Geochemical assessment of groundwater quality with special emphasis on fluoride in Tabasein Plain, Eastern Iran

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Abstract
The aim of this research was the geochemical assessment of the groundwater quality and the evaluation of the distribution pattern of fluoride concentration in water resources of the region and their connection with the prevalence of dental fluorosis occurrence in the study area. To achieve to this goal six sediment and 22 water samples were taken and analyzed. Fluoride and phosphorous concentration were remarkably high (1400 ppm and 6231 ppm respectively) in basaltic-andesite unit. Water resources located in the southern part of old lake had the highest TDS (>6300mg/L) compared with the others. Fluoride content differ from 0.64-1.71mg/L and in 27% water samples were higher than allowable amount expressed by WHO (1.5mg/L). The health effects of fluoride were investigated on 210 students at the age of 7-16 years old. The results indicated that the fluoride concentration increased in the vicinity of the igneous rocks in water resources and also increased with the time residence. The concentration of fluoride in groundwater indicated the prevalence of dental fluorosis occurrence in the study area. The intensity of the disease revealed a meaningful correlation with the age and the male gender.

Keywords: *Fluoride, Fluorosis, Geochemical, Groundwater, Tabasein plain.*

Introduction

The quality of the aquifer in arid and semi-arid regions has long been under consideration. In spite of the importance, there are still few information concerning the procedure of the water quality changes from the upstream towards the downstream. This is due to the complexity and the existence of various factors which control the quality of water (Jalali, 2009). The principal factors which control the quality of water are the chemical components of the precipitations, the soil, the minerals and the geological formations (Andre et al. 2005). The chemical composition of the groundwater is controlled by the geochemical reactions between water and soil in ventilation and saturation zone, temperature, pressure, and the age of aquifer (Nandimandalam, 2012). The quality of groundwater indicates some important information regarding the contact area in the past and present time (Appelo & Postma, 1993). In areas without industrial and agricultural activities, the determination of structural geology and mineralogy of the study area would greatly help the assessment of the correlation between the ground features and the quality of water in areas being sought.

Recently, in comprehensive hydro-chemical studies, besides the measurements of major anions and cations concentrations, some other anions and cations such as fluorides, nitrates which are influential on human health are being considered (Reimann & Banks, 2004).

Fluoride is an element that has relatively high frequency in the earth crust. Fluoride is the most electronegative element in Mendeleev Periodical Table and 13^{th} abundant element in the earth crust. Its Clarke is 585 ppm (Bowen, 1979; Hem, 1989; Weinstein & Davison, 2003). Fluoride content of acidic and intermediate rocks is generally more in comparison with basic and ultrabasic rocks. (Baily 1977; Naseem *et al.,* 2010). Based on available literatures, fluoride bearing minerals such as Flour apatite, apophyllite, phlogophite, illite, hydromuscovite, biotite, chlorite, tourmaline, hornblende, … are usually found in acidic rocks (pegmatite and granite), intermediate rock (andesite) and clay dominated units (Madhavan & Subramanian, 2002; Kumar & Saxena 2011; Raju *et al.*, 2013). Jacks *et al.,* (2005) also found very high concentrations of fluoride in calcrete samples collected from arid areas of the Indian granitic terrain. Sedimentary horizons also have apatite as an accessory mineral and fluorite also often occurs as cement in some sandstones (Vikas *et al.,* 2012). Some quantity of fluoride in groundwater is contributed from hydration of the above minerals present in the clay horizons. The presence of fluoride in water is mostly due to the natural contamination (Handa. 1975; Saxena & Ahmed 2001; Raju *et al.,* 2013).

The procedure of the fluoride entrance in the natural water environment is dependent on the leaching of fluoride–bearing minerals in natural water (WHO, 1996, 2006; Kalinic *et al.,* 2005; Chae *et al.,* 2007; Mesdaginia *et al.,* 2010). The correlation between the water fluoride concentration and the main anions and cations has been studied by some researchers (Gupta et al. 2006, Hamzaoui-Azaza *et al.,* 2009, Ferriera *et al.,* 2010; Raju *et al.,* 2013). Then fluoride content in water resources that are in contact with sediments and rocks with high fluoride concentration is higher compared with other water resources (Fregnasted *et al.,* 2001, Carrillo *et al.,* 2002). Fluoride element is essential for the growth of bones and the forming of teeth in human bodies (Fung *et al.,* 1999; Shomar *et al.,* 2004). Although the need of human body to fluoride has been proved, the amount of the need depends on so many factors including climate, water consumption, gender and the exceeding fluoride doses would create some problems in human body particularly in the dental textures (Lijun *et al.,* 2000). The World Health Organization (WHO, 2006) prescribes a fluoride concentration of 1.5 mg/L as the maximum permissible limit in drinking water. The negative effects of fluoride on human teeth due to the dietary intake of more than 6 milligrams per day have been proved. It has also been stated that the dietary intake of more than 14 milligrams per day of fluoride has an obvious negative effect on the human body skeleton (Hillier *et al.,* 2000; Peherson *et al.,* 2006; WHO, 2006). The World Health Organization (WHO) has determined the allowed limits of fluoride content in drinking water as 1.5 mg/L (WHO, 2006).

The digesting system of the human body is the main fluoride receiving passage. 70-90 % of the fluoride present in food and water is absorbed by the textures of stomach and intestine and transmitted by blood and ultimately accumulated within teeth and bones (WHO, 1996; Fawell *et al.,* 2006; Meenakshi & Maheshwari, 2008). The prevalence and the severity of the fluorosis are dependent upon the fluoride content of the drinking water, the climate, the environment temperature, the amount of daily water consumption and some other sources (Susheela & Kumar 1991; Madhavan and Subramanian 2006). The investigations on fluorosis revealed that the outbreak of fluorosis occurred while the fluoride concentration in water reached 0.9-1.2 mg/L (Fawell *et al.,* 2006, Meenakshi & Maheshwari, 2006; WHO, 2008).

In Iran the fluoride concentrations in water resources have been studied in some regions , such as Dayer City (Ramezani *et al.,* 2004); Shush aquifer of Khuzestan Country (Nouri *et al.,* 2006); Dashtestan (Dobaradaran *et al.,* 2008); Kuh-e Banan (Poureslami *et al.,* 2008); water distribution networks of Tabas (Shams *et al.,* 2009); Maku (Nadiri *et al.,* 2013); Mute area (Keshavarzi *et al.,* 2010); Boushehr (Battaleb-Looie *et al.,* 2013).

In this research the quality of water resources of the study area (Tabasein plain) was investigated using the geological and hydro-geochemical information of the region. The health effects of fluoride was also studied via the evaluation of the negative effects of fluoride-bearing drinking water on the dental fluorosis among the inhabitants of the region.

Materials and Methods

Study Area

The study area which occupies approximately 950 Km2 is a part of Tabasein plain (south eastern part of the plain) and is located 60 Km southeast of Nehbandan city. The average of the annual precipitations is 98.2 mm, Potential Evaporation (PE) of the study area is 3151mm and the average annual temperature is $22.1^{\circ C}$ which indicate the area as an arid land. The elevation of the study area varies from 751 to 1471m indicated on the topography map (Fig. 1). Based on the latest public census conducted in 2004, the population of the study region was about 4869 people.

The geology map of the study area was shown in figure 2. The area is geologically covered by two distinct lithology of Upper Cretaceous age and Cenozoic age. The lithological units belong to Upper Cretaceous age consists of three types of rocks: ultramafic rocks (cm), some clastic limestones (Kud), basic tuff and chert (ms) and basaltic-andesite flows (kua), as seen in Fig. 2. The main outcrop of ultramafic rocks is located in the west and south western part of the study area. However, there are dispersedly the other outcrops of this unit in east and north part of the study area. Basaltic-andesite flows and the pyroclastic rock units are located in the center and north part of the area. These rocks are severely weathered and faulted. The tertiary rocks formations are mostly sedimentary units such as limestone, marl and sandstone. The occurrences of these units are seen in the south part and north western part of the area as indicated in Fig. 2 .

Sampling

The sediment and water samples were plotted on topography and geology map (Figs. 1 and 2). In this research 22 water samples were taken from three Qanats, one spring, 15 water wells and three samples from a river (Fig. 1) on 28th & 29th April, 2010. Sampling was performed based on APHA (1995) so that all samples from the wells were taken after 10 minutes of pumping on the same day. All samples were filtered through 0.45 µm filter. The electrical conductivity (EC) and pH values were measured in situ using EC-PH, Model wt-410i. The samples were collected in polyethylene vials and immediately taken to the chemistry laboratory of the Rural Water and Wastewater Company in Birjand, Southern Khorasan, Iran. The samples were taken in triplicate and analyzed for anions and cations using ion chromatography (Metrohm, 861 Advanced Compact IC), while the fluoride contents of the samples were measured using SPANDS method with spectrophotometer (DR5000/HACK, LANGE).

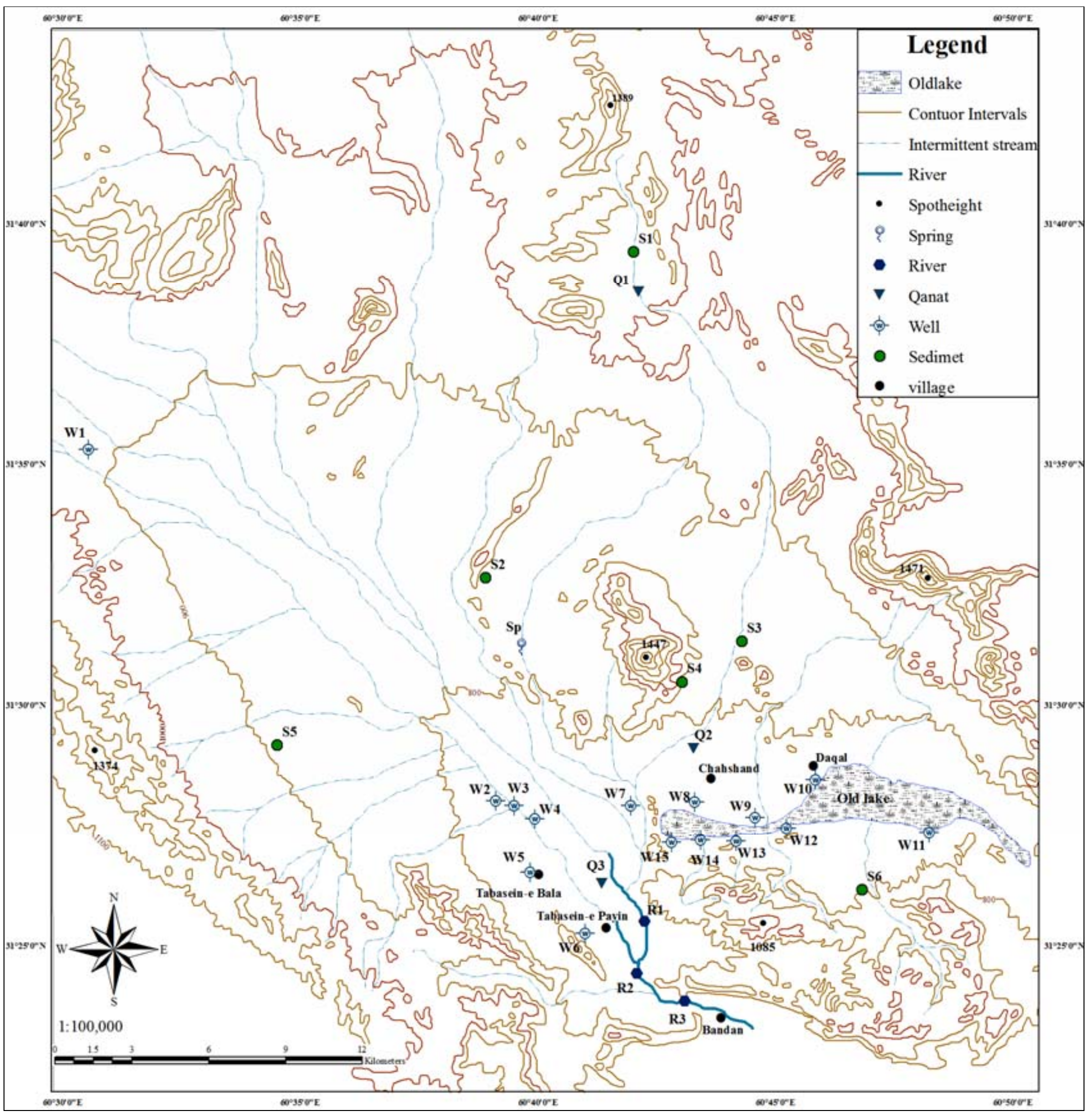

Figure 1. Topography map of the study area and the sample locations (modified after Geological Survey of Iran)

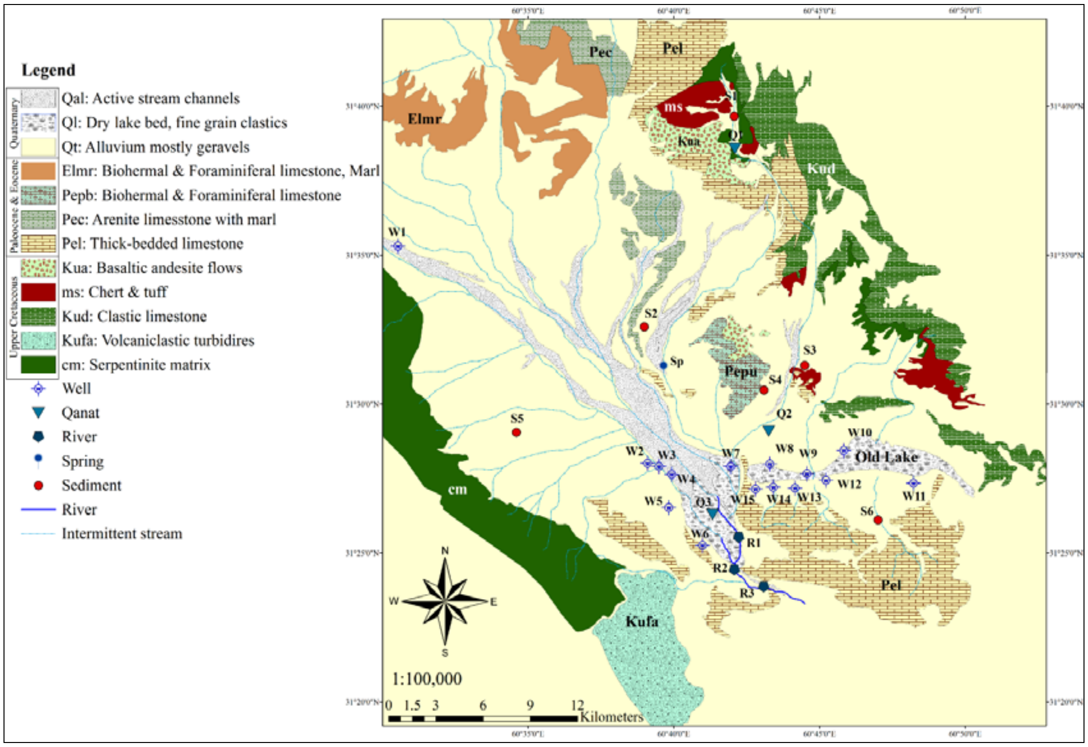

Figure 2. Geological map of the study area and the sample locations (modofied after Geological Survey of Iran, 1:100000 Geology maps of Bandan and North of Bandan)

Alkalinity (HCO_3^-) was measured using phenolphthalein and methyl orange indicator and titration method with H_2SO_4 0.02 N (accuracy= 0.1mg/L). Furthermore, the analytical error range of the charge balance for water samples was calculated and the results was less than ±%5 for all of them.

By studying the topography and geology maps (Figs. 1 and 2), field monitoring, and the results of physico-chemical analysis of water samples, it was found that among all lithological units shown in the maps, the basements of the water resources in the region are consist of six units. Thus, samples were taken from the sediments which were directly derived from these units, plotted on topography and geology map (Figs. 1 and 2). Sediment samples were analyzed through ICP-MS, ICP-OES techniques after acid digestion using Aqua-Regia for 44 elements while fluoride was measured with regard to DIN5104 (accuracy= 100ppm) in Labwest, Australia.

In this research the Dean index was used for the evaluation of the severity of this disease prevalence. In this method which is well-known as Dean Index method, the dental fluorosis is divided into 6 sub-groups (table .1)

Statistics and Software

Statistics and Software have been used for this research are as follows:

The statistical data was presented using Spearman Correlation Coefficient and Cluster Analysis Methods by SPSS 19. Also Arc GIS 9.2, AqQa and PHREEQC were used to present maps, hydrochemical data and Saturation Indices (SI) Respectively.

Results and Discussion

Hydrogeology and Hydro-geochemical Data

Table 2 contains the results of chemical analysis of sediment samples. Ultramafic rocks (cm) contain remarkably higher Mg concentration than other samples due to frequency of ultramafic minerals such olivine (Table. 2). According to the hydrochemical data and field observations and comparing the concentration of Mg in water samples W1, W2, W3, W4, W5, W6 and Q1 with content of Mg in cm unit (Table. 2), this unit covers the basements of W1, W2, W3, W4, W5, W6, and some parts of Q1. This unit is severely serpentinited. The fluoride content in this unit is very low (200 ppm, Table. 2) that could be interpreted by the origin of this unit, generated in the earliest stage of magma genesis (Kabata-Pendias and Mukherjee, 2007). Thus, the fluoride content in the water resources which are in direct contact with these rocks, mentioned above, is relatively low. The basaltic-andesite flows (kua) covers the major part of the basement of Q1, the main source of drinking water for the residents, and minor part of the basement of Q2. The fluoride content in the sediment samples directly derived from this unit is high (1400 ppm, Table. 2) in contrast with other units. Furthermore, the concentration of phosphorous in this unit is absolutely evident; thus, this high concentration is an indicator of presence of fluoride in flour apatite minerals which is common in intermediate igneous rocks (Kabata- Pendias and Mukherjee, 2007). The basic tuff and chert (ms) covers a minor part of basements of Q1 and the major part of the basement of Q2. It contains fluoride of 700ppm concentration (Table. 2) that is relatively high compared with the other samples, except Kua. It seems that shortage of Al, Fe and P content besides high concentration of Ca emphasis fluorite as a source of fluoride in this unit.

Those units in the region which were formed during Cenozoic and connected to the water resources are: thick-bedded limestone unit (Pel), arenite limestone with marl unit (Pec) and biohermal and foraminiferal limestone unit (Pepb). The fluoride content in the sediment samples derived from these units is relatively normal (400 ppm, Table 2) in comparison with the other units. The thick-bedded limestone unit (Pel) is located in the south of the study area and is the basement of W7, W8, W9, W10, W11, W12, W13, W14, Q3, R1, R2, and R3.The arenite limestone with marl unit (Pec) covers the basement of the only spring in the study area (Sp). The biohermal and foraminiferal limestone unit (Pepb) has a bedrock outcrop in the center of the study area and covers a minor fraction of the basement of Q2. The catchment area is very extensive and as it can be seen in topography and geology map (Figs. 1 and 2), it is surrounded by mountain and groundwater is conducted out the catchment via the Bandan River. The Bandan River is the only reliable surface water which is used for agricultural purposes. The origin of this river is in fact the ground water which penetrates to the surface. Besides the Bandan river there are some runoff seasonal water in the east part and south eastern part of the area which flowing into old lake in the east. The most accessible water sources are located in the south and the south eastern part of the study area.

Table 1. Dean's index criteria

Score	Criteria	Definition
0	Normal	Smooth, bright, pale creamy-white translucent surface. No white discoloration of teeth.
1	Questionable	A few white flecks or white spots mainly on the edge of the incisors and cusps.
2	Very mild	Small opaque white areas covering less than 25% of the tooth surface.
3	Mild	Opaque white areas covering less than 59% of the tooth surface.
4	Moderate	All tooth surface are affected; a marked deterioration of occlusal surface; brown stains may be present.
5	Severe	All tooth surface are affected; discrete or confluent holes; brown stains present.

Table 2. The result of chemical analysis of sediment samples

Basement	Samples	Al (%)	Fe (%)	Ca (%)	Na (%)	K (%)	Mg (%)	S (ppm)	F(ppm)	P (ppm)
Pepb	S4	7.20	10.92	10.92	1.66	1.64	2.88	308	400	629
Pec	S2	7.24	4.10	9.69	2.00	1.24	2.76	129	400	465
Pel	S6	5.61	2.61	16.04	1.90	0.88	1.88	263	400	415
Kua	S1	10.66	5.57	6.17	4.67	1.50	3.18	1435	1400	6231
ms	S3	5.57	3.24	14.00	1.63	1.03	2.57	111	700	357
cm	S5	4.50	3.99	7.27	1.23	0.71	11.63	170	200	200

Due to both high rate of evaporation and shortage of precipitation in the study area with the lack of enough joints and cracks in the rock units, it has not been observed any water-bearing formation. Then, all of the water resources are located in Quaternary sediments.

The results of the hydro-chemical analyses of the samples as well as the depths of the wells are presented in Table. 3. The electrical conductivity (EC) and the total dissolved solids (TDS) of the samples in the catchment and north of the study area (W1 and Q1) are clearly less than the other parts. These factors gradually increase from the upstream to the downstream. This could be due to changes in the aquifer media from coarser to finer material toward the downstream that causes the lower groundwater velocity and thus, the longer residence time. The maximum tenors of the TDS are present in the border of the old lake in the south eastern part of the catchment area (W8 to W15). This is due to the occurrences of the residual evaporate sediments, the shallow depths, and the increase of the groundwater age. Na Concentration like Cl, SO_4, EC, TDS & Ca from upstream toward downstream is increasing considerably. The mentioned parameters are followed by the location of water resources in (regard to being upstream or downstream) in contrast with the geochemical compositions of rock units, except Mg content of water resources located in the vicinity of ultramafic units that is higher in comparison with other ions. In the vicinity of ultramafic masses (Q1, W1, W2, W3, W4, W5, W6), Mg (meq/L) has higher concentration than Ca (meq/L) while close to the carbonated units (Pepb, Peci, Pepu), concentration of Ca is higher than Mg. Thus, ultramafic and carbonated units are responsible for adjustments of Mg and Ca contents in water resources.

Table. 3. The results of the hydro-chemical analyses of the water samples and depth of the wells.

Samples	PH	EC	TDS	Ca	Mg	Na	K	HCO3	SO4	Cl	F	P	Depth
		(μs/cm)	(mg/L)										(m)
Q1	8.14	2160	1444	22.6	16.7	484.6	0.4	330.1	506.3	210.6	1.67	28	-
Q2	8.61	2690	1738	70.9	28.2	492.2	3.1	159.9	648.4	375.4	1.41	-	-
Q3	7.89	6270	4209	270.5	117.2	1012.0	32.1	111.1	1354.0	1348.0	0.86	-	-
W1	8.05	3410	2169	42.9	70.7	637.7	6.3	233.1	702.2	573.3	0.64	-	150
W2	7.95	4360	2939	123.6	87.0	769.5	11.3	131.2	1082.0	782.4	0.94	-	70
W3	7.89	4400	2986	129.3	87.1	772.7	12.5	130.6	1106.0	794.8	0.99	-	56
W4	7.81	5030	3294	160.7	105.7	873.8	13.3	136.7	1204.0	850.5	0.80	-	48
W5	7.71	5470	3664	179.3	128.5	846.0	10.2	178.8	1415.0	950.5	0.98	-	44
W6	7.59	5770	3929	126.8	118.0	1077.0	7.8	209.9	1367.0	1103.0	1.01	-	47
W7	7.76	6990	4467	254.7	103.8	1078.0	18.8	140.3	1602.0	1303.0	1.10	-	31
W8	7.69	9820	6458	447.9	146.9	1647.0	9.0	95.2	1360.0	2595.0	0.94	-	21
W9	7.95	6480	4464	255.3	58.2	1205.0	3.1	131.2	1672.0	1133.0	1.12	-	20
W10	7.65	8190	5598	379.1	109.1	1412.0	3.1	134.2	1886.0	1626.0	1.03	-	23
W11	7.63	8910	6327	367.3	80.3	1673.0	4.3	137.3	2558.0	1402.0	1.70	-	19
W12	7.17	13600	9175	676.7	178.3	2196.0	4.7	112.9	3006.0	2868.0	1.59	-	20
W13	7.66	12180	8397	531.0	179.0	2116.0	9.8	119.6	2924.0	2446.0	1.32	-	21
W14	7.69	9510	6573	360.3	122.3	1749.0	11.7	116.5	2251.0	1922.0	1.62	-	24
W15	7.31	9320	6407	381.9	122.9	1670.0	16.4	123.3	2234.0	1840.0	1.71	-	19
R1	8.06	7900	5365	330.8	172.3	1269.0	25.4	149.5	1880.0	1589.0	0.93	-	-
R2	*7.67*	7490	5088	275.3	159.9	1250.0	22.7	140.9	1814.0	1465.0	0.86	-	-
R3	*8.28*	8120	5393	321.0	172.8	1221.0	20.3	261.2	1982.0	1522.0	1.18	-	-
Sp1	7.10	5160	3579	231.0	39.4	952.7	4.7	104.3	1290.0	826.0	0.84	-	-

Since the ratio of chloride ion concentration to the sum of the rest anions in all samples is less than 0.8 meq/L, thus it is resulted that the weathering factor is the principal factor in controlling the quality of water across the study area as stated by Hounslow 1995.

Statistical evaluations

The use of multivariate statistical analysis would help the identification and the classification of the variables involved in the chemical characteristics of water in the region. The statistical methods would lead to the interpretation and the anticipation of the groundwater quality if the hydro-geochemical data, the hydro-geology and the geological information of the study area are well-known. These methods classify the chemical parameters based on their inter-correlation, suggesting an adequate conception of water quality variations.

There are minimum, maximum, mean and standard deviation for analyzed parameters in the water samples. As it is presented, Cl, SO_4 and Na have the most standard deviation in comparison with other anions and cations.

Data standardization

The use of standard data would decrease the effects of the variables which comprise the high variances and in turn would increase the effects of the variables comprising the low variances. The standardization formula is given in equation (1).

$$Z = (X - \mu)/ б \quad (1)$$

Where, X is the parameter value, μ is the mean and б is the standard deviation (Vengopal et al., 2008). In this research the standardized data were used in statistical analyses.

Data Correlation

The linear correlation between the two variables in general, ranges from +1 to -1. When the correlation coefficient approaches +1 or -1 the relation of the two variables becomes very meaningful. The positive correlation coefficient indicates the similar behaviors of the two variables.

In this study the Spearman correlation coefficients were calculated using the SPSS19 Software (Table 5). The high correlation coefficients between calcium, magnesium, chloride and sulfate anions (Ca:SO_4 r=0.876; Mg:SO_4 r=0.686; Ca:Cl r=0.965; Mg:Cl r=0.802; Ca:TDS r=0.938; Mg:TDS r=0.762) across the whole length of the catchment area suggesting the lack of precipitations process during the transmission of water along the plain. The occurrences of the negative correlation between bicarbonates and PH with TDS, -0.477 and -0.585 respectively, indicate that these parameters gradually decrease from the relatively high quality (lower TDS) water sources in the upstream to the low quality (higher TDS) water sources in the downstream.

Table 4. Minimum, maximum, mean and standard deviation for analyzed parameters

	Ca	**Na**	**Mg**	**K**	**Cl**	**SO4**	**HCO3**	**TDS**	**EC**	**pH**	**F**
Minimum	22.64	484.67	16.69	0.56	210.49	506.26	95.09	1444.17	2160.00	7.10	0.64
Maximum	676.70	2196.40	179.06	31.94	2868.30	3006.56	329.77	9175.16	13600.00	8.61	1.71
Mean	269.98	1200.25	109.31	11.44	1341.96	1629.44	152.30	4711.90	6965.00	7.78	1.15
Std. Deviation	161.82	482.32	48.05	8.23	692.66	679.46	57.41	2009.56	2910.67	0.34	0.33

Table 5. Spearman correlation coefficient of hydro-chemical parameters of the study area

	pH	**TDS**	**Ca**	**Mg**	**Na**	**K**	**HCO_3**	**SO_4**	**Cl**	**F**
pH	1.000	-0.585**	-0.563**	-0.322	-0.584**	0.116	0.434*	-0.577**	-0.518*	-0.286
TDS	-0.585**	1.000	0.968**	0.736**	0.986**	0.179	-0.477*	0.924**	0.980**	0.399
Ca	-0.563**	0.968**	1.000	0.704**	0.955**	0.167	-0.558**	0.876**	0.965**	0.333
Mg	-0.322	0.736**	0.704**	1.000	0.682**	0.539**	-0.182	0.686**	0.802**	0.036
Na	-0.584**	0.986**	0.955**	0.682**	1.000	0.137	-0.474*	0.937**	0.954**	0.402
K	0.116	0.179	0.167	0.539**	0.137	1.000	-0.080	0.164	0.261	-0.339
HCO_3	0.434*	-0.477*	-0.558**	-0.182	-0.474*	-0.080	1.000	-0.270	-0.489*	0.032
SO_4	-0.577**	0.924**	0.876**	0.686**	0.937**	0.164	-0.270	1.000	0.866**	0.475*
Cl	-0.518*	0.980**	0.965**	0.802**	0.954**	0.261	-0.489*	0.866**	1.000	0.293
F	-0.286	0.399	0.333	0.036	0.402	-0.339	0.032	0.475*	0.293	1.000

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

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

Due to shortage of precipitation and high evaporation rate, the concentration of main ions is mostly affected by resistant time increasing and groundwater velocity decreasing whereas fluoride concentration mostly depends on the rock unit composition. Then, there is not a significant correlation between main ions and fluoride. As mentioned previously, fluoride is mostly derived from flour apatite minerals.

Cluster Analysis

Cluster Analysis is a robust method for the identification and the selection of homogeneous groups among the hydro-chemical raw data. This method comprises some algorithms which classify the raw data into groups in accordance with their correlations. The data may be classified based on the maximum correlations (EI Yaouti *et al.,* 2009).

In this research the Agglomerative Hierarchical Clustering method was applied and the Ward's method linkage was used in order to determine the similarity present within the data. The Euclidean distance is a geometrical distance in the multi-dimensional space. The Wards' method is a known method, looking at the data variances, evaluates the cluster distances. The results are shown as a dendrogram (Hamzaoui-Azaza *et al.,* 2009).

The cluster analysis was applied to the results of this research is indicated as a dendrogram in Fig. 3(a). The groundwater resources are divided into three groups based on the hydro-chemical characteristics. Then the Stiff, and Schoeller diagrams were drawn for each group using the AqQa Software as indicated in Fig. 3(b) and Fig. (4b) and all water samples were plotted on Piper diagram (Fig. 4a). The mean concentrations of the hydro-chemical parameters of each group are indicated in Table. 6. The quality of the water resources decreases from group 1 towards group 3 (Table. 6) whereas the TDS and EC tenors increase. As it was shown in correlation matrix (table. 5), the concentration of major cations and anions, have a positive significant correlation with TDS and EC such as Na, Ca, Mg, SO_4 and Cl increase from group 1 toward group 3. As regards group 1, 2 and 3 are located in upstream, middle lands and downstream and around the old lake respectively, it can be concluded that water quality is decreasing from upstream toward downstream due to enhancement of contact time and shortage of enough discharge and dilution especially in southern part of old lake. The Piper and Schoeller diagrams of each group are shown in Fig. 4. These diagrams express that the type of water in group 1 and group 2 and 3 are sodium sulfate and sodium chloride respectively. Since the location of the group 1 water resources is closer to the ranges and subsequently the shorter residence time occurred and also the lower solubility of these rocks, resulting that this group having the lowest TDS among all groups.

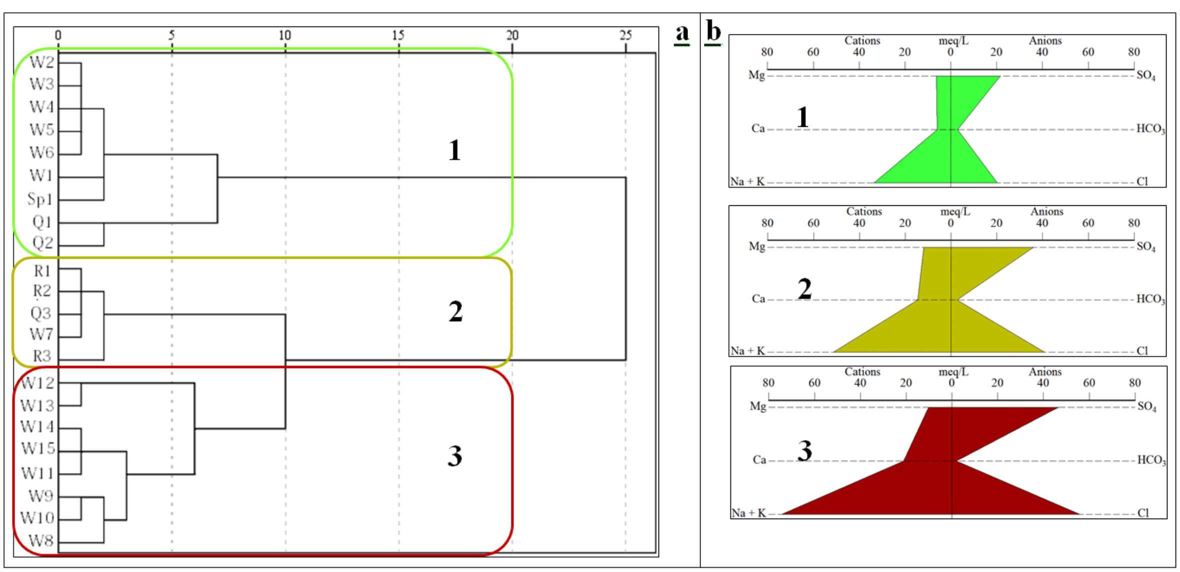

Figure 3. Tree Diagram (a) and Stiff Diagram (b) of hydro-chemical groups

Table 6. The mean of the chemical composition of the groups

Groups	PH	EC	TDS	Ca	Mg	Na	K	HCO3	SO4	Cl	F
		(μs/cm)	(mg/L)								
1	7.87	4272	2860	120.8	75.7	767.4	7.8	179.4	1036.0	718.6	1.03
2	7.93	7354	4904	290.6	145.2	1166.0	23.8	160.5	1726.0	1445.0	0.99
3	7.59	9751	6675	425.0	124.6	1709.0	7.8	121.4	2236.0	1979.0	1.38

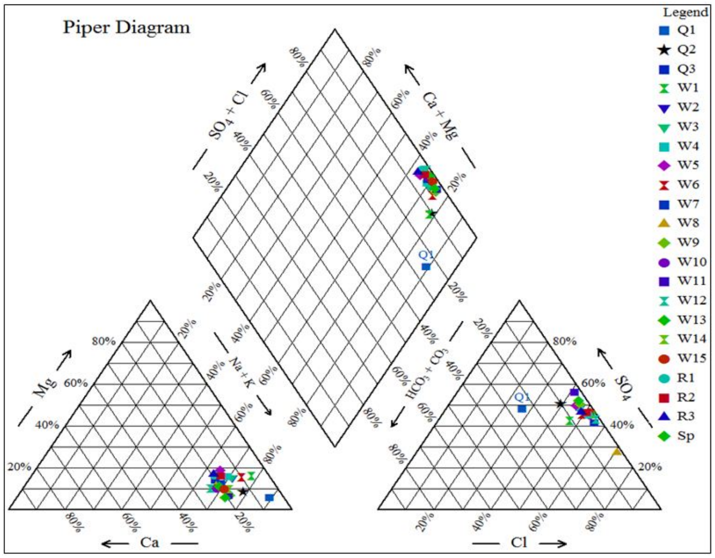

Figure 4. Piper diagram for each sample

The quality of water in group 2 decreases while the distance from the ranges and the residence time increase. The highest TDS of water is related to the group 3 due to the occurrence of its water resources in the vicinity of the residual evaporate sediments of the old lake.

Saturation Index (SI)

The saturation index is used in order to compare the solubility of different minerals in different conditions. It is calculated from the following relation:

$$SI = \log IAP/Kt \quad (2)$$

Where, IAP, is the ion activity and Kt is the constant of solubility. In this research the saturation of water resources calculated using PHREEQC software (Parkhurst & Appelo, 1999). The determination of the saturation values in water resources of the study area was carried out to evaluate the stability of the groundwater with respect to the principal and accessory minerals being dissolved in aquifer. The quality of water is interpreted based on the quantity of the dissolved minerals. If the water is exactly in the situation of threshold saturation, the saturation index (SI) would be zero. The positive SI value is the indication of mineral over-saturated condition tending to the precipitations and the negative SI value is the indication of mineral under-saturation condition tending to dissolution (De Andrade *et al.*, 2008; Cloutier *et al.*, 2008; Cidu *et al.*, 2009). The water resources saturation Index with respect to the principal and accessory minerals and fluorite mineral is indicated in Fig. 5.

The water resources of the study area are almost over-saturated with respect to all carbonate minerals and under-saturated with respect to the sulfate minerals and halite mineral as shown in Fig. 5. Saturation index of samples can be arranged as follow: Carbonate< sulfate< chloride.

Health Effects of Fluoride

The fluoride concentration of groundwater resources in the study area is presented in Table. 3. The fluoride distribution map across the study area is drawn by Geographical Information System (GIS) software on the geology map (Fig. 6).

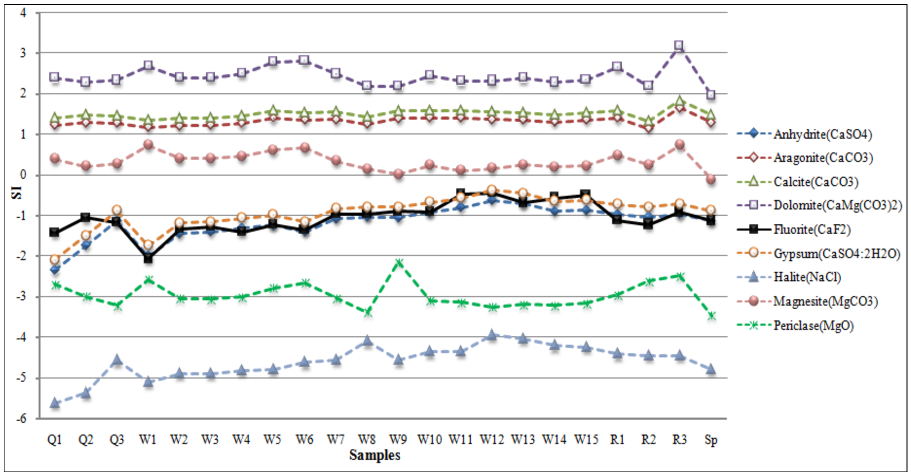

Figure 5. Saturation indices of some minerals in groundwater

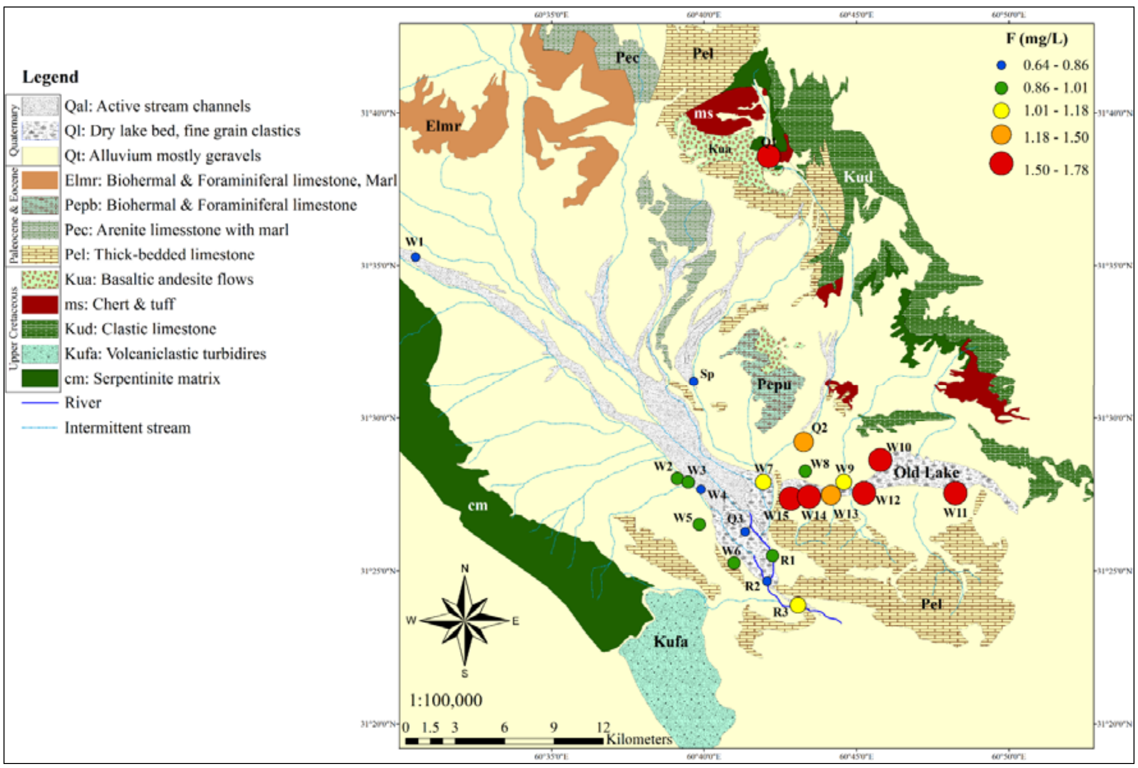

Figure 6. Fluoride concentration distribution map of groundwater of the study area

In this map the red symbols stand for the values more than the allowed limits present in the groundwater that contain 27% of all water samples. The fluoride concentration in Q1 qanat (1.67 mg/L) which is located in the upstream of the catchment area is more than the Standard limit recommended by WHO.These exceeding values are also seen in the water wells in the south part of the area (W11, W12, W14 and W15). The Q2 qanat, in spite of having relatively adequate quality, indicates a higher fluoride content i.e.1.41 mg/L in compare with upstream wells (W1-6). Different factors such as: alteration of the fluoride-bearing rocks, the high residence time, and the increase of the reaction time between the soil and water bring about the increase of fluoride solubility and the increase of fluoride contents (Abu Rukah & Alsokhny 2004; Jacks *et al.*, 2004; Kim & Jeeng, 2005). Furthermore, high water temperature accelerates the water–mineral interactions in the aquifers, including the dissolution of some fluoride-bearing minerals, such as fluorite (Mamatha & Sudhakar, 2010, Padhi & Muraliharan, 2011, Dey *et al.,* 2011, Karro & uppin, 2012). The enhancement of fluoride concentration is justified by the occurrences of basic tuffs and the basaltic-andesite lavas in the catchment areas where the fluoride content naturally increases in these rocks (comparing Table 2 and Table 3). Thus, the increase of fluoride contents in Q1 and Q2 qanats is due to the leaching of rocks and minerals present in the catchment area. High concentration of fluoride in water resources near acidic and intermediate igneous rocks was reported in other researches (Kabata- Pendias & Mukherjee, 2007, Naseem *et al.,* 2010).

In Q1, phosphate concentration is significantly higher than other water samples. It was suggested that the concentration of phosphorous was controlled by phosphate anion derived from apatite mineral; therefore, there is a positive correlation between phosphate and fluoride. As it mentioned before, high content of fluoride, EC and TDS in the water samples located in southern part of old lake W11, W12, W14 and W15 show that the most important reason for high levels of fluoride concentration in this part of catchment can be due to increase of residence time and shortage of dilution.

It is implied from the correlation matrix that there are not any correlation between fluoride and anions and cations. There is not any obvious correlation between fluoride and the principle parameters of water due to the occurrence of various origins for fluoride. This result is also stated by Gupta (2006) and Adriano (1986). In grouping of groundwater resources using cluster analysis, the most frequency of fluoride contents belong to the groups 3, 1 and 2 accordingly. The lower contents of fluoride in group 2 may be due to the lack of occurrences of some characteristics features such as lower contact time and lack of fluoride-bearing sediments. The calculation of saturation index (SI) indicates this important point that the water resources of the study area is under-saturated with respect to the fluoride-bearing minerals, particularly fluorite that its solubility is lower than others (Madhavan & Subraminian 2006), suggesting the ability of water in leaching the fluoride compounds.

The Q1 qanat has been the supplier of the drinking water in the region since the year 2000. The high concentration of fluoride in this qanat has led to the prevalence of dental fluorosis among people living in this region particularly among children.

The fluoride content in drinking water is not the only reason for prevalence of fluorosis in a region but the climatology of the region should also be accounted for. As mentioned earlier in this paper, the study area experiences the annual average temperature of the region is 22.1^{oC} and mean precipitation of 98.2 mm. Hot weather causes more water consumption and consequently people receive more fluoride through drinking water. This explanation is supported by findings from other parts of the world with hot weather and arid climate where prevalence of fluorosis in the regions with fluoride concentration of less than 1ppm in water resource is reported (Driscol *et al.,* 1983; Manjl *et al.,* 1986; Brouver *et al.,* 1988; Akpata, 1997). It should be noted that there are other drinks and food containing high concentration of fluoride such as tea as well as sea foods and dates (Newburn, 1975; Whitford, 1986; Battaleb-Looie *et al.,* 2013). Since in this region, water is their main drinking source and is consumed heavily in the area; especially at the age of 7-16 years old, therefore it could be considered as a main reason for prevalence of fluorosis in the study area.

In order to evaluate the prevalence of fluorosis in the region, 210 students between the ages of 7 to 16 years old (90 girls and 120 boys) were examined. In order to be more confident about conclusion, all the selected students were reviewed to be sure that they were born in the area, didn't move to some other area during their life and also didn't use filtered water.

In Fig. 7 some samples of dental fluorosis are presented indicating different severity of the disease. The results of the assessment with respect to the fluorosis prevalence are shown in table 6 and table 7, Separated in two categories of age and gender.

As indicated in table 7 and table 8 the severity of the fluorosis increases meaningfully with the age and male gender. The reasons of these increase the fluorosis accumulation due to increase of concentration of fluoride and its residence time within the body.

In this research the Community Fluorosis Index (CFI) was applied (relation 3) to consider a better conception of fluorosis outbreak differences in relation to the age and gender (Mandinic 2009, Vazquez-Alvarado *et al.,* 2010).

CFI= (∑ (frequency × statistical weight)) / (number of individuals) (3)

The reasons of the higher fluorosis severity in males may be for the sake of the more activities of the boys which leading to the more consumption of water and consequently receiving the more daily intake amount of fluoride. This finding was reported by other researchers conducted in other parts of the world. (Ramezani *et al.,* 2004, Wondwossen *et al.,* 2006, Ferriera *et al.*, 2010).

Table 7. The prevalence of dental fluorosis among 7-16 –years old male and female students

Total		**Female**		**Male**		
Frequency (%)	**Frequency**	**Frequency (%)**	**Frequency**	**Frequency (%)**	**Frequency**	**Dean Index**
11.9	25	13.33	12	10.83	13	0
15.24	32	13.33	12	16.67	20	1
35.71	75	42.22	38	30.83	37	2
21.9	46	20	18	23.33	28	3
13.81	29	10	9	15	20	4
1.43	3	1.11	1	3.33	2	5
100	210	100	90	100	120	_

Table 8. Dental fluorosis prevalence among 7-16 years-old students based on age and CFI

CFI	**Total**	**Fluorosis Prevalence Based On Dean Index (%)**						**Age (year)**
	Population	**5**	**4**	**3**	**2**	**1**	**0**	
0.513	39	_	5.128	10.256	30.769	23.077	30.769	7-9
1.043	69	_	8.696	23.188	44.928	13.044	10.145	9-11
1.602	88	_	20.454	26.136	34.091	13.636	5.682	11-13
2.541	14	21.429	21.427	21.429	14.286	14.286	7.143	13-16
2.142	210	1.428	13.810	21.905	35.714	15.238	11.905	7-16

Figure 7. Some dental fluorosis samples in the study area

The results indicated that the severe fluorosis is seen among the 13-16-years old group of children; moreover, the Community Fluorosis Index meaningfully increases according to the increase of the age in that the amount of this index among the 13-16- years old group is five times the amount of 7-9- years-old children.

Conclusions

The results of physicochemical analyses of water resources of the study area indicated that the lowest TDS of water was detected in the north and east parts of the catchment area (Q1, Q2, W1, W2, W3, W4, W5 and Sp), whereas the highest TDS was found around the old lake (W8 to W15) in the region.

The magnesium concentration was higher in the water resources in the vicinity of the ultramafic rocks (Q1, W1, W2, W3, W4, W5, and W6) and this would delineate clearly the effects of ultramafic rocks on the quality of the aquifer. In general, the quality of water near the ultramafic bodies and the igneous rocks was better (Q1, W1, W2, W3, W4, W5, W6) than the rest samples based on the amount of TDS.

The results of chemical analysis of sediment samples derived from basements of water resources suggesting that the ultramafic rocks, carbonate minerals and basaltic-andesite flows were the main origin of the presence of magnesium, calcium and fluoride respectively in the water resources of the region. The water resources were divided into three groups using cluster analysis. The type of water in group 1 was the sulfate type and in group 2 and 3 are chloride type.

The results of saturation index calculations indicated that the solubility of mineral increases according to the following order: carbonate minerals, sulfate minerals, and chloride minerals.

The results showed that the fluoride concentration in some water resources is higher than the allowed values. This could be the results of leaching from the rocks and minerals with high concentration of fluoride in Q1 and augmented residence time for the water resources located in south of old lake. The high concentration of fluoride, hot weather and arid climate and consequently high water consumption by the residents could be the reason for prevalence of dental fluorosis in the study area. It was also found that the prevalence and severity of the disease are more common among the boys and increased with the age.

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