1 mg/L. The Ba contents determined in twenty samples have a very heterogeneous distribution as seen in Figure 2 and Figure 4, but no sample exceeds the guide value.

Cd values were also determined at only three points. These values were close to the upper limit of the standard values.

Perhaps the most critical values in this study are Pb values. Pb values in many samples were above the LOQ, but the content of eight samples exceeded the EPA-reported threshold of 0.05 mg/L. Wastes from various factories, exhaust gases, pollution caused by mining operations and of course Pb pollution caused by natural geological formations cause significant health problems in waters.

Arsenic detected at seven points in total is generally below 20 mg/L. However, the w-28 coded sample with an As value of 137.9 mg/L far exceeds the 50 mg/L limit value reported by the EPA. Known as the "king of poisons", arsenic enters the food chain through many activities. As can enter the waters with many anthropogenic activities, geological formation and mining activities also trigger the As level in the water. It is seen that high As values are mostly close to the region where volcanic rocks and granitic rocks cut them. It is thought that the hydrothermal alterations developed due to granitic intrusions in these regions increase the As concentration in these hydrothermal alteration zones, and therefore the As values in the waters interacting with these units also increases (Figure 4).

Minor elements such as Ca, Mg, Na and K, which are more abundant in waters (Figures 2 and 4) and do not pose much threat to health compared to heavy metals and trace elements, are also extremely important especially for the sustainability of aquatic life. However, although they are important for health, very high amounts of them are still undesirable. In this respect, the determination of minor elements, in other words mineral elements, is also very important. The content of minor elements in water were determined within the limit values of EPA's surface water standards.

**Table 2. Descriptive statistics of the surface waters and analytical performance criteria of the analysis method**

Parameter	1	2	3	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	mg/L							µg/L												
	pH	Ca	Mg	Na	K	Sr	Fe	Ba	Zn	Cu	Al	Mn	Cd	Co	Ni	Pb	Cr	V	As	Rb
<b>Mean</b>	8.02	54.1	7.0	7.4	10.1	1.2	1.6	30.5	65.5	43.0	47.2	64.9	6.6	43.1	17.3	50.2	20.7	26.4	27.8	12.1
<b>Median</b>	8.07	57.4	6.9	6.9	12.1	1.1	0.4	26.2	50.1	32.5	25.3	24.0	6.6	57.4	17.4	45.4	20.7	13.5	7.8	11.4
<b>Std deviation</b>	0.43	33.5	4.9	4.0	4.9	0.5	3.7	18.1	34.6	24.0	48.3	99.7	0.0	25.5	17.3	32.8	13.4	30.1	48.6	2.1
<b>Min.</b>	7.02	1.4	0.1	0.1	0.4	0.7	0.02	8.3	22.6	13.9	12.2	10.9	6.6	13.6	10.2	10.1	11.2	9.3	7.2	9.9
<b>Max.</b>	8.68	101.5	15.0	16.0	20.3	2.4	13.1	77.0	164.4	100.2	160.0	288.6	6.7	58.2	24.4	96.7	30.2	115.4	137.9	16.1
<b>Number</b>	20	23	23	20	23	23	23	20	23	23	13	13	3	3	4	16	2	14	7	7

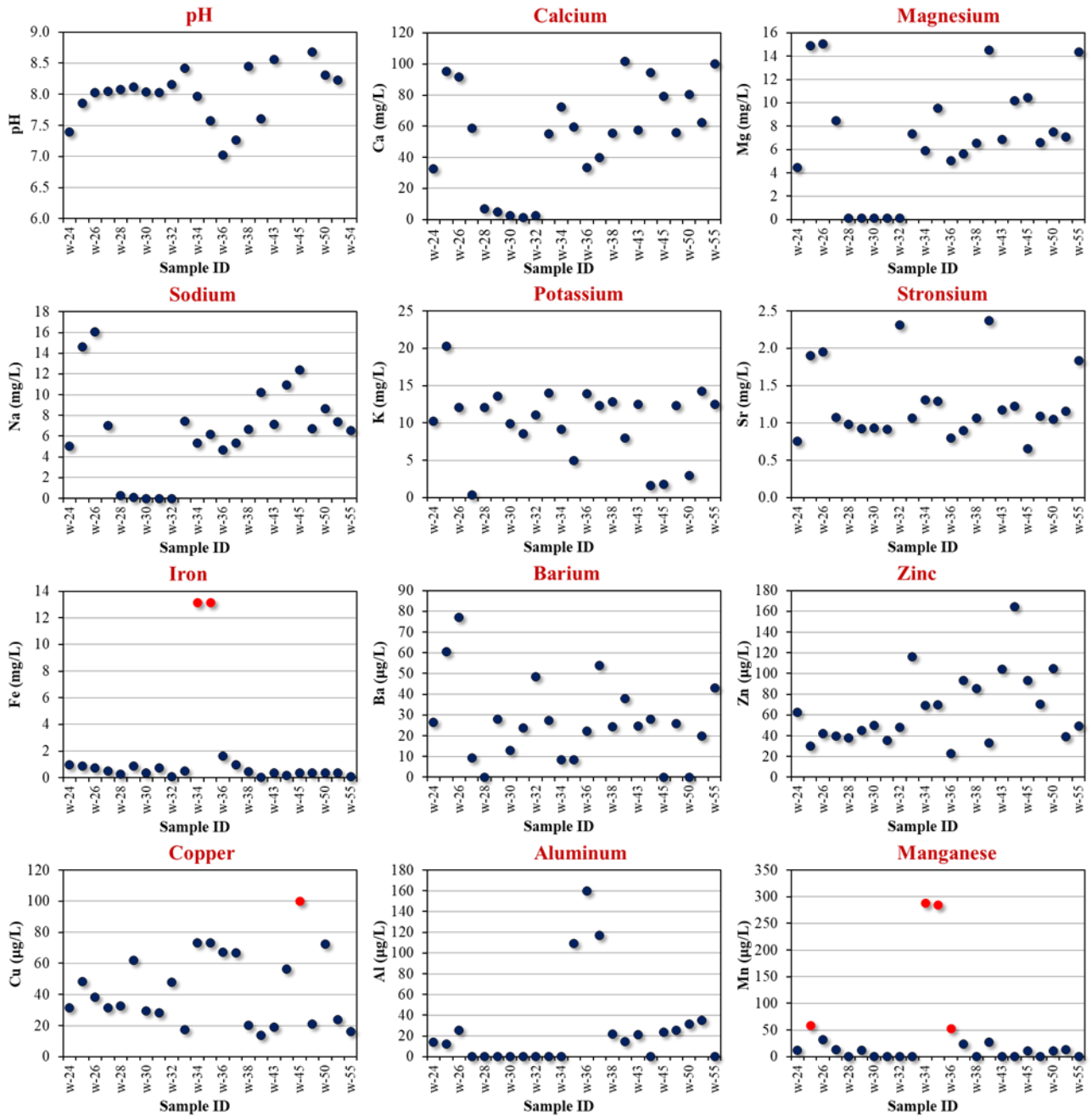


Figure 2. Distributions of pH and metal contents of the water samples

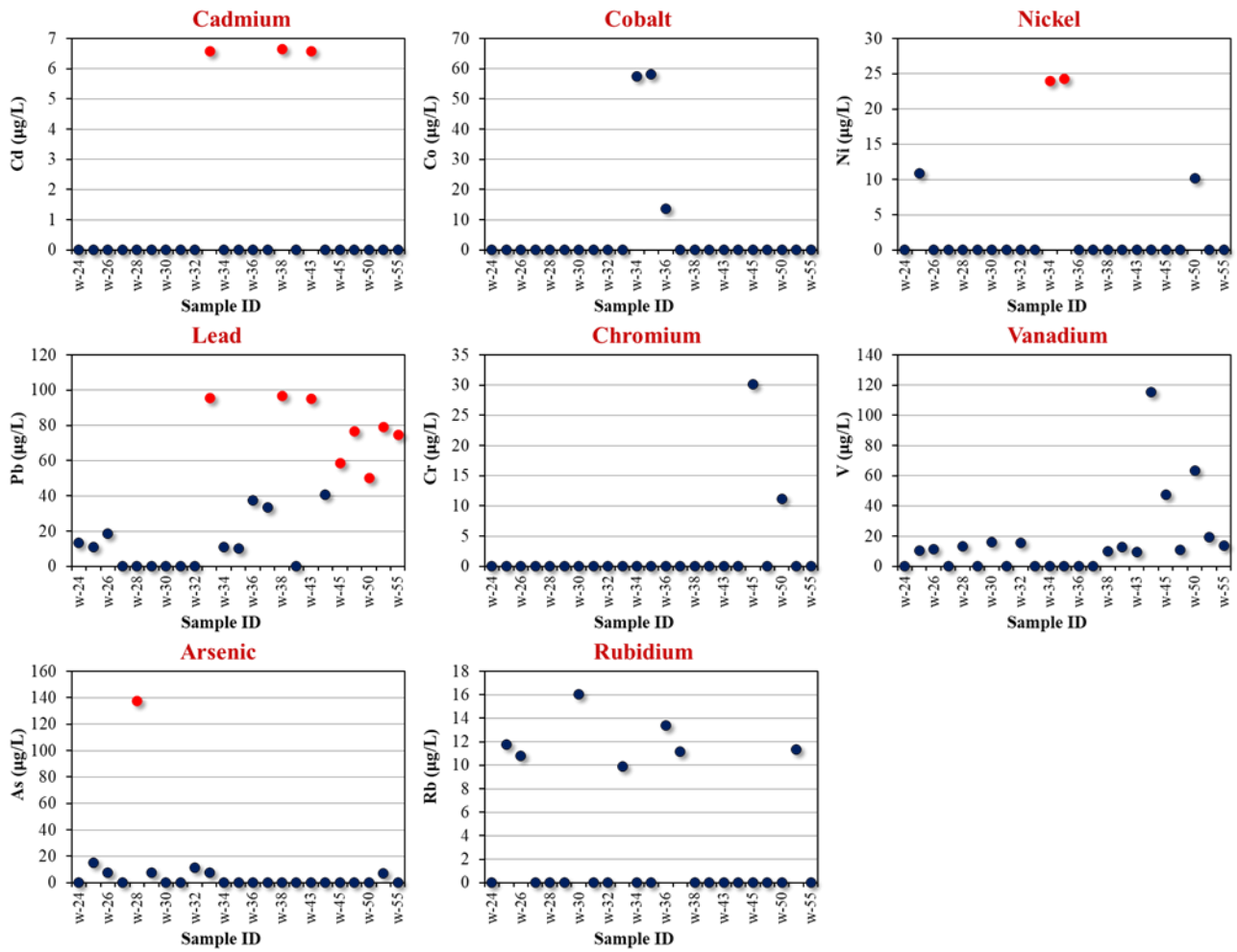


Figure 3. Distributions of metal contents of the water samples



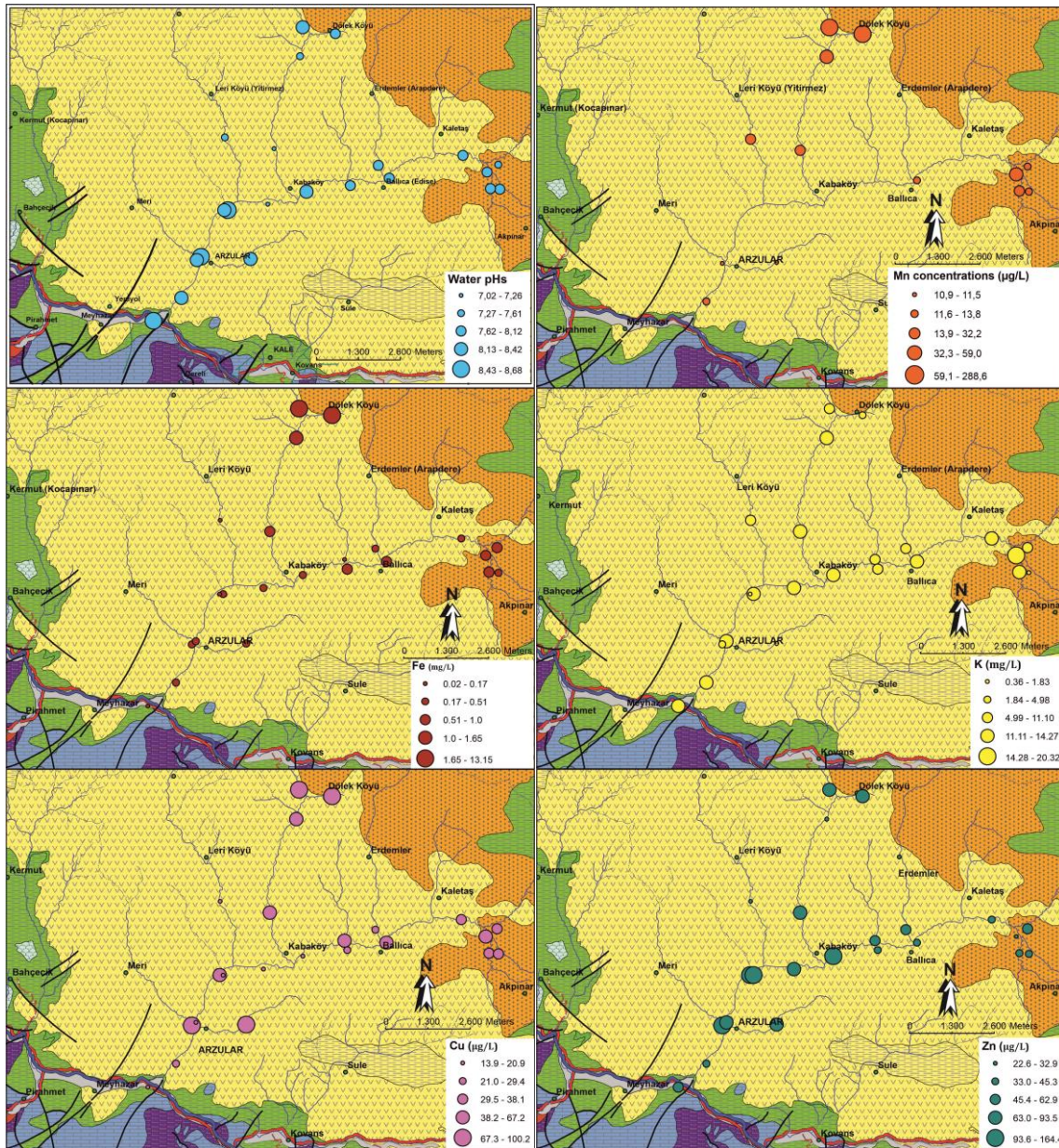


Figure 4. Dot distribution map of HMTEs, minor elements and pH values of the study area streams (Explanations of the geological map are given in Fig. 1)





Figure 4 (Continue) (Explanations of the geological map are given in Fig. 1)



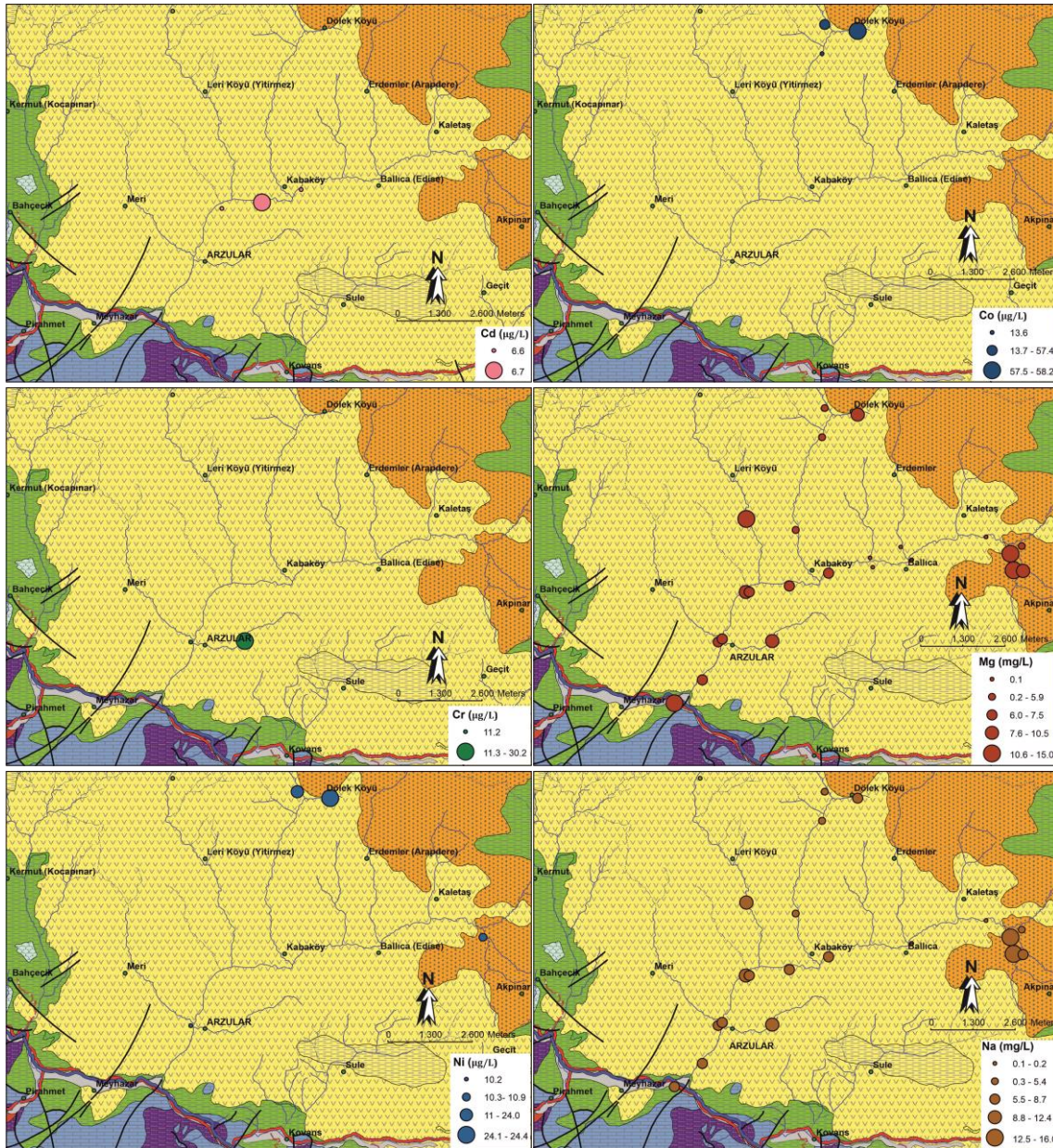


Figure 4 (Continue) (Explanations of the geological map are given in Fig. 1)

Table 3. EPA Water Quality Standards for some elements

Element Unit	Drinking water	Surface water		
		A1 class	A2 class	A3 class
pH	6.5 – 9.0	5.5 – 8.5	5.5 – 9.0	5.5 – 9.0
Al $\mu\text{g/L}$	200	-	-	-
As $\text{mg/L}$		0.05	0.05	0.1
Ba $\text{mg/L}$		0.1	1	1
Cd $\text{mg/L}$		0.005	0.005	0.005
Ca $\text{mg/L}$		-	-	-
Cr $\text{mg/L}$		0.05	0.05	0.05
Co $\text{mg/L}$		-	-	-
Cu $\text{mg/L}$		0.05	0.1	1
Fe $\text{mg/L}$	0.2	0.2	2	2
Pb $\text{mg/L}$		0.05	0.05	0.05
Mg $\text{mg/L}$		-	-	-
Mn $\text{mg/L}$	0.05	0.05	0.3	1
Hg $\mu\text{g/L}$	1	1	1	1

Mo	µg/L	-	-	-	-
Ni	µg/L	20	-	-	-
K	mg/L	-	-	-	-
Se	mg/L	0.01	0.01	0.01	0.01
Na	mg/L	200	-	-	-
Sn	mg/L	-	-	-	-
Zn	mg/L	-	3	5	5

As a result, these findings point out that the surface waters in the Arzular-Kabaköy, Kaletaş, Dölek and its surrounding areas were affected by some HMTEs such as Mn, Fe, Cd, Co, As and Pb. Although there is an anthropogenic effect especially for Ni, Cr, Co, Cd at some points, ore deposit sites and related hydrothermal alteration areas with buried ore deposits potential have been found to cause heavy metal contamination in the surface waters around these environments, therefore, more detailed studies should be done on such fields and necessary precautions should be taken in order to avert the dispersal of contamination sourced those areas.

Studies on water quality parameters and other physical properties in the region are continuing. These data are the first to be obtained, when other data are obtained then they will be evaluated separately in different articles.

### Acknowledgement

This study was supported by TUBITAK (Grant Number: 115Y146).

### Author Contribution

Corresponding author Alaaddin Vural conducted field studies during the data collection process, took part in the analysis and interpretation of the data, and undertook the writing of the article. Ali Gündoğdu both contributed to the field studies and took part in the analysis. Fatih Saka contributed to the field studies. Volkan Numan Bulut took part in the analysis. Selçuk Alemdağ contributed partially to the collection of the samples used in this article from the field. Mustafa Soylak contributed to the evaluation of the analysis data obtained.

### Conflict of Interest

The authors confirm that there is no known conflict of interest or common interest with any institution/organization or person.

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