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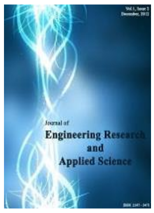

High-fluoride risk and toxicity in surface waters in Gümüşhane-Gökdere valley drainage network (NE Turkey)

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Abstract

Fluoride, which is the most reactive anion in the elements, does not exist in its pure form in nature. It is found in rock-forming minerals in the lithosphere in trace amount. It is especially, found abundantly in some pegmatites, micas (muscovite, biotite), amphibole, apatite and cryolite etc. The rocks bearing these minerals are present abundantly in Gümüşhane province which is in the most important metallogeny zone in NE Turkey. Within the scope of the study, fluoride contents of some stream waters in Gökdere Valley Drainage Network (NE Turkey) have been analyzed by potentiometric method. Taking into account the physicochemical conditions, samples were collected in the summer of 2017. The 17 water samples were collected from the Gökdere Valley. 7 of them were collected from Gökdere, 3 from Beyçam, 3 from Düğünyazı, 3 from Akgedik and 1 from Nazlıçayır locations. When the obtained fluoride analysis results are evaluated statistically, it was determined that fluoride concentrations changed between 0.19 to 9.87 mg/L, with an average concentration of 3.7 mg/L. So, fluoride contents of region's surface waters have been generally observed to exceed the allowable limit (according to WHO 2004 1.5 mg/L). When the findings are evaluated in the light of geological, geochemical and geo-statistical analyzes, it is concluded that high fluoride concentration of the surface waters in the region are directly related to geological and geochemical processes. Magmatic and metamorphic rocks containing abundant fluoride-containing minerals such as amphibole, muscovite, apatite, biotite, etc. which outcrop the region. The mineralogical content of these host rock, rock-water interactions, alteration and weathering processes of the rocks on which surface waters flow have also affect on the high fluoride content in waters. Therefore, it was concluded that the high fluoride contents in the surface waters in the region are the rocks that surfaced in the region.

Keywords: Fluoride risk/toxicity;surface water; alteration/mining area; Gümüşhane.

1. Introduction

Fluorine has atomic number with F symbol, is the most reactive element among all known ones and is 13th in terrestrial abundance [1]. It is present in several minerals such as fluorapatite, fluorite, hornblende, tourmaline, cryolite, micas (biotite, muscovite) and topaz, generally as in rock-forming minerals. Sedimentary rocks (shales, limestone, sandstone etc), metamorphic rocks (e.g. gneisses and schist) and igneous rocks (granites or basalts) contain fluoride in the range of 50-1200 ppm (50–800 ppm for sedimentary rocks and 300–1200 ppm for igneous and metamorphic rocks) [2, 3]. In general meaning, felsic igneous rocks have a higher amount of fluoride content than mafic and meta-sedimentary rocks [4, 5]. Physical and chemical processes such as hydrothermal alteration and weathering to which the host rocks are exposed cause the minerals in the rocks to deteriorate, thereby causing fluoride to be released into the environment and causing an increase in the fluoride concentrations in the environment.

In nature, fluoride is present in water, soil, animals and plants in trace amounts, and occurs generally as free fluoride ions in waters/ground waters and its concentrations, for example, in groundwater, is found in trace amounts, but it is also found in excessive amounts such as 25 mg/L [6]. Although it is accepted that the origin of fluoride in water is due to many factors, it is reported that the most important source of fluoride in the waters is the fluorides released due to the degradation of fluoride-containing minerals in the rocks due to the water/wall rock interaction. Besides, geothermal water, volcanic activity, evaporation and precipitation of calcite, ion exchange etc. are also possible source of fluoride in aquatic environments [7–10].

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Apart from natural conditions, human activities such as agricultural activities and brick kilns cause increases in fluoride concentrations [11]. When all these data are evaluated together, it can be generalized that climatic conditions, pH value, water temperature, the anion exchange-capacity of a water bearing material (OH^- for F^-), solubility of minerals being fluorine bearers, and the nature of geological environments the water passes through, as well as the periods of contacts with individual formations and geological aspects also play important roles effecting fluoride concentrations.

Fluorine is a necessary micronutrient element for human as well as all other living things, but overdose exposure can be toxic [12]. Due to the increasing sensitivity of fluoride in the society, since the beginning of the 20th century, many researches have been carried out by many researchers from different disciplines about the fluoride content of the environment and its effects on the environment and public health [1, 10, 21, 13–20]. When evaluated within normal limits, surface waters are considered to contain a maximum of 0.3 mg/L fluoride. Expected value is usually between 0.03 to 0.3 mg/L. When considering Turkey Surface Water Quality Regulation 2016 and the Reports 1994, 2004 of the World Health Organization's Drinking Water Quality Parameters [22–24], drinking water containing F^- of around 1 mg/L is considered to be ideal for dental health of children under 10 years; the permissible F^- content in potable water is accepted as 1.5 mg/L and F^- concentrations in excess of this limit are considered to pose a risk to health of human. Scientific studies on fluoride have shown that F^- content above 2 mg/L causes dental problems, which is seen mottling of tooth. Concentrations high than 4 mg/L cause different health problems such as arthritis, brain effects, cancer, cardiovascular diseases etc. and painful brittle joints, bone deformation in the skeletal system [10]. In the world, a lot of countries such as New Zealand, South Africa, Morocco, Libya, India, Algeria, China, Egypt, Iran, Jordan and Turkey suffer from fluorosis because they consume fluoride-rich waters as drinking water is widely available [18,19]. Therefore, fluorosis is an important health issues for many countries and affects millions of people in many geographies around the globe. Although the world's water resources are limited, with the increasing population, these resources have been widely used for drinking and irrigation purposes. Uncontrolled flowing surface waters are also utilized by people in Gümüşhane and its surroundings especially in areas with low population density, as in many locations of the world. The detailed investigation of the physicochemical properties and quality parameters of these waters consumed without any research in the region is of great importance for human health. Such a detailed study on water quality parameters is carried out within the scope of another study, and in this study the F^- content of the waters of the region was studied. Considering the general geological features of the study area and the geochemical processes it is exposed to, the F^- content of the waters of the region has been considered important and it has been concluded that it contains risks for human and environmental health. Therefore, this study aimed to investigate some water quality and geochemical parameters of surface waters in Gökdere Drainage Network of Souteast of Gümüşhane in Northeast Turkey, with special focus on assessing the risk of fluoride risk and the origin of fluorine in the surface water as a component that declares and limits the use of this water.

1.1. Study area

Gökdere Drainage Network is situated souteast of the Gümüşhane province in North East Turkey, between longitudes 553320E and 4463289N, and latitudes 561776E and 4469433N. According to Meteorological Service of Turkish State data, the climate is inland in the region, with mild/hot and dry summers and cold and snowy winters. The region's average temperature ranges from -6.4 to -5.0 °C in winter and from 15.5 to 19.1 °C in summer. The mean annual maximum of daily air temperatures is 17.9°C between 1967 and 2017. The annual rainfall is 457.6 $kg.m^{-2}$ on average (1967 to 2017).

Surface waters subject to the study are mainly Gökdere and Beyçam Streams and their tributaries. The main streams, the Gökdere and Beyçam, extend from southeast to northwest in the center of the two main valleys extending obliquely to each other and meet at the intersection of the valleys Fig. 1. Akgedik, Düğünyazı, Nazlıçayır, Beyçam and Gökdere are representative sub-drainage networks for study of fluoride risk areas. There are totally 17 samples location in the region.

1.2. Geological setting

The geology of the region, including the study area, includes a small summary of the geology of a significant part of the Eastern Black Sea Region [25–29]. The basement of Gümüşhane and its environs is composed of Kurtoğlu Metamorphics [30] and cut by unmetamorphized granitic plutons [31–34]. The metamorphic rocks outcrop east-southeast of the study area. Gümüşhane Granitoid is exposed in a very large area to the south of the study area, although it is mainly exposed in the center of Gümüşhane. This rock is composed of K-feldspar granites in the study area. The basement rocks are unconformably overlain by the Early-Middle Jurassic volcani-clastic Şenköy formation [35–36]. The volcano-clastic unit passes upwards into the Late Jurassic and Early Cretaceous shallow platform carbonate rocks called as Berdiga formation by [37]. Berdiga formation outcrops in the north-northeast of the area. These carbonates are conformably overlain by Late Cretaceous clastic units, called Kermutdere formation by [38]. The Kermutdere formation, which outcrop at the Çukut, Tamzı and Kovans villages in the northeast of the study area, starts with sandy limestone at the base, passes upward to red pelagic limestones and then to turbiditic series consisting of sandstone, siltstone marl and limestones (Fig. 1). All these units are cut by Late Cretaceous intrusions [39–45] at the northeast of Gümüşhane. Late Cretaceous plutonic, volcanic and sedimentary rocks are stratigraphically overlain by Middle-Late Eocene volcanic and volcanic-clastic rocks in the north-northeast of the study area, called Alibaba formation [38, 46–50]. The Alibaba formation, which crops out in the north-northeast of the area, is cut by co-aged calc-alkaline granitoids [51–54]. Actual travertine occurrences and mineral water leaks related to these occurrences are also observed in different parts of the study area. In addition, weak hydrothermal alteration development in different lithological units in different parts of the area, arenization etc. products as addition to hydrothermal alteration in granitic rocks are also observed [55–56].

1.3. Materials and methods

In summer 2017, a total number of 17 surface water samples in the area were taken from representative location distributed throughout sub-drainage network belong to five villages of Gümüşhane (Fig. 1). Considering the drainage network of the the area, 7 samples from Gökdere village, 3 samples from Beyçam, Akgedik and Düğünyazı villages and 1 sample from Nazlıçayır village were collected.

Since the region is a rural area and the increase in population in the region in the summer period, anthropogenic effect will also increase on surface water. In addition, due to evapotranspiration contamination and increase in ion concentrations would be high, summer was preferred for sampling. The geographical coordinates of sampling point were determined by a pocket-GPS tools at each sampling site. Unstable hydro-chemical parameter including pH, total dissolved solids (TDS), oxidation–reduction potential (ORP), Electrical conductivity (EC) and temperature of the surface water were analyzed in situ in a flow-through cell using a multi-parameter water quality meter (U-50, Horiba, Japan) that was calibrated previously.

The surface water samples were taken and filtered (0.45 lm) in new prerinsed 100 mL polyethylene bottles. The samples were stored at 4 °C in the dark environment until analyzed. Sub-samples for cation analysis were acidified to a pH<2by ultrapure nitric acid. The cations and anions were determined by the Central Laboratory of Gümüşhane University, with ion chromatography and inductive-coupled plasma-mass spectrometry (ICP-MS). Quality control for analysis was achieved by using duplicate sub-samples and standard materials, and by preparation and analysis of blank samples. Later, the obtained data were statistically evaluated, and the results were given Table 1 and 2.

EC of the water samples is used to obtain the total dissolved solids (TDS) concentration in water by dividing the EC values expressed in lS/cm by 1.56 [57]. Bicarbonate ion concentration of the samples were measured by volumetric titrations using 0.01 N H_2SO_4. Sulfate was measured using turbidity meter and chloride ion concentration was determined by volumetric titrations using $AgNO_3$. The results obtained from these analyzes will be evaluated in detail by taking into account regional and seasonal changes in another study. In this study, fluoride contents of surface waters in the field have been investigated by considering the recent environmental fluoride awareness. In this study piper diagram, correlation coefficients and descriptive statistics are given. GW-Chart program [58] is used to plot the Piper diagram. IBM-SPPS v.21 software was used for statistical analysis of the data. The fluoride concentrations of surface waters in the region have been determined by potentiometric method using fluoride ion selective electrode and their result and descriptive statistic were given in Table 3.

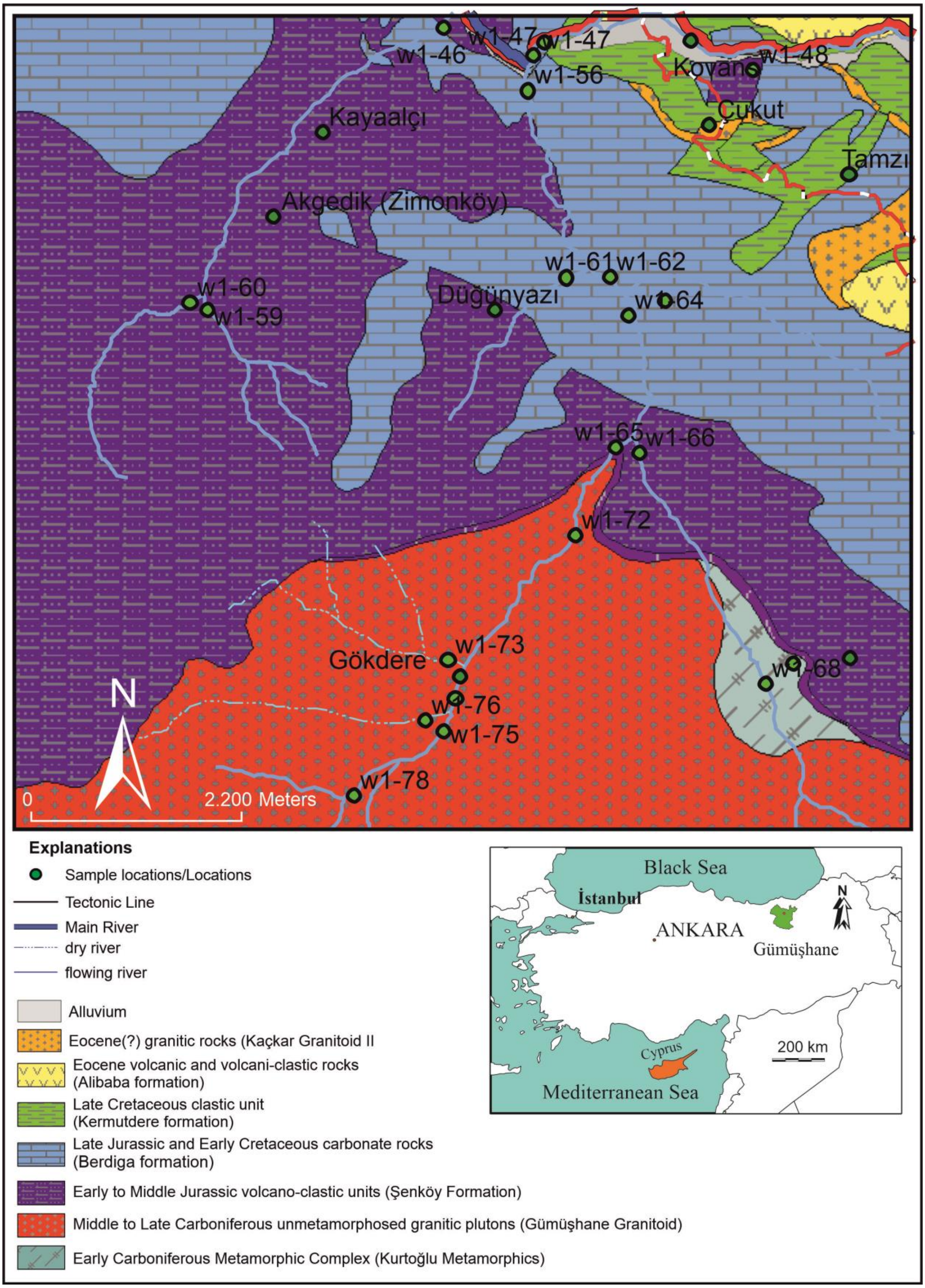

Figure 1. The geological map of the area and sampling points (after [47]).

2.Results and discussion

The statistics for various chemical and physical parameters of surface water such as mean, maximum, minimum, kurtosis, skewness, standard deviation (std.dev.), variance (var.) and significant level for normality test are given in Table 1 and 2. The normality of the data was checked using tests of one sample Kolmogorov–Smirnov and Shapiro-Wilk. As the number of data remained below 20, the Shapiro-Wilk test results were taken into account. The Shapiro-Wilk test results show that pH, Ca, M, Na, K, and HCO_3 are normally distributed (significant levels are 0.14; 0.43; 0.54; 0.14; 0.42; 0.40 respectively) (Table 2). Others, especially F and Cl show non-normality that the kurtosis and skewness parameters of them in Table 1 also show compatibility the non-normality of the data.

pH of the samples varies between 7.96 and 8.64 mean that waters are mainly alkaline. The mean concentration of major anions and cations in surface water is: $K^+ < Cl^- < F^- < Na^+ < Ca^{2+} < SO_4^{2-} < Mg^{2+} < CO_3^- < HCO_3^-$. Maximum and minimum concentrations of fluoride are 0.19 mg/L in Düğünyazı drainage network in carbonate rocks and 9.87 mg/L in Beyçam drainage network in Kurtoğlu metamorphic rocks (gneisses). The average of fluoride concentrations is 3.90 mg/L (Table 3). HCO_3^- is a dominant anion ranging 103.82 and 171.17 mg/L. Sulfate ranges between 3.00 and 17.00 mg/L, Cl^- ranges between 1.7 to 4.55 mg/L, while magnesium concentration as the dominant cation, ranges from 7.05 to 22.85 mg/L. Sodium concentration ranges from 1.75 to 7.69 while potassium concentrations are notably low, ranging from 0.04 to 1.96 mg/L.

As mention above, according to Turkey Surface Water Quality Regulation 2016 and the Reports 1994, 2004 of the World Health Organization's Drinking Water Quality Parameters [22–24], the recommended concentration of fluoride in drinking water is 1.5 mg/L. The comparison between fluoride concentrations of the area and recommended concentration shows that about 58.82% of samples (10 samples) exceed the recommended value (Table 3). However, the permissible limits of fluoride concentrations are proposed to vary with climatic conditions [19, 59] (Table 4), because the amount of water consumed and consequently the amount of fluoride ingested being influenced primarily by air temperature. In the study area, according to Meteorological Service of Turkish State, annual average of maximum daily air temperature is 17.9 and upper range of recommended fluoride content in USPHS 1962 is 1.2 mg/L. The permissible fluoride concentration according to the climatic conditions was found to be above this limit in the study area in 10 samples locations.

Table 1. Descriptive statistics of some anion and cation of surface water.

	Min.	Max.	Mean	Std. Dev.	Var.	Skewness		Kurtosis	
						Statistics	Std. Er.	Statistics	Std. Er.
F	0.19	9.87	3.90	3.55	12.58	0.25	0.55	-1.47	1.06
pH	7.96	8.64	8.23	0.18	0.03	1.00	0.56	0.77	1.09
Temp	24.20	25.10	24.36	0.22	0.05	2.93	0.56	10.07	1.09
Hardnes	111.20	276.40	159.16	49.96	2495.57	1.12	0.56	0.54	1.09
Ca	3.78	10.13	7.39	2.17	4.70	-0.77	0.79	-0.07	1.59
Mg	7.05	22.85	13.29	5.22	27.28	0.83	0.79	1.21	1.59
Na	1.75	7.69	5.60	1.93	3.72	-1.44	0.79	2.78	1.59
K	0.07	1.96	1.02	0.71	0.50	0.13	0.79	-1.77	1.59
CO_3	18.40	27.60	23.00	2.66	7.05	0.00	0.79	3.00	1.59
HCO_3	103.82	171.17	131.88	23.53	553.86	0.32	0.79	0.13	1.59
CL	1.70	4.55	2.82	0.97	0.94	0.71	0.56	-1.02	1.09
SO_4	3.00	17.00	7.89	3.93	15.43	1.19	0.56	0.81	1.09
TDS	100.10	306.80	203.73	76.56	5861.81	0.05	0.56	-1.76	1.09

When the bar diagram of the fluoride concentrations of the region is examined, the distribution of fluoride values by region is shown in Fig. 2. It is seen that fluoride concentrations are higher than the control values at 6 sample points in Gökdere village. at all sampling points in Beyçam village and 1 sampling point in Akgedik village while Düğünyazı and Beyçam sampling locations's concentration of fluoride are under control values.

Table 2. Normality test of the data.

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
F	0.26	17.00	0.01	0.86	17.00	0.01
pH	0.17	16.00	0.200*	0.92	16.00	0.14
Temp	0.31	16.00	0.00	0.64	16.00	0.00
Hardnes	0.21	16.00	0.05	0.86	16.00	0.02
Ca	0.30	7.00	0.06	0.92	7.00	0.43
Mg	0.23	7.00	0.200*	0.93	7.00	0.54
Na	0.30	7.00	0.06	0.86	7.00	0.14
K	0.23	7.00	0.200*	0.91	7.00	0.42
CO_3	0.36	7.00	0.01	0.78	7.00	0.02
HCO_3	0.22	7.00	0.200*	0.91	7.00	0.40
CL	0.25	16.00	0.01	0.87	16.00	0.03
SO_4	0.24	16.00	0.02	0.88	16.00	0.04
TDS	0.18	16.00	0.18	0.88	16.00	0.05

*. This is a lower bound of the true significance./ a. Lilliefors Significance Correction

Table 3. F^- concentration of the study are according to sub-drainage areas.

Locations	ID	F^- (mg/L)
Akgedik	w-46	0.33
	w-57	9.33
	w-60	0.21
Düğünyazı	w-56	0.23
	w-61	0.19
	w-62	0.26
Nazlıçayır	w-63	0.22
Beyçam	w-66	6.95
	w-67	9.87
	w-68	6.48
Gökdere	w-64	3.81
	w-65	6.69
	w-72	5.76
	w-73	5.26
	w-74	5.24
	w-75	0.29
	w-76	3.20
Mean		**3.78**
Median		**4.53**
Std. Deviation		**3.55**
Min.		**0.19**
Max.		**9.87**
LOQ		**0.01**

Table 4. Range of recommended fluoride concentration as per [59].

Annual mean of max. daily air temperature (^oC)	**Recommended fluoride concentration (mg/l)**		
	Lower	Optimum	Upper
10–12	0.90	1.20	1.70
12.1–14.6	0.80	1.10	1.50
14.7–17.7	0.80	1.00	1.30
17.8–21.4	0.70	0.90	1.20
21.5–26.2	0.70	0.80	1.00
26.3–32.5	0.60	0.70	0.80

The fluoride toxicity is affected by high ambient temperature, alkalinity, and by calcium and magnesium contents of water. So, correlation coefficients between these parameters were calculated. Since the parameters such as major cations and anion (such as F, Cl etc.) generally did not show a normal distribution. the correlation of the elements with each other was examined by calculating the Spearman's rho correlation coefficients (Table 5). The correlation coefficients range between -1 and +1. If it is +1, it can be said that there is an excellent positive linear relationship between the variables. If it is -1 then there is an excellent negative linear relationship between the variables. The zero (0) means there is no linear relationship between the variables. There was no negative or positive relationship between fluoride and other parameters. As to chloride, there was a weak positive correlation between chloride and pH and hardness, while a weak negative correlation was found with Mg, Ca, K (Table 5). As a general trend, fluoride concentrations are high in alkaline waters [60]. Although this correlation could not be determined in the correlation analysis due to the fact that the pH values were close to each other and the number of samples was low, high fluoride concentrations confirmed this trend for the area as the waters in the area were considered alkaline (pH of the waters in the area ranged from 7.96 to 8.64).

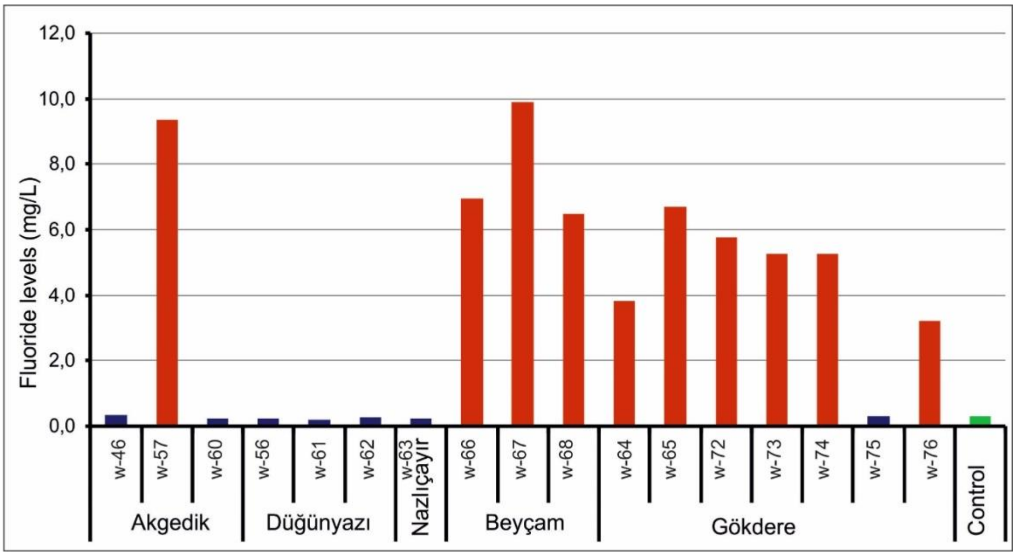

Figure 2. the bar diagram of the fluoride concentrations of the study area.

Piper diagram show the type of waters in region that it is a trilinear representation of cation, anion, and the proportion of combined cation and anion proportion and is used for two main purposes, is to classify water type and is to determinate if a series of water compositions represent the mixing of two end member [61]. In plotting the piper diagram, the relative abundance of major cations with unit concentrations is plotted on the cation triangle and the relative abundance of major anions is also plotted on the anion triangle. The two data points on the cation and anion triangles are then combined into the quadrilateral area that shows the overall chemical property of the water (Fig. 3).

In this study, using a Piper diagram, the waters were classified according to their content of major anions and cations. The piper diagram show that carbonate type of water exists (Fig.3). Also. the plot shows that the waters are is categorized in the Mg/SO4 and Mg/HCO3 zone. Although the surface waters did not differ according to the sub-drainage networks in the field. the fluoride concentrations were remarkably high in the granitic rocks and gneisses (metamorphic rocks) (Fig.1 and Fig.3). So, it can be said that the spatial distribution of the surface waters with high fluoride is controlled by the host rock that outcrop in the area. As mentioned, fluorite is the main fluorine mineral occurring in nature. especially in magmatic and metamorphic rocks and is commonly found as an accessory in mainly granitic rocks and granitic gneiss. Rock-forming minerals such as micas (both biotite and muscovite and also illite), amphiboles and apatite contain moderate amounts of fluorine in their structure [4, 62]. F- enrichment in waters is caused by water-rock interactions in the surface or aquifer.

Table 5. Spearman's rho correlation coefficients (r) of the major ions, cation, F, Cl, pH, hardness and TDS.

		F	pH	Hardness	Ca	Mg	Na	K	CO_3	HCO_3	CL	SO_4	TDS
Spearman's rho	F	1.00											
	pH	-0.27	1.00										
	Hardnes	0.00	0.37	1.00									
	Ca	0.04	-.786*	-0.14	1.00								
	Mg	0.07	-0.71	-0.21	0.964**	1.00							
	Na	-0.11	0.00	0.11	0.46	0.50	1.00						
	K	0.11	-0.29	0.18	0.57	0.64	0.21	1.00					
	CO_3	0.13	-0.67	-0.40	0.27	0.27	-0.67	0.13	1.00				
	HCO_3	-0.27	-0.11	-0.56	-0.24	-0.29	-0.22	-.873*	0.20	1.00			
	CL	0.02	0.541*	0.45	-0.46	-0.57	-0.61	-0.54	0.13	0.42	1.00		
	SO_4	0.11	0.28	0.19	-.786*	-.857*	-0.21	-0.36	-0.53	-0.11	0.17	1.00	
	TDS	-0.19	.638**	.709**	-0.63	-0.68	-0.14	-0.58	-0.47	0.22	.866**	0.24	1.00

***. Correlation is significant at the 0.05 level (2-tailed).**

****. Correlation is significant at the 0.01 level (2-tailed).**

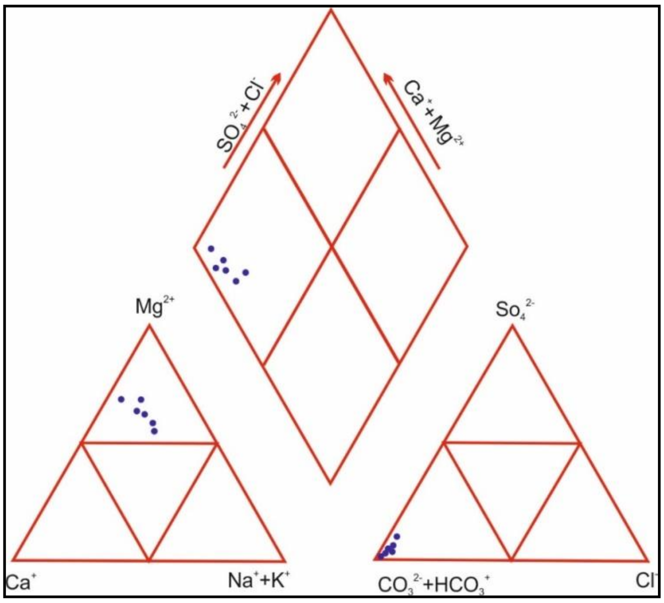

Figure 3. Piper diagram indicating of water types.

Also, as a result of hydrothermal alteration occurring clays in the rocks, are enriched with minerals such as sericite and illite (micas). Dissolution of fluorite, anion exchange with micaceous minerals and the release of fluoride from these minerals also result in the enrichment of fluoride in waters [62].

Considering this data, the main reason for the high concentration of fluoride in surface water in the area was predicted as this process. There have been many recent studies of high fluoride contents in both surface waters and groundwater [1, 9, 18, 20, 60, 63, 64].

In the study conducted by [18] in Muteh area of Isfahan-Iran, the source of fluoride toxicity was investigated. Determined by authors that fluoride concentration in this area was up to 9.2 mg/L with highest fluoride concentration at Muteh gold mine. In order to determine the source of fluoride in that area, the data were analyzed with factor analysis by the researchers. The authors concluded that the source of fluoride is of geological origin and that fluoride-bearing minerals in metamorphic and granitic rocks are amphibole and mica group. [20] carried out a study on fluoride chemistry of groundwater in Inner Mongolia and Shanxi, China. They applied principal component analysis to examine the main factors in the F- geochemistry in these regions, two severely F-affected areas in China. They found that F concentrations is in the range 0.3–5.6 mg/L and concluded that F occurrence in Shanxi could have been the result of mineral weathering and water–rock interactions in the aquifer while in Inner Mongolia may have been attributed to multiple effects including water–rock interaction processes, mining activities and agriculture.

Researchers [1] carried out a study on geochemical processes controlling the high fluoride contents in groundwaters in Taiyuan basin, northern China. They determined high fluoride groundwater with F^- concentration up to 6.20 mg/L in area. According to results of their regional hydrogeochemical investigation, hydrolysis of silicate minerals, evaporation and cation exchange are responsible for the increase in average contents of major ions in region’s groundwater. They concluded that in the recharge and flow-through area of the northern Taiyuan basin, interactions between groundwater and fluoride-bearing minerals were the major factor for high F^- concentration, whereas in the discharge area of the northern basin, the evaporation as well as the mixing of karst water had greater contribution to high fluoride concentration.

In another study conducted by [60], researchers studied geochemical source and spatial distribution of fluoride in groundwater in Taiyuan basin (China). According to their results of the geochemical model, they concluded that evaporation was the important factor responsible for the enrichment of F^- in their study area. In addition. F^- concentration in groundwater was controlled by the dissolution of the fluorine minerals such as fluorite. The authors suggested that the spatial distribution of high fluoride groundwater is also closely related to the host rock and geomorphology of the area. When the results of this study and other studies related to the subject are evaluated together. it is seen that high fluoride concentration in surface waters in the region are directly related to geological processes. Mineralogical content. water-rock interactions. alteration and weathering processes of the rocks on which surface waters flow are also effective in the enrichment of fluoride in waters.

3.Conclusions

The aim of this study was to understand the status and geochemistry of fluoride contents of surface waters and toxicity risk in the Gökdere valley drainage network. In the region, it is determined that fluoride contents are between 0.19 mg/L and 9.87 mg/L with average 3.90 mg/L. 58.82% of the sample exceed the Turkey Surface Water Quality Regulation 2016 and the Reports 1994, 2004 of the World Health Organization's Drinking Water Quality Parameters’ recommended value [22–24] 1.5 mg/L. However, the concentration of fluoride in waters can be generally controlled by many factors, both anthropogenic and natural, including phosphate fertilizer containing fluoride, geothermal water mixing with meteoric waters and the dissolution of fluorite, apatite and F-bearing silicate minerals such as micas etc. In this study area, it was seen that fluoride concentrations in the region’s surface water are result of geological and geochemical processes. So, high fluoride concentration is related to the occurrence of granitic (plutonic) and granitic gneiss (metamorphic) rocks, containing fluoride-bearing minerals such as apatite, biotite, amphibole and mica etc. Leaching of fluoride from these host rocks, evapotranspiration, longer water-rock interaction time are major factors affecting fluoride concentration in surface water in the region. Although metamorphic rocks in the region do not outcrop as granitic rocks. however, they outcrop in a wide area. But granitic rocks give a very wide outcrop in the region. Considering that the high fluoride concentrations of surface waters in the study area are dominantly caused by granitic and metamorphic rocks. It is thought that surface waters and even ground waters in many places in the region have high fluoride concentration risk and toxicity.

Therefore, it is considered necessary to investigate the fluoride risk and toxicity of surface groundwater in the region. especially drinking water.

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References

[1] Guo Q, Wang Y, Ma T, Ma R. Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China. Journal of Geochemical Exploration 2007; 93:1–12.
[2] Kabata-Pendias A, Pendias H. Trace elements in soils and plants. Boca Raton, FL, USA: CRC Press Inc; 2001.
[3] Jacks G, Bhattacharya P, Chaudhary V, Singh KP. Controls on the genesis of some high-fluoride groundwater in India. Applied Geochemistry 2005; 20:221–228.
[4] Ozsvath DL. Fluoride concentrations in a crystalline bedrock aquifer Marathon County, Wisconsin. Environmental Geology 2006; 50:132–138.
[5] Burnham CW. Magmas and hydrothermal fluids. In: Barnes HL (ed.), Geochemistry of hydrothermal ore deposits. New York: Wiley; 1997:61–123.
[6] Harrison PTC. Fluoride in water: a UK perspective. Journal of Fluor Chemistry 2005; 126:1448–1456.
[7] Kim K, Jeong GY. Factors influencing the occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula. Chemosphere 2005; 58:1399–1408.
[8] Rafique T, Naseem S, Bhanger MI, Usmani T. Fluoride ion contamination in the groundwater of Mithi sub-district, the Thar Desert, Pakistan. Environmental Geology 2008; 56:317–326.
[9] Kim Y, Kim JY, Kim K. Geochemical characteristics of fluoride in groundwater of Gimcheon, Korea: Lithogenic and agricultural origins. Environmental Earth Sciences 2011; 63:1139–1148.
[10] Ayenew T. The distribution and hydrogeological controls of fluoride in the groundwater of central Ethiopian rift and adjacent highlands. Environmental Geology 2008; 54:1313–1324.
[11] Kundu MC, Mandal B. Agricultural activities influence nitrate and fluoride contamination in drinking groundwater of an intensively cultivated district in India. Water Air Soil Pollut 2009; 198:243–252.
[12] Ayoob S, Gupta A. Fluoride in drinking water: a review on the status and stress effects. Critical Reviews in Environmental Science and Technology 2006; 36:433–487.
[13] Handa B. Geochemistry and genesis of fluoride-contamination ground waters in India. Ground Water 1975; 13:275–281.
[14] Corbett RG, Manner BM. Fluoride in the ground water of northeastern Ohio. Ground Water 1984; 22:1317.
[15] Sarma DRR, Rao SLN. Fluoride concentrations in ground waters of Visakhapatnam, India. Bulletin of Environmental Contamination and Toxicology 1997; 58:241.
[16] Wang Y, Reardon EJ. Activation and regeneration of a soil sorbent for defluoridation of drinking water. Applied Geochemistry 2001; 16:531–539.
[17] Krunić O, Parlić S, Polomčić D, Jovanović M, Erić S. Origin of fluorine in mineral waters of Bujanovac valley (Serbia, Europe). Geochemistry International 2013; 51:205–220.
[18] Keshavarzi B, Moore F, Esmaeili A, Rastmanesh F. The source of fluoride toxicity in Muteh area, Isfahan, Iran. Environmental Earth Sciences 2010; 61:777–786.
[19] Meenakshi VK, Garg K, Renuka AM. Groundwater quality in some villages of Haryana, India: focus on fluoride and fluorosis. Journal of Hazardous Materials 2004; 106:85–97.
[20] Hu S, Luo T, Jing C. Principal component analysis of fluoride geochemistry of groundwater in Shanxi and Inner Mongolia, China. Journal of Geochemical Exploration

2013; 135:124–129.
[21] Zango MS, Sunkari ED, Abu M, Lermi A. Hydrogeochemical controls and human health risk assessment of groundwater fluoride and boron in the semi-arid North East region of Ghana. Journal of Geochemical Exploration 2019; 207:106363.
[22] WHO. Fluorides and Oral Health: Report of a WHO Expert Committee on Oral Health Status and Fluoride Use, Technical Report Series 846, World Health Organization, Geneva. 1994.
[23] WHO. Drinking-water Background document for development of WHO Guidelines for Drinking-water Quality. Geneva: World Health Organization. 2004.
[24] YSKY. Yerüstü Su Kalitesi Yönetmeliği, Resmi Gazete Sayı: 29797, Tarih:10 Ağustos 2016. 2016.
[25] Vural A. Evaluation of Soil Geochemistry Data of Canca (Gümüşhane-Ne Turkey) By Processing Inverse Distance Weighting and Kriging Interpolation Methods-First Findings. Bulletin of the Mineral Research and Exploration 2019; 158:195–216.
[26] Vural A, Ersen F. Geology, mineralogy and geochemistry of manganese mineralization in Gumushane, Turkey. Journal of Engineering Research and Applied Science 2019; 8:1051–1059.
[27] Vural A, Kaygusuz A, Dönmez H. Geological, Geochemical and Geochronological Investigation of Avliyana Antimonite Mineralization. 8th Geochemistry Symposium. 02-04 May 2018 Antalya: 2018:123–124.
[28] Vural A, Kaygusuz A. Paleozoyik Yaşlı Artabel Plütonunun (Gümüşhane) Petrografik ve Jeokimyasal Özellikleri. 3. Uluslararası GAP Matematik-Mühendislik-Fen ve Sağılık Bilimleri Kongresi. 29 Kasım-01 Aralık 2019. Şanlıurfa, Türkiye: İKSAD; 2019.
[29] Vural A. Investigation of the radiation risk to the inhabitants in the region close to the hydrothermal alteration site, Gümüşhane/Turkey. Journal of Engineering Research and Applied Science 2019; 8.
[30] Topuz G, Altherr R, Schwarz WH, Dokuz A, Meyer HP. Variscan amphibolite-facies rocks from the Kurtoğlu metamorphic complex (Gümüşhane area, Eastern Pontides, Turkey). International Journal of Earth Sciences 2007; 96:861–873.
[31] Yılmaz Y. Petrology and structure of the Gümüşhane granite and surrounding rocks, NE Anatolia. 1972.
[32] Vural A, Kaygusuz A. Petrology of the Paleozoic Plutons in Eastern Pontides: Artabel Pluton (Gümüşhane, NE Turkey). Journal of Engineering Research and Applied Science 2019; 8.
[33] Kaygusuz A, Arslan M, Siebel W, Sipahi F, Ilbeyli N. Geochronological evidence and tectonic significance of Carboniferous magmatism in the southwest Trabzon area, eastern Pontides, Turkey. International Geology Review 2012; 54:1776–1800.
[34] Kaygusuz A, Arslan M, Sipahi F, Temizel İ. U-Pb zircon chronology and petrogenesis of Carboniferous plutons in the northern part of the Eastern Pontides, NE Turkey: Constraints for Paleozoic magmatism and geodynamic evolution. Gondwana Research 2016; 39:327–346.
[35] Kandemir R. Gümüşhane ve Yakın Yörelerindeki Erken-Orta Jura Yaşlı Şenköy Formasyonu’nun Çökel Özellikleri ve Birikim Koşulları. Trabzon: 2004.
[36] Eren M. Gümüşhane-Kale Arasının Jeolojisi ve Mikrofasiyes incelemesi. Trabzon: 1983.
[37] Pelin S. Alucra (Giresun) Güneydoğu yöresinin petrol olanaklan bakımından jeolojik incelemesi. Trabzon: Karadeniz Teknik Üniversitesi Yayını, Yayın No. 87; 1977.
[38] Tokel S. Stratigraphical and volcanic history of Gümüşhane region. 1972.
[39] Kaygusuz A, Siebel W, Şen C, Satır M. Petrochemistry and petrology of I-type granitoids in an arc setting: The composite Torul pluton, Eastern Pontides, NE Turkey. International Journal of Earth Sciences 2008; 97:739–764.
[40] Kaygusuz A, Siebel W, İlbeyli N, Arslan M, Satır M, Şen C. Insight into magma genesis at convergent plate margins. A case study from the eastern Pontides (NE Turkey). Neues Jahrbuch Für Mineralogie 2010; 187/3: 265–287.
[41] Kaygusuz A, Arslan M, Siebel W, Şen C. Geochemical and Sr-Nd isotopic characteristics of post-collisional calc-alkaline volcanics in the Eastern Pontides (NE Turkey). Turkish Journal of Earth Sciences 2011; 20: 137–159.
[42] Kaygusuz A, Şen C. Calc-alkaline I-type plutons in the eastern Pontides, NE Turkey: U-Pb zircon ages, geochemical and Sr-Nd isotopic compositions. Chemie der Erde 2011; 71: 59–75.
[43] Kaygusuz A, Aydınçakır E. Petrogenesis of a Late Cretaceous composite pluton from the eastern Pontides: the Dağbaşi pluton, NE Turkey. Neues Jahrbuch Für Mineralogie -

Abhandlungen 2011; 188:211–233.
[44] Sipahi F, Kaygusuz A, Saydam Eker, Vural A, Akpınar İ. Late Cretaceous arc igneous activity: the Eğrikar Monzogranite example. International Geology Review 2018; 60:382–400.
[45] Karslı O, Dokuz A, Uysal İ, Aydın F, Chen B, Kandemir R, Wijbrans J. Relative contributions of crust and mantle to generation of Campanian high-K calc-alkaline I-type granitoids in a subduction setting, with special reference to the Harşit Pluton (Eastern Turkey). Contributions to Mineralogy and Petrology 2010; 160: 467–487.
[46] Arslan M, Aliyazıcıoğlu İ. Geochemical and petrological characteristics of the Kale (Gümüşhane) volcanic rocks: Implications for the Eocene evolution of eastern Pontide arc volcanism, northeast Turkey. International Geology Review 2001; 43:595–610.
[47] Güven İ. Doğu Pontidlerin 1/25000 Ölçekli Kompilasyonu. Ankara: MTA Genel Müdürlüğü; 1993.
[48] Kaygusuz A, Arslan M, Siebel W, Şen C. Geochemical and Sr-Nd isotopic characteristics of post-collisional calc-alkaline volcanics in the Eastern Pontides (NE Turkey). Turkish Journal of Earth Sciences 2011; 20: 137–159.
[49] Aslan Z, Arslan M, Temizel İ, Kaygusuz A. K-Ar dating, whole-rock and Sr-Nd isotope geochemistry of calc-alkaline volcanic rocks around the Gümüşhane area: implications for post-collisional volcanism in the Eastern Pontides, Northeast Turkey. Mineralogy and Petrology 2014; 108: 254–267.
[50] Kaygusuz A, Şahin K. Petrographical, geochemical and petrological characteristics of Eocene volcanic rocks in the Mescitli area, Eastern Pontides (NE Turkey). Journal of Engineering Research and Applied Science 2016; 5 (2): 473-486.
[51] Karslı O, Chen B, Aydın F, Şen C. Geochemical and Sr-Nd-Pb isotopic compositions of the Eocene Dölek and Sarıçiçek Plutons, Eastern Turkey: Implications for magma interaction in the genesis of high-K calc-alkaline granitoids in a post-collision extensional setting. Lithos 2007; 98: 67–96.
[52] Kaygusuz A, Öztürk M. Geochronology, geochemistry, and petrogenesis of the Eocene Bayburt intrusions, Eastern Pontide, NE Turkey: implications for lithospheric mantle and lower crustal sources in the high-K calc-alkaline magmatism. Journal of Asian Earth Sciences 2015; 108: 97–116.
[53] Eyüboğlu Y, Dudas FO, Thorkelson D, Zhu DC, Liu Z, Chatterjee N, Yi K, Santosh M. Eocene granitoids of northern Turkey: Polybaric magmatism in an evolving arc–slab window system. Gondwana Research 2017; 50: 311–345.
[54] Kaygusuz A, Yücel C, Arslan M, Sipahi F, Temizel İ, Çakmak G, Güloğlu ZS. Petrography, mineral chemistry and crystallization conditions of Cenozoic plutonic rocks located to the north of Bayburt (Eastern Pontides, Turkey), Bulletin of the Mineral Research and Exploration 2018; 157: 75-102.
[55] Vural A. Assessment of metal pollution associated with an alteration area: Old Gümüşhane, NE Black Sea. Environmental Science and Pollution Research 2015; 22:3219–3228.
[56] Vural A, Gündoğdu A, Akpınar I, Baltacı C. Environmental impact of Gümüşhane City, Turkey, waste area in terms of heavy metal pollution. Natural Hazards 2017; 88.
[57] Todd DK. Groundwater, hydrology. 2nd ed. New York: Wiley; 1980.
[58] Winston RB. Graphical User Interface for MODFLOW, Version 4: U.S. Geological Survey Open-File Report 00-315 2000:27.
[59] USPHS. Public Health Service Drinking Water Standards (1962) USPHS, Publication 956. USGPO, Washington, DC, p 1962. 1962.
[60] Li X, Hou X, Zhou Z, Liu L. Geochemical provenance and spatial distribution of fluoride in groundwater of Taiyuan basin, China. Environmental Earth Sciences 2011; 62:1635–1642.
[61] Eby GN. Principles of environmental chemistry. Thomson Edmunds WM; 2004.
[62] Rukah YA, Alsokhny K. Geochemical assessment of groundwater contamination with special emphasis on fluoride concentration, North Jordan. Chemie Der Erde Geochemistry 2004; 64:171–181.
[63] Young SM, Pitawala A, Ishiga H. Factors controlling fluoride contents of groundwater in north-central and northwestern Sri Lanka. Environmental Earth Sciences 2011; 63:1333–1342.
[64] Mamatha P, Rao SM. Geochemistry of fluoride rich groundwater in Kolar and Tumkur Districts of Karnataka. Environmental Earth Sciences 2010; 61:131–142.