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The Effect of the Seasons on the Variation of Arsenic, Boron, and Other Parameters in the Waters in Iğdır

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Arsenic,
boron,
electrical conductivity,
toxic elements,
water quality

Abstract: In this study, we investigated and determined the amount of various toxic elements like manganese (Mn), cobalt (Co), nickel (Ni), boron (B), and arsenic (As) in underground drilling and surface natural springs drinking waters in Iğdır province and districts Ararat Mountain side by the ICP- MS technique in dry and rainy months. The several properties of samples of drinking water, such as pH, total dissolved solids (TDS), electrical conductivity (EC), salinity (Sal), Cl^-, NH_4^+, and NO_3^- were measured with the mobile YSI Professional Plus multiparameter. The results of the analysis were compared to the limit values of the World Health Organization (WHO), the American Environmental Protection Agency (EPA), the European Union Standard (Council of the European Union Standards: ECS), and the National Drinking Water Standard (TSE). The mass amount of toxic elements of Mn, Co, Ni, B, and As in the analysis regions for volcanic rocks near water samples was detected to be 357 mg kg^{-1}, 16.5 mg kg^{-1}, 22.4 mg. kg $^{-1}$, 5 mg kg^{-1}, and 3.8 mg kg^{-1}, respectively. The maximum concentration of Mn, Co, Ni, As, and B toxic elements in drinking water in the study area was detected in September 2017 in the dry season as 417.88 μg.L^{-1}, 0.35 μg.L^{-1}, 3.06 μg L^{-1}, 37.16 μg.L^{-1}, and 1185.45 μg L^{-1}, respectively; and in May 2017 and June 2017, in the rainy season as 133.67 μg L^{-1}, 0.45 μg L^{-1}, 2.26 μg L^{-1}, 50.98 μg L^{-1}, and 1075.61 μg L^{-1}, respectively. In the analysis sample of drinking water in September 2017, one of the dry months, the variation in the average of the Mn, Co, Ni, As, and B toxic elements decreased compared to December 2017, March 2017, and June 2017. Depending on the water quality parameters, a significant amount of positive effect among EC, Log [TDS], and Log [Cl^-] parabolically were determined and calculated as R^2=0.906. As a result, in this study, we revealed that the toxic element amount varies considerably depending on the seasons of the year.

Iğdır Sularında Mevsimlerin Arsenik, Bor ve Diğer Parametrelerin Değişimine Etkisi

Anahtar Kelimeler:
Arsenik,
bor,
elektriksel iletkenlik,
toksik elementler,
su kalitesi

Özet: Bu çalışmada, Iğdır ili ve ilçeleri Ağrı dağı eteklerinde yer altı sondajı ve yerüstü doğal kaynak içme sularında mangan (Mn), kobalt (Co), mikel (Ni), mor (B) ve arsenik (As) toksik elementlerin değişimi ICP-MS yöntemi kullanarak tespit edilerek incelendi. Çalışma kurak ve yağışlı aylarda yapıldı ve pH, toplam çözünmüş katı madde (TDS), elektriksel iletkenlik (EC), tuzluluk (Sal), Cl^-, NH_4^+ ve NO_3^-, içme suyu örneklerinde mobil YSI Professional Plus multiparametresi kullanılarak gerçekleştirilimiştir. Analiz sonuçları Dünya Sağlık Örgütü (WHO), Amerikan Çevre Koruma Ajansı (EPA), Avrupa Birliği Standardı (Avrupa Birliği Standartları Konseyi: ECS) ve Ulusal İçme Suyu Standardı (TSE) sınır değerleri ile karşılaştırıldı. Analiz bölgelerindeki volkanik kayaçların Mn, Co, Ni, B ve As toksik element ICP-MS kütle sonuçları sırasıyla 357 mg kg^{-1}, 16.5 mg kg^{-1}, 22.4 mg kg $^{-1}$, 5 mg.kg^{-1} ve 3.8 mg kg^{-1} olarak tespit edilmiştir. Çalışma alanındaki içme sularındaki maksimum Mn, Co, Ni, As ve B konsantrasyonları Eylül 2017'de, kurak mevsimde sırasıyla 417.88 μg.L^{-1}, 0.35 μg L^{-1}, 3.06 μg L^{-1}, 37.16 μg L^{-1} ve 1185.45 μg L^{-1} olarak tespit edilmiştir. Mayıs 2017 ve Haziran 2017'de yağışlı mevsimde sırasıyla 133.67 μg.L^{-1}, 0.45 μg.L^{-1}, 2.26 μg L^{-1}, 50.98 μg L^{-1} ve 1075.61 μg L^{-1} olarak belirlenmiştir. Kuru aylardan biri olan Eylül 2017'de içme suyu analiz örneğinde Mn, Co, Ni, As ve B toksik element ortalamalarındaki değişim Aralık 2017, Mart 2017 ve Haziran 2017'ye göre azalmıştır. Su kalitesi parametreleri üzerinde, EC ile Log [TDS] ve Log [Cl^-] arasında parabolik olarak önemli miktarda pozitif etki belirlenmiş ve R^2= 0.906 olarak hesaplanmıştır. Sonuç olarak, bu çalışmada su kaynaklarındaki toksik element miktarının mevsimlere bağlı olarak önemli değişimler gösterdiğini ortaya koyduk. Bu durum insan ve çevre sağlığı üzerinde olumsuz etkilerinin olabileceği muhakkaktır.

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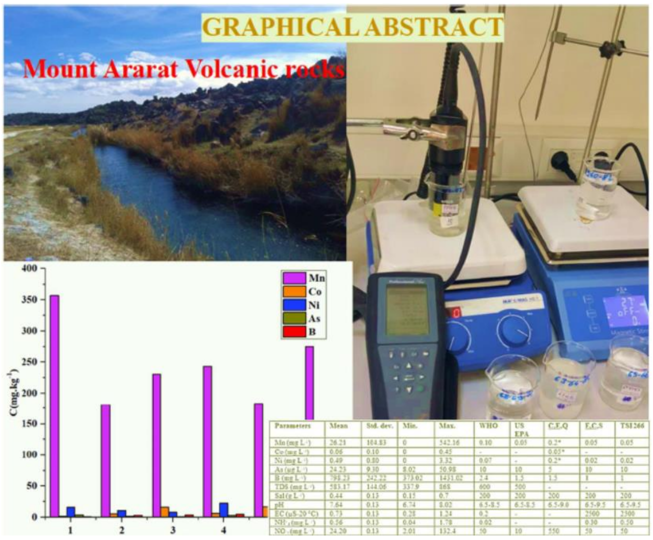
Graphical Abstract



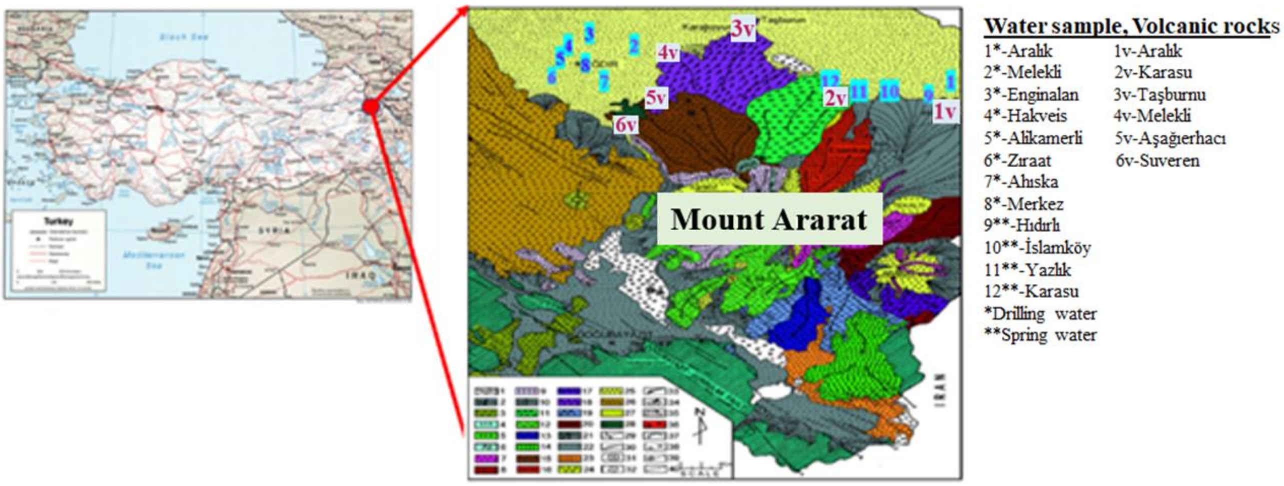
1. INTRODUCTION

Nowadays, the mass amount of As and B elements in water resources have exceeded the amount 10 µg L^{-1} and 2,4 mg L^{-1} limits (that amount exhibits toxic effect) accepted by WHO due to natural mineral fields, factory wastes, and volcanic rocks. This problem with drinking water causes diseases, like lung, kidney, bladder, and cardiovascular cancers in the people of countries, such as Bangladesh, Bolivia, China, the US, Canada, Bolivia, and Turkey (Halim, 2010; Sigfusson et al., 2011; Munoz et al., 2013; Elwakeel, and Guibal, 2015; Bacquart et al., 2015). A researcher has demonstrated that manganese, which is a toxic element in the running waters of Sicily affected by the Etna Volcano, has been raised above the tolerated limits (Roccaro, 2007) in European and National regulations. Also, the paper revealed that the source of manganese in water source stems from the oxidation of potassium permanganate. Another paper determined that Total Dissolved Soluble (TDS) value in underground waters was to be 1 000-35.00 mg L^{-1} (Desalting handbook, 2003). Smedley et al. claimed that there is a compatibility between arsenic and the concentration of iron hydroxides in colloids in the waters on earth (Smedley and Kinniburgh, 2002). Pique et al. reported that high amounts (>200 µg L^{-1}) of dissolved arsenic in water solutions in non-thermal groundwater were released by reduction of Fe (>14 mg L^{-1}) during the adsorption process of arsenic (Pique et al., 2010). Wilkie and Hering maintain that the arsenic waters they collected for the study in 2010 were rapidly catalyzed as a result of microorganism activities in arsenic waters. Folch found that As concentration in deep drilling thermal waters was detected to be > 100 µg L^{-1} and this may be caused by volcanic basaltic rocks (Folch, 2010). A correlation between the extent of Ca-(Na)-HCO_3 borne CO_2 in underground waters and the extent of its salinity was founded (Pique et al., 2010). In another study, Gates (2011) revealed that the reason why the high concentrations of arsenic in drinking waters in California, the USA is higher than the accepted 10 µg L^{-1} is the volcanic ashes in the aquifer. It is also stated that in cases when the B toxic element is higher than 3000 µg L^{-1} value, a positive correlation is observed between the TDS of water and measurement values. As for the underground waters in Canada, a positive correlation was detected between As and high amounts of salt (Webster, 1999). The salt in spring waters was observed so solving due to the water-rock interaction resulting from geo-chemical alteration, and an increase in the dissoluble TDS in waters. Again, these researchers revealed that secondary minerals and Ca concentrations in waters have a strong parabolic relationship. It is also maintained that dissolved concentrations in the spring waters in Canada changed in line with the geological structure of the region (Frape and Fritz, 1984). Meteor water was detected to decrease the quality of water even further with its effect on toxic elements in volcanic areas (Rowe et al., 1995). In a study revealing the impact of the volcanic aquifer of Djibouti on groundwater, water quality parameters such as EC, pH, temperature, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Na^+, Ca^{2+}, Mg^{2+}, K^+, Br^-, F^-, and trace metals (Li, Ba, B, Sr, Si, Al, Cr, Fe, Mn, Mo, Pb, Co, Cu, Ni, Zn, Ti, V, As, Se) in the water were identified and multivariate statistical analysis, binary diagram study was researched. They reported that seawater salinity interacted with the gulf basalt aquifer and exceeded the WHO values of As and Se in drinking water (Fakir et al., 2001; Cardona et al., 2004; Vengosh et al., 2005; Ghabayen et al., 2006; Bouchaou et al., 2008; Djabri et al., 2008; El Yaouti et al., 2009; Moussa et al., 2012; Belkhiri et al., 2012; Zghibi et al., 2014; Ahmed et al., 2017). In addition, it was observed in these studies that there is a correlation between As and Se ratios. Another study revealed the quality of the water in the 950 km long drainage channel, which was started to be built in 1968 to dry the marshy land in the Iğdır plain; average pH was measured as 8.06, Ca as 43.35 mg L^{-1}, Mg as 37.16 mg L^{-1}, NH_4^+ as 0.04 mg L^{-1}, B as 0.03 mg L^{-1}, Cl^- as 85.2 mg L^{-1}, NO_3^- as 2.86 mg L^{-1}, and electrical conductivity as 1045.85 µS cm^{-1} (Demirtaş, 2008). In addition, the water-soluble salts of the element B, which has many economic and technological uses, demonstrate the presence of B minerals in this study area (Ayers and Patrick, 1976; Mohajeri et al., 2003, Chew et al., 1979).

In this study, for the first time, we investigated the water standards, such as pH, TDS, EC, Sal, and the amount of several elements like Cl^-, NH_4^+, and NO_3^- of the Mn, Co, Ni, B, and As in drinking waters and the rate of exposure to meteor waters by seasons. Toxic elements in water cause various diseases in humans and other living metabolisms when they exceed standard limits. Therefore, it is very important to determine the concentration of these in the waters used as drinking water and to determine the factors affecting their concentrations in the water. These toxic elements' state of exposure to the volcanic areas in their place of origin was revealed. In addition, statistical evaluation was performed on drinking water quality. The toxic elements were analyzed of volcanic rocks in these water regions performed by Mn, Co, Ni, B, and As in the ACME laboratory by ICP-MS the method of AQ252.

1.2. Study Area

The examinations of toxic elements of As, B, Mn, Co, and Ni in drilling and spring waters and drinking water were conducted in Iğdır province, districts, and villages (Figure 1). The drill and underground waters used for drinking and agricultural purposes in Iğdır province and districts were opened by Turkish Iller Bank and have an average depth of 106 m out of a total of 15 drilling wells that are used as drinking water, approximately 94500 people annually use an average of 6068281 m^3 of water to maintain their daily life activities (Iğdır Municipality 2018).



(1) Alluvium and alluvial fan, (2) Moraine, (3) Lava of Tendürek volcano, (4) Hyaloandesite, (5) Hyaloandesite, (6) Andesite, (7) Hypersthene basalt, (8) Basalt, (9) Basalt, (10) Moraine and fluvial-glacial fan, (11) Hyalobasalt, (12) Hypersthene andesite, (13) Hypersthene andesite, (14) Hypersthene andesite, (15) Hypersthene andesite, (16) Hypersthene andesite, (17) Basalt, (18) Basalt, (19) Hyalobasalt, (20) Basalt, (21) M: Morain, FGY: Fluvial and glacial fans, (22) Alluvium of Dogubeyazıt plain, (23) Basalt, (24) Andesite, (25) Andesite and associated pyroclastic rocks, (26) The Zondağ volcanic association, (27) Continental deposits of Igdir-Aralik depression, (28) Undifferentiated basement rocks, (29) Tensional Fracture, (30) Caldera wall, (31) Eruption centre, (32) Crater, (33) Flow direction, (34) Slope waste and debris, (35) Alluvial cone, (36) Permanent ice cap, (37) Cirque glacier, (38) Marsh, (39) Strike-slip fault, (40) Fault and inferred fault.

Figure 1. Geology map of the Ararat volcanic center (Yılmaz et al., 1998).

The study area is generally dry in July and August months of the year, and in September and October 2017. The region, which is very cold and snowy in winter, has a continental climate. Although the elevation of the region is 850-900 m, a microclimate effect occurs due to the topographic structure of the basin. According to the measurements of the Iğdır-Meteorology Directorate, the rainfall rate in Iğdır between January 2016 and December 2017 is presented in kg. m^{-2} (Figure 2, Directorate Turkish State Meteorological Service 2018.)

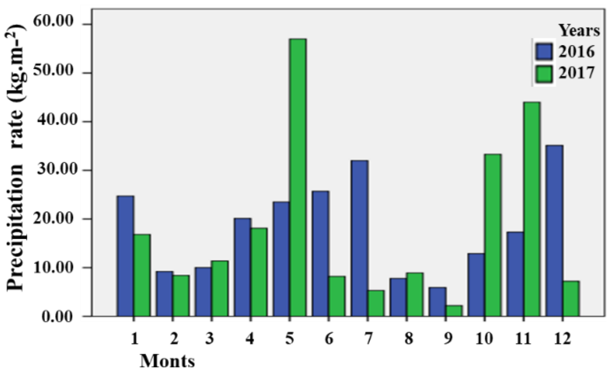


Figure 2. Monthly Total Precipitation Rate (kg m^{-2}).

2. MATERIAL AND METHOD

Water samples collected from the study area were taken into sample containers as three samples from each source in December and September 2017, and the average values of the results were analyzed. The glass containers used for the sample collection were sterilized with an aqueous (1/20 by volume) solution of acetic acid and hydrochloric acid and completely cleared of heavy metals. The bottle sample containers were dried in the oven to make the sample ready for collection after being rinsed with ultra-pure water. Mobile multiparameter (YSI Professional Plus) was calibrated with pH (4.00, 7.00, and 10.00), NO_3^-, NH_4^+, Cl^-, conductivity, and salinity standard solutions before carrying each on-site sample of water. The cations in the sample waters were taken from each sample of water into three sample containers and acidified with HNO_3 with pH=2. Then, the water samples were measured with "Agilent Technologies 7700 Series" ICP-MS located in Igdir University Central Research Laboratory. The measurement values of three samples from each water source were averaged and SPSS 22.00 program was used to analyze the toxic elements by month (December 2016, March 2017, June 2017, and September 2017). Two-way ANOVA was used as the analysis method. The group variances were determined homogeneous in this analysis (Levene's homogeneity test was used). The volcanic rock samples were ground 3 microns after gathering the areas, Aralık, (1) Karasu (2), Taşburnu (3), Melekli (4), Aşağıerhacı (5), and Suveren (6), respectively. Before was taken constant weight within the desiccator the samples were dried in an oven at 105 °C. The samples were dissolved in ACME laboratories according to AQ252 the method (1: 1: 1 HNO_3: HCl: H_2O). They performed quantitative analysis of Mn Co Ni As and B with ICP-MS.

3. RESULT AND DISCUSSION

Arsenic, boron, manganese, nickel and cobalt, Electrical Conductivity, pH, Salinity, Total Dissolve Solid, chloride, nitrate, and ammonium in the waters collected from the study area were examined in December 2016, March, and September months of 2017. Some of these are, The Regulation of the World Health Organization (WHO), the Environment Protection Agency of the United State of America (US EPA 816-F-09-004 | 2018) Guidelines for Canadian Drinking (CEQ), European Community Standards (ECS, the European Union Directive of 211) and the TS 266 standard of the Turkish Standard Institute. The physical and chemical quality parameters indicated for the water in these regulations are given in Table 1. This study aimed to investigate the physical and chemical content of the drinking water spring, and drilling used in Iğdır province, and to assess the risk to human health.

Table 1. Some quality parameters of water statistical results.

Parameters	Mean	Std. dev.	Min.	Max.	WHO	US EPA	C,E,Q	E,C,S	TSI 266
Mn (mg L^{-1})	26.21	104.83	0	542.16	0.10	0.05	0.2*	0.05	0.05
Co (mg L^{-1})	0.06	0.10	0	0.45	-	-	0.05*	-	-
Ni (mg L^{-1})	0.49	0.80	0	3.32	0.07	-	0.2*	0.02	0.02
As (µg L^{-1})	24.23	9.30	8.02	50.98	10	10	5	10	10
B (mg L^{-1})	798.23	242.22	373.02	1431.02	2.4	1.5	1.5	1	1
TDS (mg L^{-1})	583.17	144.06	337.9	868	600	500	-	-	-
Sal (g L^{-1})	0.44	0.13	0.15	0.7	200	200	200	200	200
pH	7.64	0.13	6.74	8.02	6.5-8.5	6.5-8.5	6.5-9.0	6.5-9.5	6.5-9.5
EC (µS-20 °C)	0.73	0.13	0.28	1.24	0.2	-	-	2500	2500
NH^+_4 (mg L^{-1})	0.56	0.13	0.04	1.78	0.02	-	-	0.30	0.50
NO^-_3 (mg L^{-1})	24.20	0.13	2.01	132.4	50	10	550	50	50
Cl^- (mg L^{-1})	118.76	0.13	8.06	207.18	250	250	250	250	250

According to these data, it was detected that in the drinking water of Aralik district, the WHO, US EPA, ECS, and TS EN ISO 11885 standards of manganese which are 50 µg L^{-1} was detected to be maximum in June 2017 with 542.16 µg L^{-1} and minimum in December 2017 with 133.67 µg L^{-1}. Measurements at other water sources were detected to be considerably below the standard limits. The change of the manganese element in water samples is demonstrated (Figure 3a). The highest average change of manganese by month comprised in march 2017, followed by September, December, and June 2017 respectively. The average variation of manganese is indicated (Figure 3b).

The researchers have claimed to create harmful effects if the concentration is higher than 0.1 mg L^{-1} in concentration in agricultural irrigation waters for only tomato plants.

In our study, the limit values in drinking water were maximum in June 2017 in Enginalan village drilling water with 0.449 µg L^{-1} and minimum in 2017 December in the Hidirli hamlet and Islamkoy spring waters which remained below the ICP-MS measurement values. The varying of cobalt in water samples has been indicated (Figure 3c). The highest average varying of cobalt by month comprised in June 2017, followed up by March, December, and September 2017 respectively. The average varying of cobalt has been indicated (Figure 3d). In the foregoing four standards for drinking water, the maximum concentration value of a nickel is taken as 20 µg. L^{-1}. The region's maximum amount was detected in the sample of the drilling well of the Aralik district in March 2017 at 3.32 µg L^{-1}, and the minimum was detected in Hidirli hamlet, Islamkoy, Yazlik, and Karasu spring waters which remained below the ICP-MS measurement values. The variation in nickel element in water samples is presented (Figure 3e). The average varying of nickel by month was higher in December and March 2017 than in June and September 2017. The average varying of nickel has been indicated (Figure 3f).

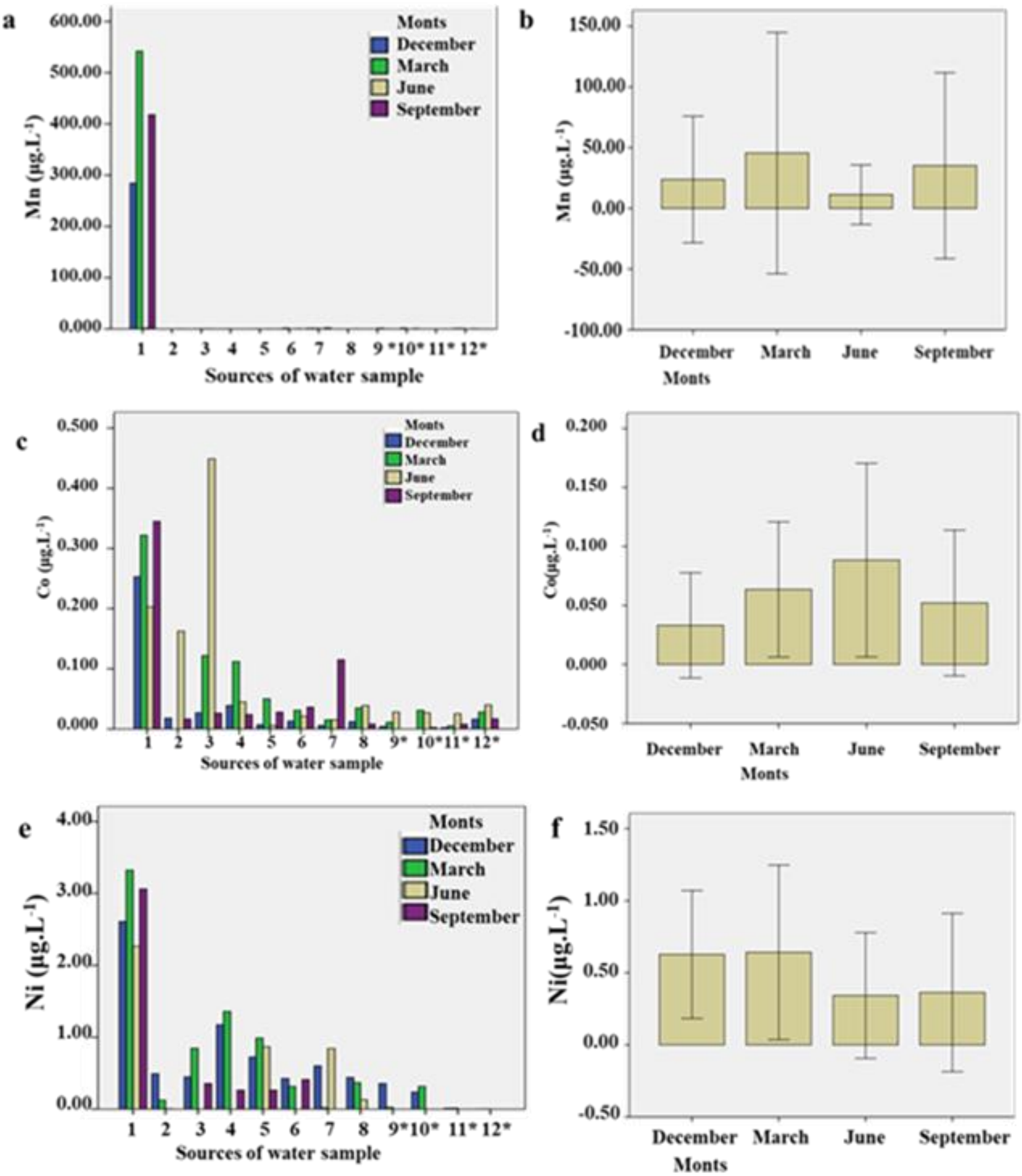


Figure 3. The Mn ions in waters of sample a. Changed concentration by months in respect of; and b. Average confidence intervals (µg L^{-1}); The Co ions in waters of sample c. Changed concentration by months in respect of; and d. Average confidence intervals (µg L^{-1}); The nickel ions in waters of sample e. Changed concentration by months in respect of; and f. Average confidence intervals (µg L^{-1})

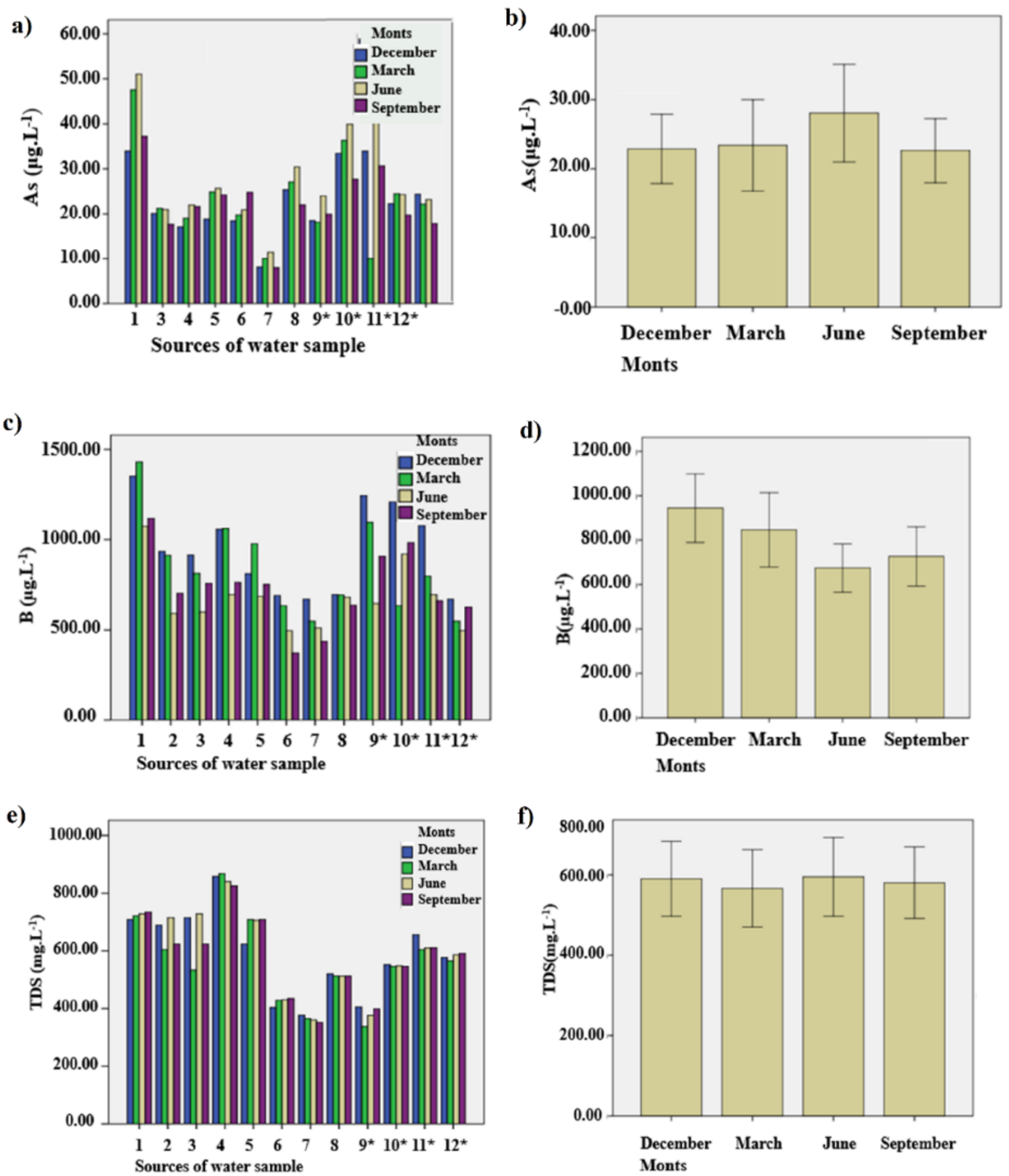


Figure 4. The As ions in waters of sample a. Changed concentration by months in respect of; and b. Average confidence intervals (µg L^{-1}); The B ions in waters of sample c. Changed concentration by months in respect of; and d. Average confidence intervals (µg L^{-1}); The TDS in waters of sample e. Changed concentration by months in respect of; and f. Average confidence intervals (mg L^{-1})

Regarding the concentration of arsenic we measured, the forgoing four standards take 10 µg L^{-1} as the maximum mass in drinking water. In the study area, the maximum amount was detected in the sample taken from the drilling water in the Aralık district in March 2017 with 50.98 µg L^{-1}, whereas the minimum value was detected in the Ziraat drill water in December 2017 with 8.124 µg L^{-1}. The variation of the arsenic element in water samples is given (Figure 4a). The maximum monthly average change in arsenic comprised in June 2017. The variance was higher in March and June 2017 than in December and September 2017, respectively. The average variation of arsenic is given (Figure 4b). The maximum concentration values of boron we measured, in the foregoing WHO, ECS, and TS EN ISO 11885 standards is taken as 1 mg L^{-1} while it is 2.4 mg L^{-1} in EPA. In the study area, the maximum value was detected in the drilling water of

Aralik in 2017 December with 1431.019 μg L^{-1}, and the minimum value was detected in the Ziraat drilling water in September 2017 with 373.0 μg L^{-1}.

The variation of boron in water samples is given (Figure 4c). The highest average change in boron by month comprised in December 2017, followed by March, September, and June 2017 respectively. The highest varying comprised in December 2017, and March 2017. The average change of boron is given in Figure 4d. Regarding the Total Dissolved Solid (TDS) measured, according to the foregoing WHO ECS, and TS EN ISO 11885 standards, amounts 1.500 mg L^{-1} are defined as fresh water and 1500 mg L^{-1} are defined as bitter water. EPA, on the other hand, takes the maximum value of 500 mg L^{-1}. In the study area, the maximum amount was detected in the sample of Hakveis village drilling water in March 2017, with 868.00 mg $L^{-1,}$ and the minimum was detected in Hidirli hamlet spring water in March 2017 with 337.9 mg L^{-1}. The TDS change in water samples is given (Figure 4e). The average change of the total water dissolved solids (TDS) by months is close to each other. However, the average change in September 2017 was lower relative to other months. The Total Dissolved Solid average change of solute is given (Figure 4f).

In terms of salinity measured, the foregoing WHO, ECS, and TS EN ISO 11885 standards take 2 g L^{-1} as the maximum value. In the study area, the maximum value was detected in the drilling water of Hakveis village in March 2017, with 0.68 g L^{-1} whereas the minimum value was detected in Hıdırlı hamlet water in June 2017, with 0.15 g L^{-1}. The salinity change in water samples is given (Figure 5a). Although the average change of salinity in all measured months was the same, the change in September 2017 was relatively lower. The average change of salinity is given (Figure 5b). The standards of pH change we measured in second-quality drinking water are classified in the foregoing WHO, EPA, ECS, and TS EN ISO 11885 standards as 6.5 to 9.5. In the study area, the maximum pH was detected in the central district's drilling water in September 2017, with pH=8.2 and the lowest value was recorded in the Karasu spring water in September 2017, with pH=7.0. The pH change in water samples is given (Figure 5c). Although the average change of pH in all measured months was the same, the change in March 2017 and June 2017 was relatively small. The average change in pH is given (Figure 5d). In the ECS regulation, 2500 μS cm^{-1} (20°C) was identified as the upper limit standard of drinking water conductivity. In the instant measurements made in the study area, the maximum value was measured in the Hakveis drilling water in September 2017 at 1.24 μS cm^{-1} (17°C), and the minimum value was recorded in Ahiska drilling water in March 2017, with 0.46 μS cm^{-1} (17°C). The electrical conductivity change in water samples is given (Figure 5e). The average change in Electrical Conductivity increased in March, December, June, and September 2017 respectively. It was observed that the least change in conductivity comprised in March 2017. The average variation of Electrical Conductivity is given (Figure 5f).

Regarding the NH_4^+ standard in water, 0.50 mg L^{-1} was identified as the upper limit in the ECS regulation. In the instant measurements of the waters in the study area, the maximum values were detected in the Alikamerli drilling water in December 2017, with 1.78 mg L^{-1} while the minimum value was detected in Hidirli hamlet natural spring water in June 2017, with 0.05 mg L^{-1} Ammonium changed in water samples is given (Figure 6a). The average change of ammonium was less in March and June 2017 than in December and September 2017.

The minimum change in ammonium concentration was detected in March 2017. The average change of ammonium is given (Figure 6b). The maximum standard of Nitrate, we measured, in the drinking waters settled by the foregoing WHO, ECS, and TS EN ISO 11885 is 50 mg L^{-1} while the limit settled by EPA is 45 mg L^{-1}. In the study area, the maximum value was detected in the sample taken from the drilling water of Aralik district in December 2017 with 132.4 mg $L^{-1,}$ and the minimum was detected in Ahiska drilling water in September 2017, with 2.01 mg L^{-1}. Ammonium changes in water samples are given (Figure 6c).

The average change in nitrate was lower in December 2017 relative to other months. The maximum change in nitrate concentration was detected in December 2017. The average change of ammonium is given (Figure 6d). The standard for maximum concentration of Free Chloride measured, in drinking waters settled by the foregoing WHO, ECS, and EPA is 250 mg L^{-1} while the TS EN ISO 11885 standard is 600 mg L^{-1}. In the study area, the maximum value was detected in the samples from the drilling water of Aralik district in June 2017, with 207.18 mg L^{-1} whereas the minimum value was detected in the Ahiska drilling water in March 2017 with 40.06 mg L^{-1}. Free chloride changes in water samples are given (Figure 6e).

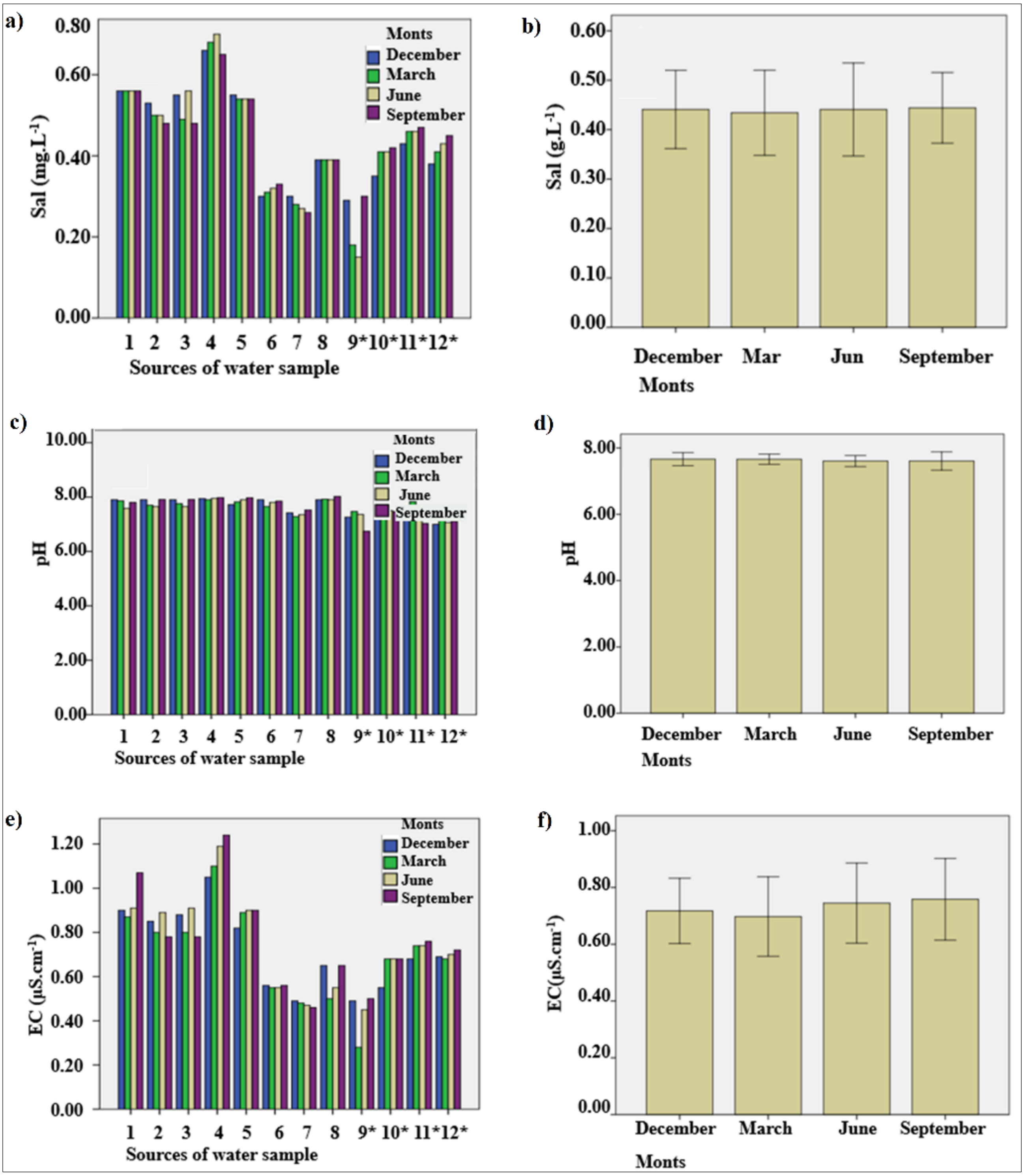


Figure 5. The salinity in waters of sample a. Changed concentration by months in respect of; and b. Average confidence intervals (g L^{-1}); The pH in waters of sample c. Changed pH by months in respect of; and d. Average confidence intervals; The EC in waters of sample e. Changed conductivity by months in respect of; and f. Average confidence intervals (µS cm^{-1})

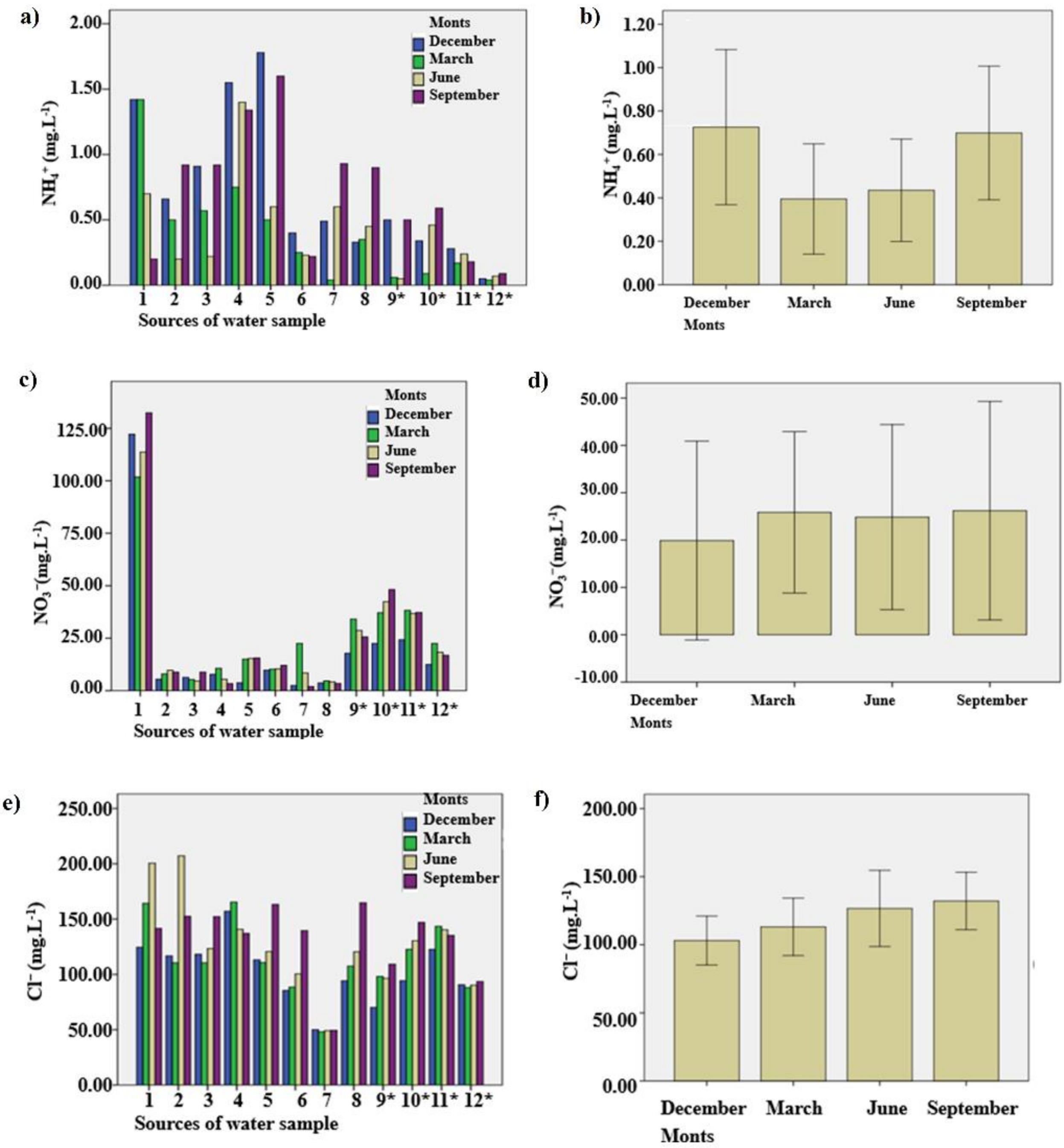


Figure 6. The NH_4^+ ions in waters of sample a. Changed concentration by months in respect of; and; b. Average confidence intervals (mg L^{-1}); The NO_3^- ions in waters of sample; c. Changed concentration by months in respect of; and d. Average confidence intervals (mg L^{-1}); The Cl^- ions in waters of saμple; e. Changed concentration by months in respect of; and f. Average confidence intervals (mg L^{-1})

The average change in chloride was lower in December 2017 relative to other months. The average change of Free Chloride increased in December, March, and September 2017 respectively. The average change of Free Chloride is given (Figure 6f).

The highest was detected of Mn to be 357 mg L^{-1} first (in the sample of Aralık) and the least in the second (in the Karasu sample) 181 mg L^{-1} with ICP-MS, in the volcanic rocks from areas of the water samples. The highest was detected Co to be 16.5 mg L^{-1} fifth (in the sample of Aşağıerhacı) and the least in the first (in the Aralık sample) 1.6 mg L^{-1} with ICP-MS, in the volcanic rocks from areas of the water samples. The highest was detected of Ni to be 22.4 mg L^{-1} fourth (in the sample of Melekli) and the least in the third (in the Taşburnu sample) 8.2 mg L^{-1} with ICP-MS, in the volcanic rocks from areas of the water samples. The highest was detected of As to be 3.8 mg L^{-1} first (in the sample of Aralık) and the least in the third (in the Taşburnu sample) 0.9 mg L^{-1} with ICP-MS, in the volcanic rocks from areas of the water samples. The highest was detected of boron to be 5 mg L^{-1} fourth (in the sample of Melekli) and the least in the first and fifth (in the Aralık and Aşağıerhacı samples) 1 mg

L^{-1} with ICP-MS, in the volcanic rocks from areas of the water samples. The detection of manganese, cobalt nickel, and arsenic boron in the volcanic rocks is given (Figure 7).

It was determined by analyzing the sample water, and the volcanic rock directly related to solubility the concentration and change of Mn, Co, Ni, As, and B ions of the cations. In addition, the concentration of manganese ions in drilling well waters increased in June 2017. It has been supported by the presence of soluble compounds on the Mn amount in the water depending on the volcanic rock samples, to by the increasing the high manganese concentration in the rainy seasons and the water samples in the locality. It has been realized with a mean of 29.01 mg L^{-1} and a standard error of ± 13.13 in December, June, March, June, and September 2017. The highest concentration of Co was measured in June 2017. When the dissolubility of cobalt salts and the month of May when the rainfall is the highest is taken into consideration, this situation demonstrates a direct proportion. It can be to explain the high concentration of Co, in water samples, especially in drilling waters compared to spring waters, not only by the low impact of volcanic rocks on water but also by the presence of insoluble Co compounds in the rocks. The mean and standard error of our measurements were realized as 0.059 ± 0.014.

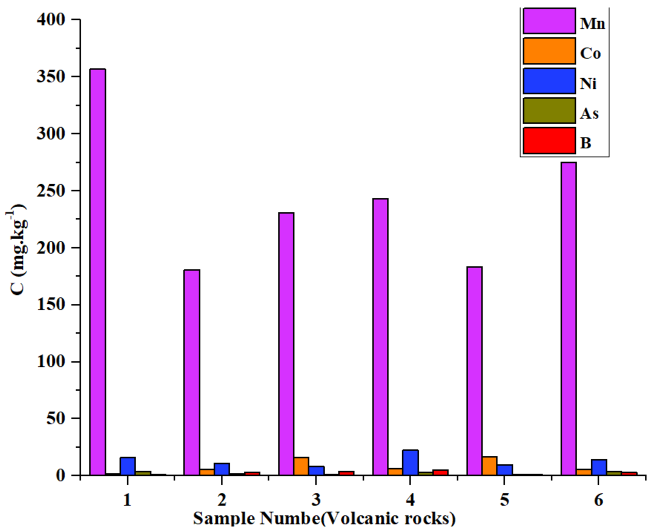


Figure 7. Analyzing volcanic rock samples with ICP-MS (ACME).

Although Ni concentration was highest in March 2017, there is no correlation when the dissolubility of nickel salts and May 2017 when the rainfall was the highest is taken into consideration. This demonstrates that the precipitation rate does not have much effect on nickel dissolubility. It can be explained by the low concentration of nickel compared to other toxic elements in sample water, with has been insoluble compounds in volcanic rocks. The mean and standard error of our measurements were realized as 0.494 ± 0.115. The highest amount of arsenic was measured in June 2017. This is evidence that water-dissoluble arsenic compounds are present in volcanic rocks or water aquifer environments during the rainy period. It was determined arsenic ratio, both in the highest 1st (Aralık) drilling water, in the latest in 6th drilling water (Ziraat) 50.98 µg L^{-1} 8.02 µg L^{-1} respectively, and the volcanic rocks of vicinity samples water (first, and sixth) 3.8 mg L^{-1}, 3.5 mg L^{-1} respectively. It can be explained, with ıt's negligible effect of volcanic rocks on the area of this drilling water where least detected As, (to the sixth drilling). The mean and standard error of our measurements has realized as 24.229 ± 1.342. Boron concentration was highest in the drilling well water in March 2017. Boron was determined the highest 4th sample of volcanic rocks and the least in the 1st and 5th samples 5 mg L^{-1} and 1 mg L^{-1} respectively. But, the maximum amount of B measurement was detected with 0.5 µg L^{-1}, in their study on the drainage sewage water (Demirtaş A, 2008). In addition, in December 2017, when rainfall was lower than average, B concentration was highest in nine water sources relative to other months, while it was highest in March 2017 in the other three water sources. The mean and standard error of our measurements has determined as 7.98 ± 0.350.

4. CONCLUSION

The findings of this study were summarized below;

- The number of toxic elements in the drinking waters of Igdir city has exceeded the standard.
- High concentration levels of toxic B, As, Mn, Ni, nitrate, ammonium, and, chlorine in the municipal drinking water network in Igdir were determined to threaten human health.
- The volcanic rock geology of the aquifer, characteristic of anthropogenic, and micro-climate of interaction have immense effects on the content of waters in Iğdır province depending on the seasonal year.
- We can say that the risk of seeing a pandemic disease may be increased due to the high concentration of Mn, Co, Ni, B, and As elements in water contents in Igdir.
- To prevent the increase of several diseases among people who live in Igdir province, the drinking water must be purified before being supplied to the city network according to the standards of fresh drinking water.
- The quality standards of drinking water are crucial for the healthy survival of human beings and living beings. So, we can say that this study contributed to the evaluation of water sources in Igdir province.

5. REFERENCES

Ahmed A.H., Rayaleh W. E., Zghibi A., Ouddane B. (2017). Assessment of chemical quality of ground water in coastal volcano sedimentary aquifer of Djibouti. Journal of African Earth Sciences, 131, 284-300.

Ayers, O.E., R.E. Patrick (1976) Hydrogen gas generators for use in chemical lasers, U.S. Pat. 3,948,699.

Bacquart T., Frisbie S., Mitchell E., Grigg L., Cole C., Small C., Sarkar B. (2015). Multiple inorganic toxic substances contaminating the groundwater of Myingyan Township. Myanmar: Arsenic. manganese. fluoride.

iron. and uranium. Science of The Total Environment, 517, 232-245.

Belkhiri L., Mouni L., Boudoukha A. (2012). Geochemical evolution of groundwater in an alluvial aquifer: case of El Eulma aquifer. Journal of African Earth Sciences, 66e67. 46e55.

Bouchaou L., Michelot J.L., Vengosh A., Hsissou Y., Qurtobi M., Gaye C.B., Bullen T.D., Zuppi G.M. (2008). Application of multiple isotopic and geochemical tracers for investigation of recharge salinization, and residence time of water in the SousseMassa aquifer, southwest of Morocco, Journal of Hydro-environment, 352, 267e287.

Cardona A., Carrillo-Rivera J., Huizar-Alvarez R., Graniel-Castro E. (2004). Salinization in coastal aquifers of arid zones: an example from Santo Domingo, Baja California Sur, Mexico, Environmental Geology, 45, 350-366.

Chew, W.M., Murfree, J.A., Martignoni, P., Nappier, H.A., Ayers, O.E. (1979) Amine-borane
as hydrogen generating propellants, U.S. Pat.4,157,927.

Debels P., Fıgueroa R., Urrutia R., Barra R., Niell X. (2005). Evaluation of water quality in the Chilla'n river (Central Chile) using physicochemical parameters and a modified water quality index. Environmental Monitoring and Assessment, 110, 301-322.

Demirtaş A. (2008). Drainage Water Quality in Iğdır PlaiN. Atatürk University Journal of The Agricultural Faculty, 39(1), 23-33.

EC (Council of the European Union), (2014). Council Directive 98/83/EC – on the quality of water intended for human consumption. Official Journal of the European Communities.

El Yaouti F., El Mandour A., Khattach D., Benavente J., Kaufmann O. (2009). Salinization processes in the unconfined aquifer of Bou-Areg (NE Morocco): a geostatistical. geochemical. and tomographic study. Applied Geochemistry, 24, 16e31.

Elwakeel K.Z., and Guibal E. (2015). Arsenic(V) sorption using chitosan/$Cu(OH)_2$ and chitosan/CuO composite sorbents. Carbohydrate Polymers, 134, 190-204.

Environmental Protection Agency (Washington-EPA) (2018).

Fakir Y., Zerouali A., Aboufirassi M., Bouabdelli M. (2001). Exploitation et salinite des aquiferes de la Chaouia cotiere. littoral atlantique. Marocco. Journal of African Earth Sciences, 32, 791-801.

Frape S.K., Fritz P., Mcnutt R.H. (1984). Water-Rock İnteraction And Chemistry Of Ground-waters From The Canadian Shield. Geochimica et Cosmochimica Acta, 48, 1617-1627.

Gates J.B., Nicot J.P., Scanlon B.R. and Reedy R.C. 2011. Arsenic enrichment in unconfined sections of the southern Gulf Coast aquifer system. Applied Geochemistry, 26(4), 421-431.

Ghabayen S., McKee M., Kemblowski M., (2006). Ionic and isotopic ratios for identification of salinity sources and missing data in the Gaza aquifer. Journal of Hydro-environment, 318, 360-373.

Halim M.A., Majumder R.K., Nessa S.A., Hiroshiro Y., Sasaki K., Sahac B.B., Saepulohd A., Jinno K. (2010). Evaluation of processes controlling the geochemical constituents in deep groundwater in Bangladesh: Spatial variability on arsenic and boron enrichment. Journal of Hazardous Materials, 180, 50-62.

Iğdır-Meteorology Directorate, (2017) https://mgm.gov.tr/eng/forecast-cities.aspx

Iğdır Municipality Directorate of Water and Sewerage Affairs
http://www.igdir.bel.tr/page.php?kat=67&altkat=13&konumid=2

Kannel P.R., Lee S., Lee Y.S., Kanel S.R., Khan S.P. (2007). Application of water quality indices and dissolved oxygen as indicators for river water classification and urban impact
Assessment. Environmental Monitoring and Assessment, 132, 93-110.

Lambert R.S.J., Holland J.G., Owen P.F. (1974). Chemical petrology of a suite of calc-alkaline lavas from Mount Ararat. The Journal of Geology, 82, 419-438.

Lizcano I.J., Radha K.P., Fan. L.T., Erickson L.E. (1974). Identification of parameters in transient water quality models from stochastic data.

Madonia P., Cangemi M., Bellomo S., D'Alessandro W. (2013). Influence of volcanic activity on the quality of water collected in roof water catchment systems at Stromboli Island (Italy). Journal of Geochemical Exploration, 131, 28-36.

Mohajeri, N., Robertson, T., Raisi, A.T. (2003) Hydrogen storage in amine borane complexes, orazine hydrogenation to cyclotriborazane: Molecular modelling and experimental borazane
thermolysis, Fsec Final Report for Task III-B. Report date: December 1.

Moussa A.B., Zouari K., Valles V., Jlassi F. (2012). Hydrogeochemical analysis of groundwater pollution in an irrigated land in capbon peninsula. Arid Land Research and Management, 26, 1e14.

Munoz M.O., Werna H., Johnssona F., Bhattacharyaa P, Sracekc O., Thunvika R., Quintanilla J, Bundschuha J. (2013). Geogenic arsenic and other trace elements in the shallow hydrogeologic system of outhern Poopó Basin. Journal of Hazardous Materials, 262, 924-940.

Notsu K., Fujitanib T., Ui T., Matsudad J., Ercan T. (1995). Geochemical features of collision-related volcanic rocks in central and eastern Anatolia. Journal of Volcanology and Geothermal Research, 64, 171-192.

Pique A., Grandia F., Canals A. (2010). Processes releasing arsenic to groundwater in the Caldes de Malavella geothermal area NE Spain. Water Research, 44, 5618-5630.

Roccaro, P., Barone C., Mancini G., Vagliasindi F. G. A. (2007). Removal of manganese from water supplies intended for human consumption: a case study, Desalination - Journal, 210, 205-214.

Rowe J.G.L., Brantley S. L., Fernandez J.F., Borgia A. (1995). The chemical and hydrologic structure of Poas Volcano. Journal of Volcanology and Geothermal Research, 64, 233-267.

Sancho A. (2010). Geological and human influences on groundwater flow systems in range-and-basin areas: the case of the SelvaBasin, (Catalonia. NE Spain). PhD Thesis, Universitat Auto`noma de Barcelona.

Shrestha S., Kazama F. (2007). Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan. Environ. Model. Softw, 22, 464-475.

Smedley P.L., Kinniburgh D.G. (2002). A review of the source.behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 17(5), 517-568.

Tankersley K.B., Dunning N.P., Thress J., Owen L.A., Huff W.D., Fladd S.G., Bishop K.J., Plog S., Watson A.S., Carr C., Scarborough V.L. (2016). Evaluating soil salinity and water management in Chaco Canyon, New Mexico. Journal of Archaeological Science, 9, 94-104.

Teychene B., Collet G., Gallard H., Croue J.P. (2013). A comparative study of boron and arsenic (III) rejection from brackish water by reverse osmosis membranes. Desalination, 310, 109-114.

TSI - TS 266/T1 (2014). Water intended for human consumption.

TSI 266. (2005). Standards for Drinking Waters, Turkish Standards Institution, Ankara, Turkey.

Vengosh A., Kloppmann W., Marei A., Livshitz Y., Gutierrez A., Banna M., Guerrot C., Pankratov I., Raanan H. (2005). Sources of salinity and boron in the Gaza strip: natural contaminant flow in the southern Mediterranean coastal aquifer. Water Resources Research, 41.

Watson I. C., Morin O.J., and Henthorne L. (2003). Desalting handbook for planners. Bureau of Reclamation. Desalination and Water Purification Research and Development Program Report, 72, 316 http://www.usbr.gov/research/AWT/report pdfs/report072.pdf (21.07. 2014).

Webster J.G. (1999). The source of arsenic (and other elements) in the Marbel -Matingao river catchment Mindanao Philippines. Geothermics, 28, 95-111.

Wilkie J.A., Hering J.G. (1996). Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and cooccurring solutes. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 107, 97-110.

World Health Organization, (2011). Guidelines for drinking-water quality. fourth edition.

Zghibi A., Merzougui A., Zouhri L., Tarhouni J. (2014). Understanding groundwater chemistry using multivariate statistics techniques to the study of contamination in the Korba unconfined aquifer system of Cap-Bon (North-east of Tunisia). Journal of African Earth Sciences, 89, 1-15.