Chapter

# GIS and Statistical Evaluation of Fluoride Content in Southern Part of Upper Rasyan Aquifer, Taiz, Yemen

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## Abstract

Fluorosis continues to be an endemic problem in Yemen. More areas are being affected by fluorosis in different parts of this country. The present study aims to identify the intensity and the spatial extent of fluoride concentration in groundwater of the southern part of the upper Wadi Rasyan, Taiz, Yemen. 93 sampling points were selected; the sampling included all types of sources of groundwater and all types of aquifers. The results show that 71% of samples exceed the WHO drinking water guidelines value of 1.5 mg/l, and there are wide variation for groundwater's content of fluoride in the same aquifer (whether, volcanic and alluvial) and in the same of groundwater type, and these variations between the different water types or between the different depths of water (alluvial and volcanic aquifers) are not significantly different. The high concentration of fluoride in groundwater of the volcanic aquifer is likely because of the nature of geology formations by the water-rock interaction result of long-time residence of water in contact with the geology formation. The high concentration of fluoride in the alluvial aquifer likely resulting the waste of urban and industrial activates sources, the over exploration of groundwater, the arid climatic and the activities agriculture.

**Keywords:** fluoride, spatial distribution, GIS, Al-Burayhi and Hedran, Al-Hawban, upper Wadi Rasyan, Taiz and Yemen

## 1. Introduction

Fluorine has the highest chemical reactivity among all known elements and occurs mainly as free fluoride ions in natural waters, although some fluoride complexes also exist under specific conditions [1]. In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature and the action of other chemical elements [2]. Fluoride ion in drinking water is known for both beneficial and detrimental effects on health. Fluoride in small amounts is an essential component for normal mineralization of bones and formation of dental enamel [3]. However, excessive intake of fluoride can cause dental and skeleton fluorosis [4, 5]. Due to its strong electronegativity, fluoride is attracted by positively charged calcium in teeth and bones [6]. Fluorosis is a considerable health problem worldwide, which is afflicting millions of people in many areas of the world, for example, East Africa [7–9] and India [10–12]. According to World Health Organization (WHO) Guidelines for Drinking Water Quality [13], the limit value for fluoride is 1.5 mg/L. The value of 1.5 mg/L is a guiding value, which may be changed based on climatic conditions like temperature, humidity, volume of water intake, fluoride from other sources, etc. for different regions of the world [14]. The source of water supplies in Yemen is mostly from groundwater accumulated during previous and current times [15]. Fluorosis continues to be an endemic problem in Yemen. More areas are being affected by fluorosis in different parts of the country. Recently, a report from General Authority of Rural Water Projects (GARWP) indicates markedly increasing in fluoride content in groundwater (between 2000 and 2006) in districts of some governorates such as Sana'a, Ibb, Dhamar, Taiz, Al-Dhalei and Raimah. The highest fluoride concentration in drinking water was reported in some districts of Sana'a governorate, especially Sanhan [16]. Most Yemenis dwelling in rural areas use deep well water for drinking and household works, and a large number of these wells are contaminated with fluoride in a concentration of 2.5–32 mg [14]. The present study aims to identify the intensity and the spatial extent of the existing groundwater contamination by fluoride in the study area and tries to identify sources pollution responsible for the current pollution of the affected areas through an analytical study in the southern part of the upper Wadi Rasyan of Taiz governorate in Yemen.

## 2. Materials and methods

To achieve the objectives mentioned above, there has been:

1. Identifying and understanding of the characteristics of the study area (topographic and hydrological analysis): location, topography and hydrological characteristics using arc Map GIS.

2. Inventing sources of pollution and production of their maps: inventory of number, type and intensity of human activities and the village's distribution that is likely to contaminate the groundwater in the study area, view inventory results on the map using arc Map GIS and using this map in the interpretation of the results of the spatial assessment of groundwater quality of the study area.

3. Inventing of wells in the study area and displaying them on the map using arc Map GIS.

4. Determining sampling points based on type of wells (dug well and bore well), type of aquifers (alluvial and volcanic), the different depths (from 9 to 500 m) and their location according to the hydrology system and the pollution sources in order to appropriate selection of sampling point and production of the map of sampling points, by using the arc Map GIS.

5. Taking, transporting and analyzing samples.

6. Data processing and interpreting by using arc Map GIS and Minitab 18 program software.

7. Viewing the results of the analysis on the maps in order to know the spatial distribution of fluoride concentration in groundwater of the study area. The spatial distribution of fluoride in groundwater samples in the study area is represented as a thematic layer using IDW tool in the arc Map GIS software program that was used to the prediction of an unknown value for fluoride of the rest of the study area that was not covered by analysis and thus gave the spatial distribution of the fluoride that used in assessing the suitability of groundwater for drinking in the study area as a whole.

8. Using the results of the groundwater assessment quality to propose alternative strategies to deal with groundwater.

9. Preparing the final reports (article).

### 2.1 Sampling

The sampling was collected in polyethylene bottles of 1000-ml capacity after rinsed with distilled water and the water of the well, through months in August, September and October, 2014. The fluoride concentration of groundwater samples was determined using DR 2800 spectrophotometer.

### 2.2 Statistical methods

The Fisher test was used when comparing dichotomous data separately and Pearson's correlation coefficient for continuous variables. On the other hand, after verifying the hypotheses of normality and homogeneity, we used the nonparametric Kruskal-Wallis H to test whether three or more samples were drawn from the same population, or from populations with identical characteristics (distribution with the same median). An analysis of variance was used to study the difference in means between the different samples greater than or equal to three and in the multivariate analysis between our samples two by two we chose the Bonferroni test. In the study, Al-Hawban, Al-Burayhi and Hedran and Al-Dhabab sub-basins were all different samples. After, we performed logistic regression analysis. Fluoride was included as a dichotomous variable (lower or greater than 1.5 mg/L). Other variables with p-values $< 0.2$ in the univariate analysis were entered into the multivariate logistic regression model, which where taken into account in the multivariate logistic analysis. We studied the cause-effect association between the fluoride (lower or greater than 1.5 g/ml) and the included variables using odds ratio (OR). In our first model (crude model), we were satisfied only on the univariate analysis between each variable (independent factors) and the dichotomous concentration of fluoride (dependent variable). In a second model, we performed a simultaneous analysis between the independent variables and the dichotomous dependent variable of fluoride. In order to assess the accuracy of the estimates, we have indicated the 95% confidence interval (IC to 95%) of the average data. A p-value of less than 0.05 at 95% confidence level was considered as statistically significant.

## 3. Results

### 3.1 Results characteristics analysis of the study area

#### *3.1.1 Location of the study area*

The study area represents the southern part of the Upper Wadi Rasyan catchment area, Taiz governorate, Yemen. The study area is estimated at 472 square kilometers which is densely populated and includes Taiz city which represented the third largest and important cities in Yemen (**Figure 1**).

#### *3.1.2 Results of topography analysis of the study area*

The results of the topographic analysis (morphology, elevation and slopes degree) of the study area are illustrated in **Figures 2–4**.

From the topographic analysis of the study area, we find that the group of mountains and plateaus that surrounding the study area made it semi-closed. Therefore,

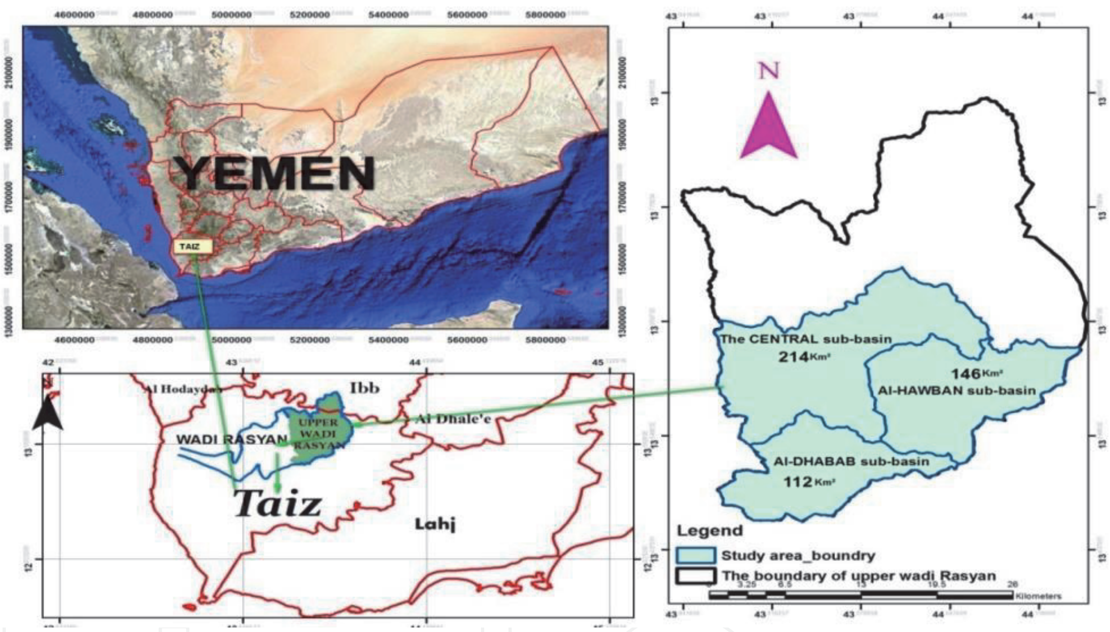


**Figure 1.**
*Location of the study area [17].*

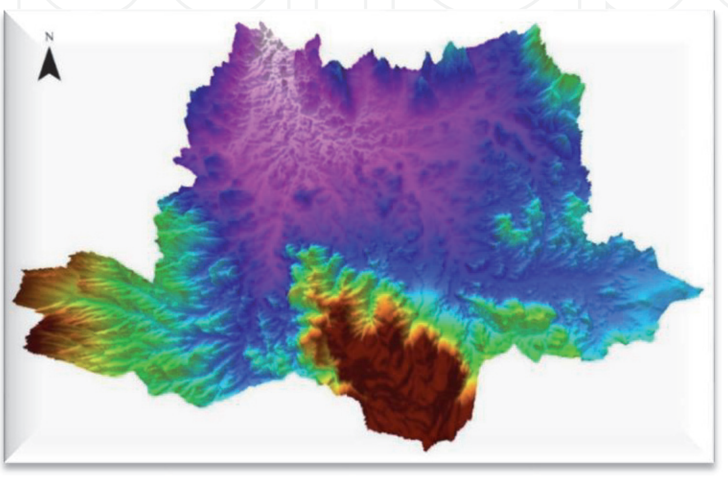


**Figure 2.**
*Topography of the study area.*

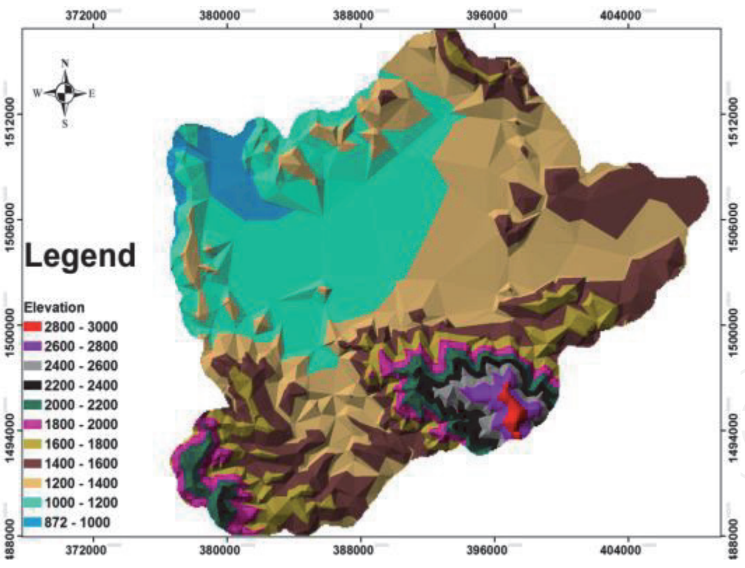


**Figure 3.**
*The elevation in the study area.*

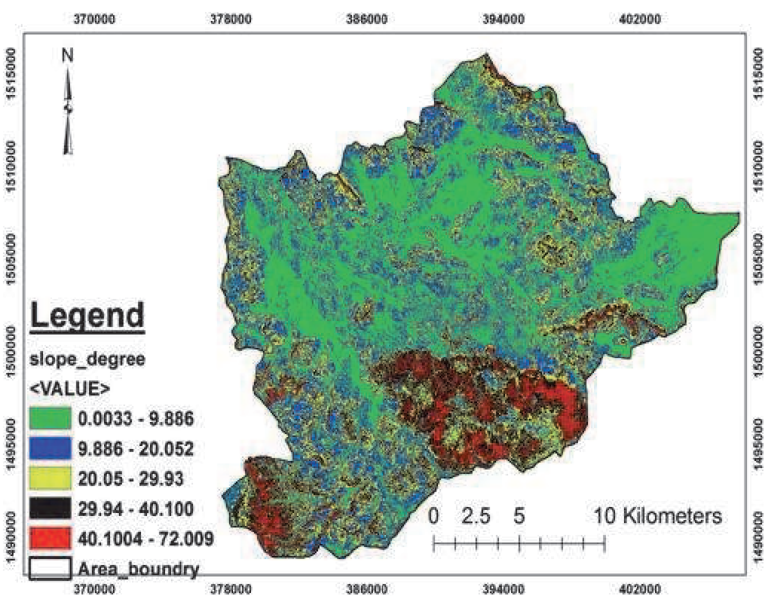


**Figure 4.**
*The slope degree in the study area.*

the north-west corner of the study area formed the outlet for the runoff network as shown in **Figure 5**. According to the digital elevation model of the study area that was obtained from the NASA site and topographic analysis, the elevations in the study area concentrated in the south and southwest, where the height of the mountain of Sabir was up to 3000 m above sea level, whereas Jabal Habashi has a maximum height of 2400 m above sea level. The lowest elevation is located in the north-west and is 872 m above sea level, and in the east, elevations are between 1200 and 1600 m above sea level (**Figure 3**). **Figure 4** shows the map of the degrees of slope in the study area. The degree of slope determines the flow intensity of the floods and, therefore, the extent of water (or water and pollutants) infiltration into the ground.

### *3.1.3 Results of hydrology analysis of the study area*

The results of the hydrological analysis [the hydrological limits, direction of surface runoff and then the flow direction of pollutant at the surface (hydrology system) and the hydrological level (main valleys and its tributaries)] of the study

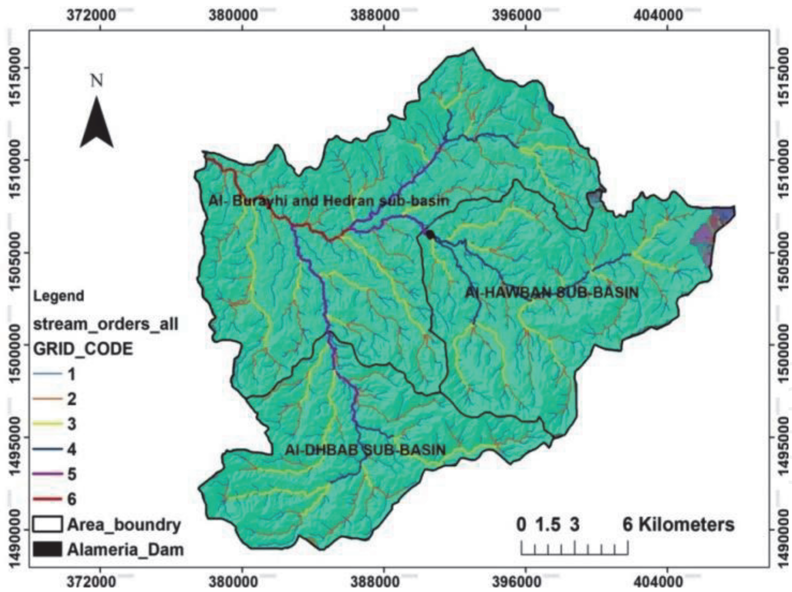


**Figure 5.**
*Hydrology system in the study area.*

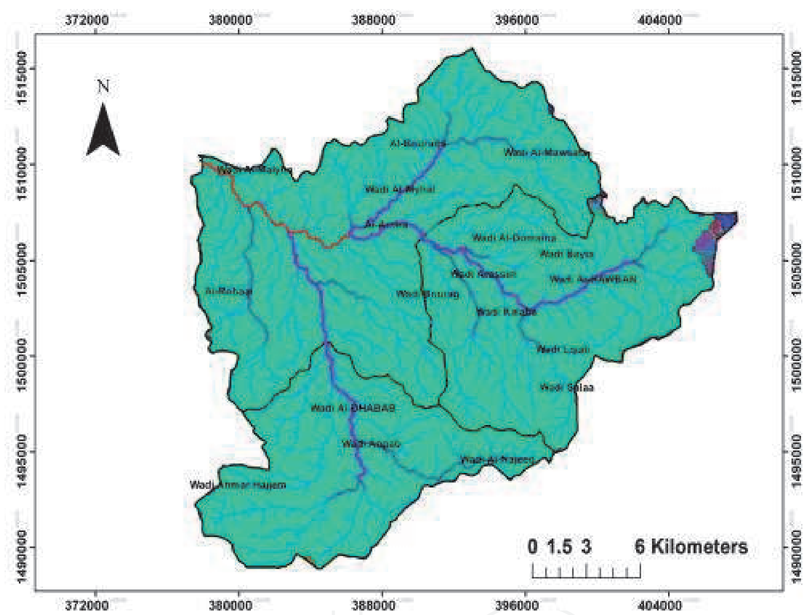


**Figure 6.**
*Main valleys and its tributaries in the study area.*

area are illustrated in **Figures 5** and **6**. From the hydrology map of the study area, we found that the watershed drainage (the hydrology system) in the study area is dendritic and the direction of water surface is into the north-west corner of the study area. Based on hydrological characteristics, the study area has been divided into three main sub-catchment area or sub-basins as shown below:

1. Al-Hawban sub-basin has 146 $km^2$.

2. Al-Dhabab sub-basin has 112 $km^2$.

3. Al-Burayhi and Hedran sub-basin (Central sub-basin) has 214 $km^2$.

*3.1.4 Geomorphology and geology of the study area*

The geology of Yemen is a part of the Arab Shield which consists of a Proterozoic crystalline subsoil covered by a Paleogene sedimentary sequence (Mesozoic sediments). In the west of the country, the sedimentary sequence is covered by Yemen volcanic (Cenozoic volcanic) [18]. The study area occupies the southwestern corner of the Arabian Shield, and the geological complexity of the region is mainly due to its position at the junction of the Red Sea and the Gulf of Aden rift systems. Geological map and geological cross sections for the study area were derived from the geological map of the upper Wadi Rasyan, scale 1: 100,000; that prepared by Dar Yemen Consulting Company [19]. As shown in **Figure 7**, the geomorphology of the study area is dominated by the tertiary volcano that covers most of the region.

Geomorphology of the study area was characterized as modern rock units, which was formed during the Cenozoic (Cenozoic volcanic group), which was formed by a series of eruptions and volcanic eruptions that were affected by Yemen in general and the province of Taiz, especially during the third geological age as a result of movements of the successive continental shelf separation tectonics along the fault line of large expanses of the Gulf of Aden, in the southern Dead Sea to north and the emergence of the Red Sea gorge and the separation of the Arabian plate from the African plate where it was accompanied by the emergence of streaks parallel to the axis of the Red Sea, which represented the levels of weakness and

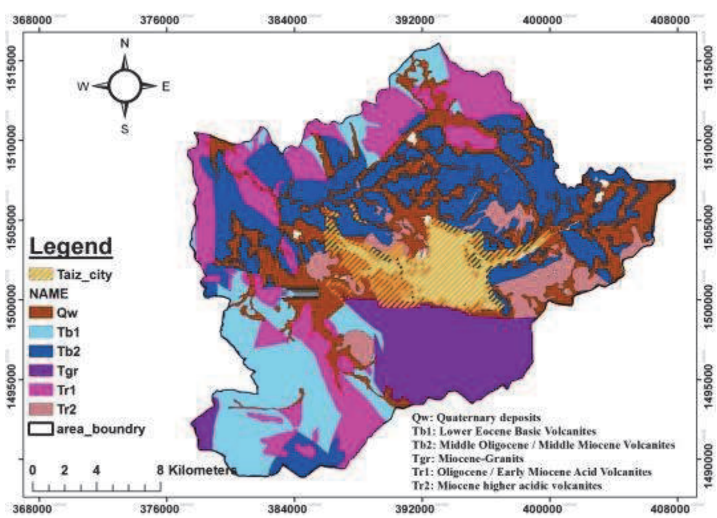


**Figure 7.**
*Geomorphology of study area (the source of basic map [19]).*

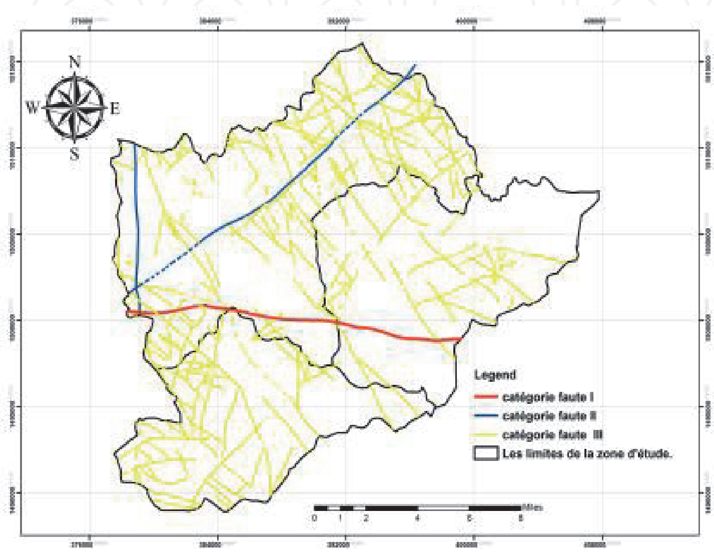


**Figure 8.**
*Geology faults in the study area (the source of basic map [19]).*

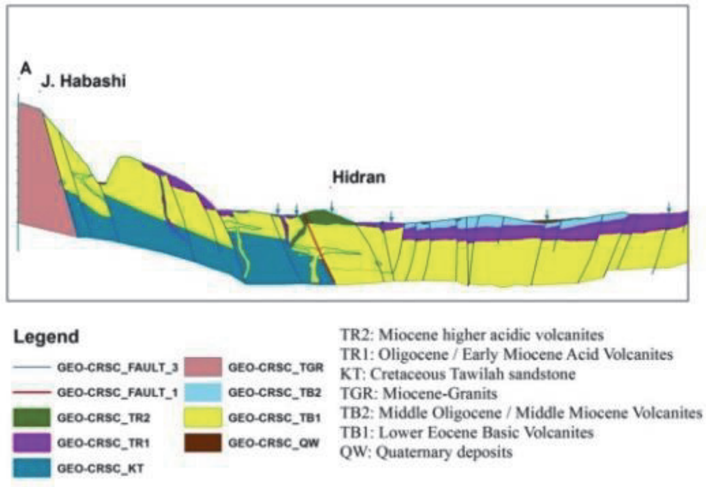


**Figure 9.**
*The geology cross-section of Jabal Habashi to Hedran (the source of basic map [19]).*

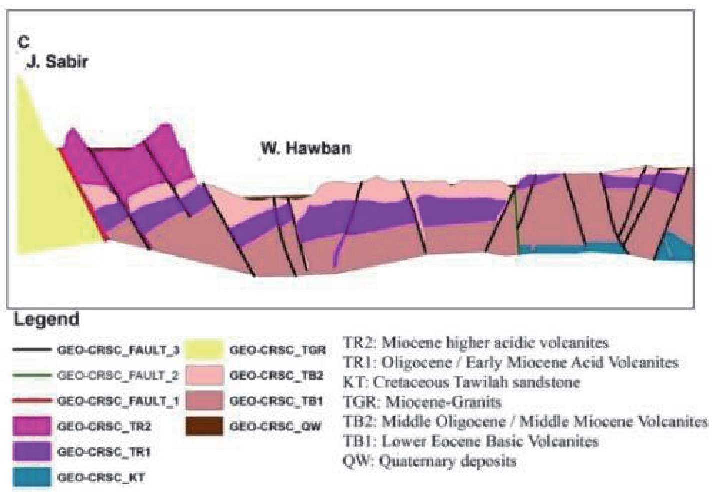


**Figure 10.**
*The geology cross-section of Jabal Sabir to Al-Hawban (the source of basic map [19]).*

pathways of magmatic systems [20]. A major crack extends from the east to the west of the study area. There are also local cracks stretching group north-west to south-east perpendicular to the main fault (**Figure 8**).

According to [19], the geology of the study area consists of Cretaceous Tawilah Sandstone (Kt), Lower Basalt (Tb1), Low Volcanic Acids (Tr1), Basic Volcanic Medium (Tb2), Second Volcanic Acids (Tr2), Granite (Tgr): *granite in the mountain of Sabir contains some older volcanic rocks* and finally Quaternary (QW): Wadi sediments are deposited by seasonal floods and wind-deposited soils derived from the alteration of volcanic ash and tufa mainly of (Tr1). Thickness can be up to 70 m. **Figures 9** and **10** illustrate geological cross-sections of some study areas.

### *3.1.5 Hydrogeology of the study area*

According to [19], groundwater in the study area is being produced from three aquifers: the Quaternary alluvium, the Tertiary fractured volcanic and the Cretaceous Tawilah Sandstone. Cretaceous Tawilah Sandstone in the study area is located in the lower classes, in the southwest of the study area and extends to the north, as shown in **Figure 11**.

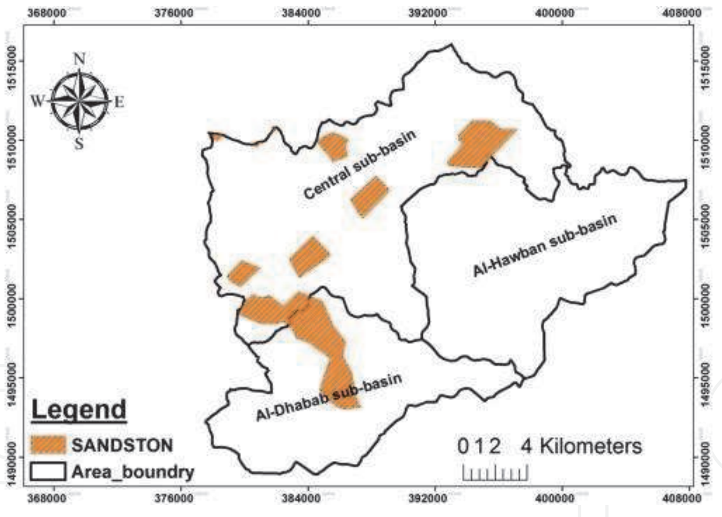


**Figure 11.**
*Cretaceous Tawilah sandstone in the study area (the source of basic map [19]).*

Alluvial aquifers form the highest and shallow aquifers in the region. These sediments exist along the Wadis path (**Figure 6**). The total thickness rarely exceeds 30–40 m, but they can locally reach considerable thicknesses (up to 70 m). Hydraulic properties vary from site to other. Intergranular groundwater flow is dominant [19].

Volcanic aquifers consist of the tertiary volcanic sequence. The thickness of this sequence may exceed 600–700 m. Groundwater flows mainly in this type of aquifers through the cracks/faults. The sandstone aquifer includes Tawilah Sandstone, Southwest of the study area (Al-Dhabab), and this formation is soaked to an expected depth of more than 500 m. In general, sandstone is largely silicified and fractured, so that the dominant groundwater flow in this aquifer is of intergranular type and mixed fracture. The quality of this aquifer is excellent to good [19].

#### *3.1.5.1 Groundwater recharge*

Groundwater aquifers in the study area are recharged by many sources of water, as follows:

1. In Al-Hawban sub-basin, the aquifers are recharged with rainwater (either pure or loaded with wastewater that is disposed of in floodwaters), wastewater disposed of in sewers, industrial wastewater in the eastern part of the sub-basin where there is an industrial food complex.

2. In Al-Burayhi and Hedran sub-basin, the aquifers are recharge with the floods coming from the Al-Hawban sub-basin that loaded with liquid and solid waste types, domestic wastewater that is transported from the city of Taiz across the sewerage network is deposited in sedimentation ponds in this sub-basin, wastewater used to irrigate crops in this sub-basin, irrigation water, which goes downloaded with high concentrations of salts, sedimentation ponds for industrial wastewater in the western part of the sub-basin, the floods that coming from the Al-Dhabab sub-basin to the south-west of the Al-Burayhi and Hedran basin, these floods reach the Al-Burayhi and Hedran sub-basin, which is mostly pure but soon to be contaminated by the remnants of industrial activities located west of the Al-Burayhi and Hedran sub-basin.

3. In the Al-Dhabab sub-basin, rainwater is almost the only source of recharge for the aquifers.

#### *3.1.5.2 Groundwater flow*

According to [19], in general, the groundwater movement in the study area is a function of the hydrological system into the north-west corner of the study area (toward the Al-Burayhi and Hedran sub-basin). In the volcanic aquifers, the direction of the groundwater movement is subject to the direction of the faults.

### *3.1.6 Results of inventory's contamination source in the study area*

The results and spatial distribution maps of village and inventory's contamination source in the study area are shown in **Figures 12** and **13**.

The sampling sites are illustrated in **Figure 14**.

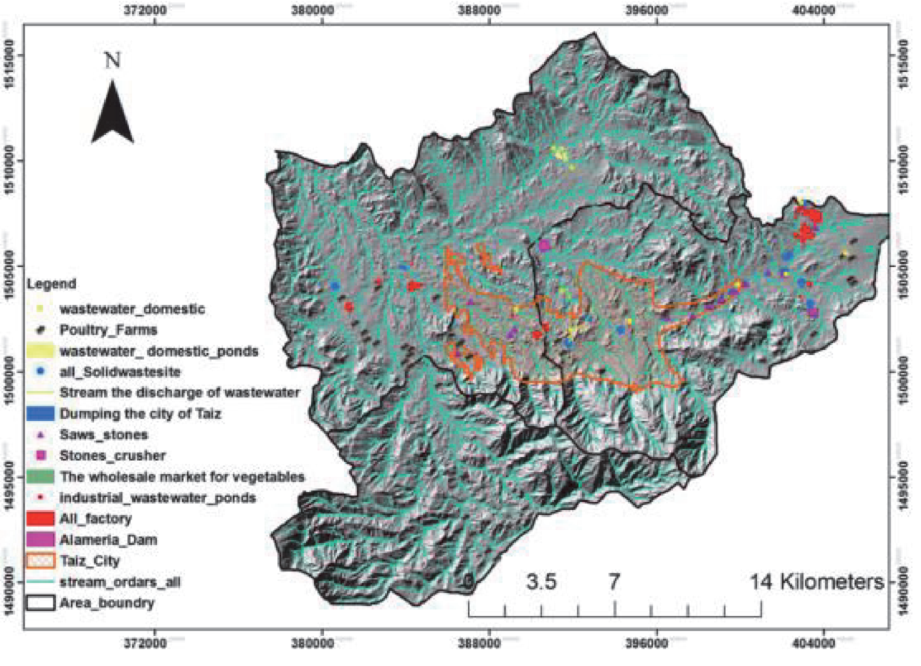


**Figure 12.**
*Spatial distribution of pollution sources in the study area.*

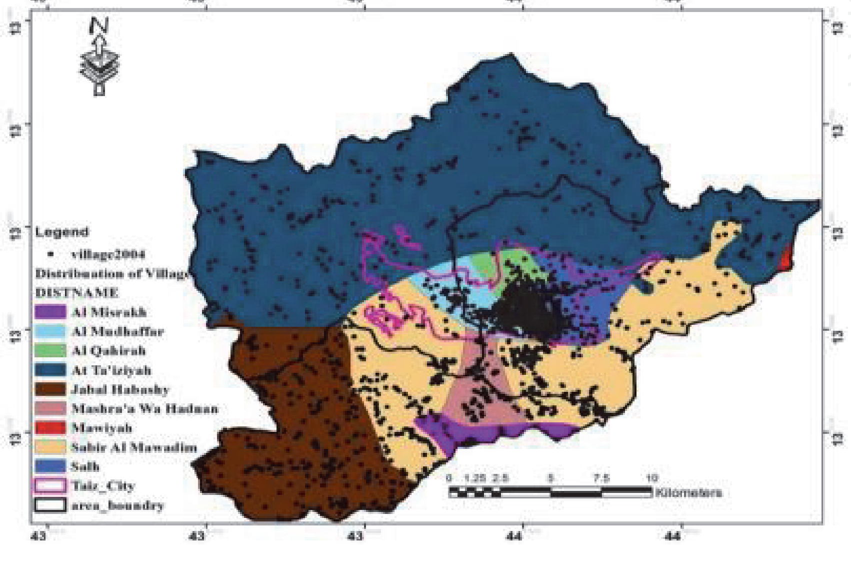


**Figure 13.**
*Village's distribution in the study area.*

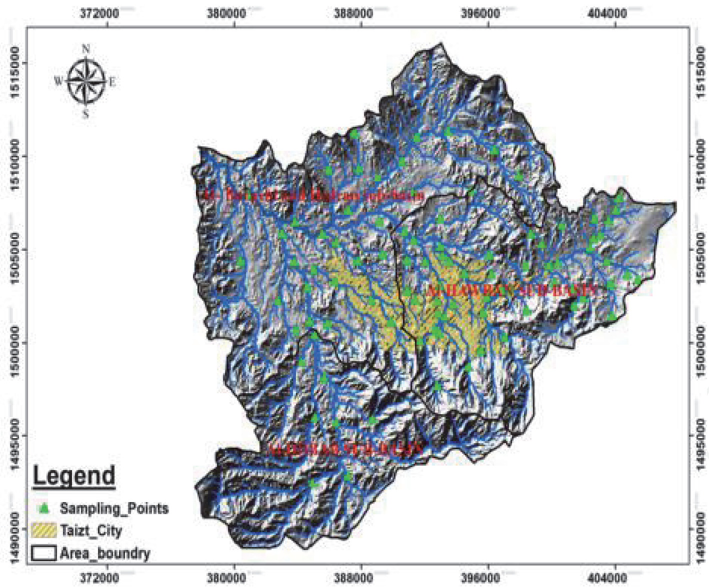


**Figure 14.**
*Sampling sites.*

## 3.2 Results analysis of fluoride's concentration in groundwater of the study area

### *3.2.1 Descriptive statistic of results*

A summarized statistic descriptive of results of fluoride's concentration (mg/L) in groundwater of the study area is shown in **Table 1**, and the minimum, maximum, means and standard deviation of results based on each sub-basin are illustrated in **Table 2**.

We used boxplot tool in order to provide a simplified presentation of how the values of fluoride's concentration are distributed, the boxplot (**Figure 15**) illustrated, the values' distributions are dissimilarities in their distribution in three sub-basins.

| Variable | Min | Q1 | Median | Q3 | Max | Mean | StDev |
|---|---|---|---|---|---|---|---|
| F- mg/L | 0.100 | 1.470 | 1.890 | 2.980 | 6.000 | 2.353 | 1.449 |

**Table 1.**
*Descriptive statistics of F- mg/L for all samples.*

| | Al-Hawban, sub-basin | Al-Burayhi and Hedran, sub-basin | Al-Dhabab, sub-basin |
|---|---|---|---|
| No. of wells | 56 | 29 | 8 |
| Minimum | 0.98 | 0.1 | 0.58 |
| Maximum | 5.81 | 5.45 | 1.11 |
| Mean | 2.32 | 2.66 | 0.85 |
| S.D | 1.15 | 1.26 | 0.189 |

*SD, standard deviation.*

**Table 2.**
*Descriptive statistics of fluoride values mg/L in groundwater samples of the study area by sub-basin.*

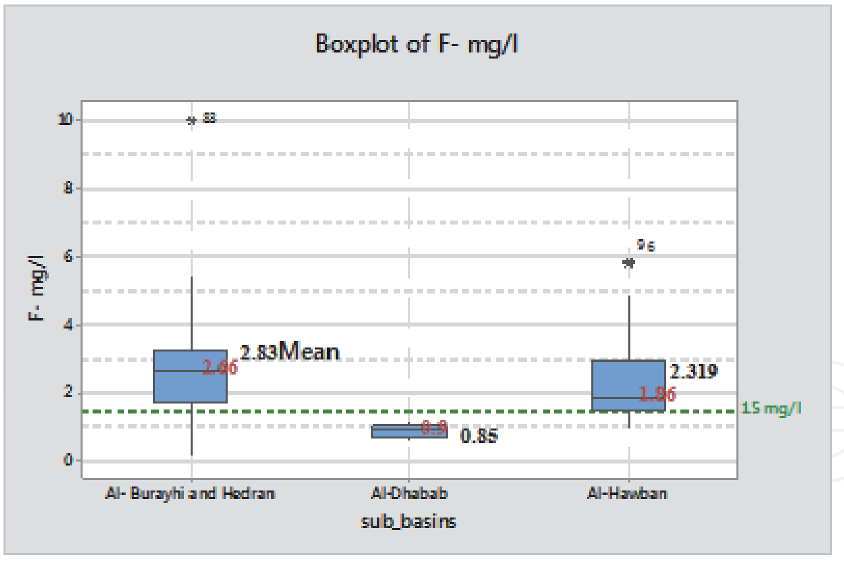


**Figure 15.**
*Box plot to provide a simplified presentation of how the values of fluoride's concentration are distributed in groundwater of three sub-basins.*

### *3.2.2 The correlation analysis*

The correlation analysis between the fluoride concentration and the different physicochemical parameters showed that the fluoride concentration is positively correlated with the Cl, EC, TDS, K, Na, Mg and T. H at the significance level of 0.01 and with the parameters Ca and HCO3 at the significance level of 0.05 (**Table 3**).

### *3.2.3 The relationship between the concentration of fluoride and the water type*

**Figure 16** illustrated how the values of fluoride's concentration are distributed according to water type, and **Figure 17** show the comparison of the mean of F-mg/L according to water type with 95% confidence interval.

From the results of fluoride contain in the 93 samples, we found that the very high fluoride's concentration (4.501–6 mg/L) was associated with the water type both of Na-Cl (5 samples), Na-HCO3 (1 sample) and Mg-Cl (1 sample), the high fluoride's concentration (3.01–4.5 mg/L) was associated with the water type both of Na-Cl (8), Na-SO4 (3), Mg-Cl (1), Na-HCO3 (2) and Ca-HCO3 (1), the moderately abundant of fluoride's concentrations (1.5–3.0 mg/L) was associated with the water type both of Ca-Cl (4), Ca-HCO3 (2), Ca-SO4 (2), Mg-Cl (2), Mg-SO4 (1), Na-Cl (13), Na-HCO3 (16) and Na-SO4 (4), the optimal fluoride's concentration (0.5–1.5 mg/L) was associated with the water type both of Ca-HCO3 (5), Mg-HCO3 (5), Na-Cl (8), Na-HCO3 (7) and Na-SO4 (1) and one sample with water type of Na-SO4 has fluoride's concentration lower than 0.5 mg/L as shown in **Table 4** and **Figure 19**. The distribution of water type according to sub-basins of the study area is illustrated in **Figure 18**, and the spatial distribution of both of water type and fluoride concentrations is illustrated in **Figure 19**.

There are variations for the fluoride concentration in the same of water type as shown in **Table 4**. Normal concentration of fluoride in Al-Dhabab sub-basin was associated with Ca-HCO3 and Mg-HCO3 water type; however, the sources of samples (wells No. 32 and 43, and spring No. 44) in Al-Hawban with the Ca-HCO3 water type showed high values of fluoride concentration 3.66, 2.36 and 1.96 mg/L containing fluoride concentration that exceeds the WHO drinking water, respectively. These sources are located in the southwest of Al-Hawban sub-basin, likely the sources of fluoride results of geology formation of the Sabir's mountain granits,

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| | | **C°** | **pH** | **EC (µs/cm)** | **TDS (mg/L)** | **T.H (mg/L)** | **T.A (mg/L)** | **Ca (mg/L)** | **Mg (mg/L)** | **Na (mg/L)** | **K (mg/L)** | **Fe (mg/L)** | **Cl (mg/L)** | **SO4 (mg/L)** | **HCO3 (mg/L)** | **NO3 (mg/L)** | **F- (mg/L)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| F- mg/L | P C | 0.086 | −0.055 | 0.491** | 0.491** | 0.394** | 0.014 | 0.211* | 0.427** | 0.453** | 0.489** | 0.072 | 0.536** | 0.168 | 0.262* | 0.014 | 1 |
| | Sig. (2-tailed) | 0.414 | 0.602 | 0.000 | 0.000 | 0.000 | 0.897 | 0.043 | 0.000 | 0.000 | 0.000 | 0.490 | 0.000 | 0.107 | 0.012 | 0.895 | |
| | No | 93 | 93 | 93 | 93 | 92 | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 93 | 92 | 93 | 93 |

*PC, Pearson Correlation.*
*Correlation is significant at the 0.05 level (two-tailed).*
**Correlation is significant at the 0.01 level (two-tailed).*

**Table 3.**
*Correlation between fluoride and different physico-chemical parameters.*

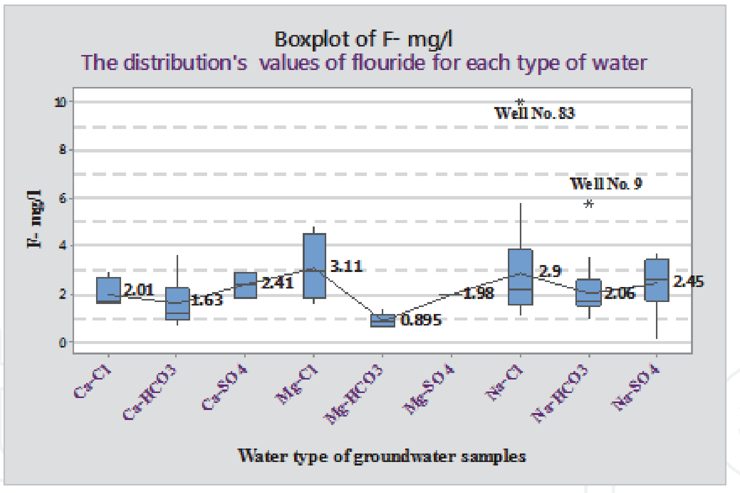


**Figure 16.**
*The distribution's values of fluoride according to water type.*

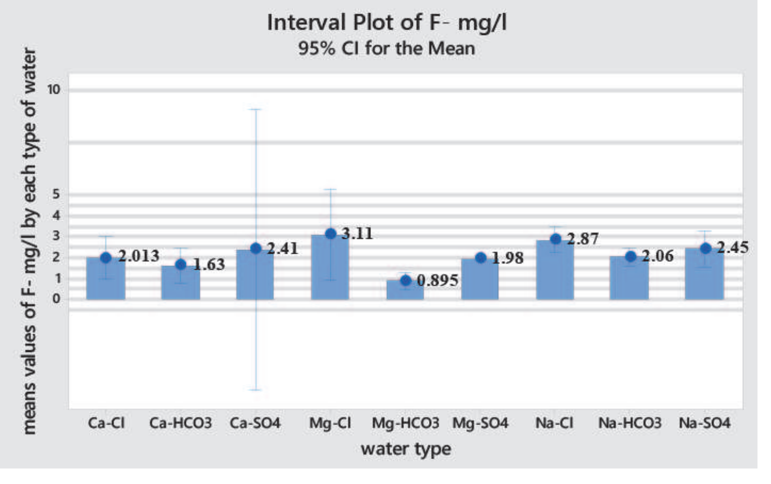


**Figure 17.**
*Comparison of the mean of F- mg/L according to water type with 95% confidence interval.*

| Concentration of fluoride (mg/L) | Type of water and number of samples |
|---|---|
| 0.5–1.5 | Ca-HCO3 (5), Mg-HCO3 (5), Na-Cl (8), Na-HCO3 (7) and Na-SO4 (2) |
| 1.5–3.0 | Ca-Cl (4), Ca-HCO3 (2), Ca-SO4 (2), Mg-Cl (2), Mg-SO4 (1), Na-Cl (13), Na-HCO3 (16) and Na-SO4 (4) |
| 3.01–4.5 | Na-Cl (8), Na-SO4 (3), Mg-Cl (1), Na-HCO3 (2) and Ca-HCO3 (1) |
| 4.501–10.0 | Na-Cl (5), Na-HCO3 (1) and Mg-Cl (1) |

**Table 4.**
*Classification of F- mg/L and their relation to the water type.*

according to [21]. The groundwater with high concentration of fluoride is associated with the granits rocks.

For the Na-Cl water type, we found that 26 samples out of 34 samples have high concentration of fluoride, 12 samples located in the Al-Burayhi and Hedran sub-basin [(wells No. 83, 80, 78, 77, 68, 65, 88, 82, 87, 79, 75 and 92), where 4 samples of them (wells No. 83, 80, 78 and 77) have 4 of highest values of fluoride's concentration of out of 5 the highest values)] and 14 samples located in the Al-Hawban sub-basin (wells No. 6, 12, 2, 11, 1, 36, 30, 25, 42, 29,24, 28, 55 and 34); however, there are 8 wells with water type of Na-Cl that have fluoride's concentration equalizer or

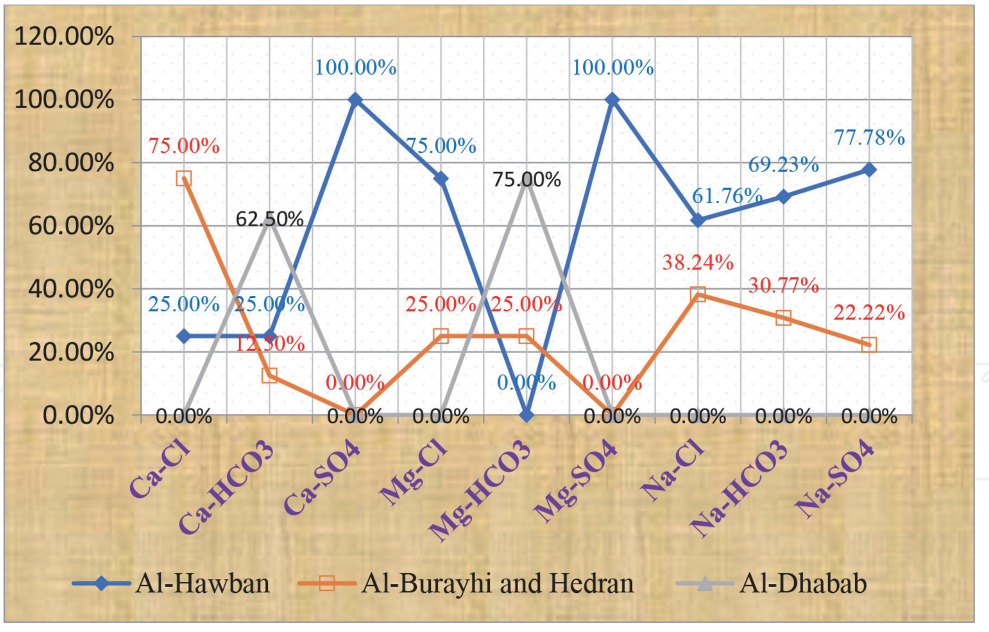


**Figure 18.**
*The distribution of water type according to sub-basins of the study area.*

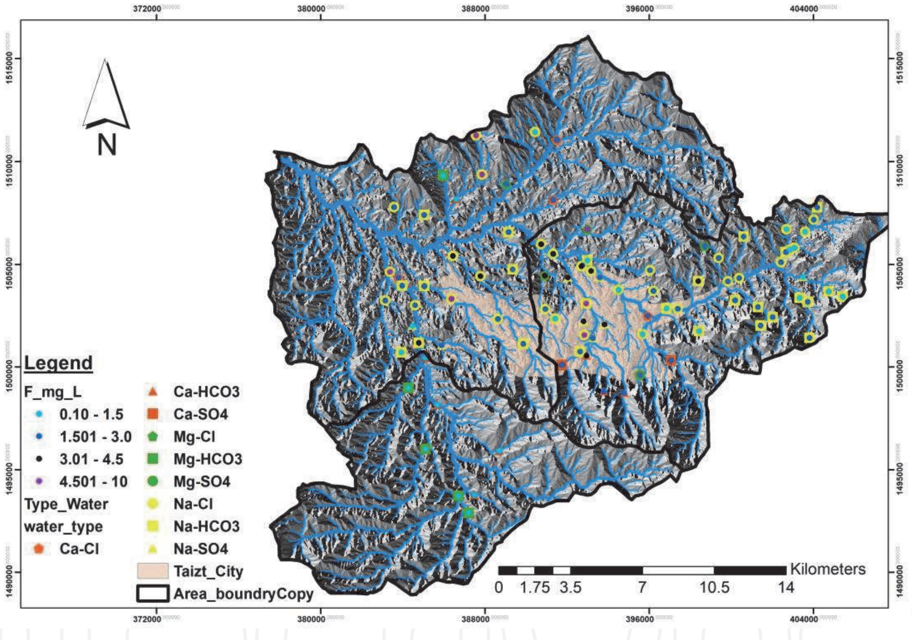


**Figure 19.**
*The spatial distribution both of water type and the F- mg/L in the study area.*

lower than 1.5 mg/L [(7 wells located in the Al-Hawban sub-basin (wells No. 54, 37, 49, 53, 51, 40 and 5) and one well (No. 72) located in the Al-Burayhi and Hedran sub-basin)]. The wells with the Na-HCO3 water type have 19 groundwater samples out of 26 samples (wells and one spring) with a high fluoride's concentration [(11 wells and one spring in Al-Hawban (dug wells No. 9, 22, 27, 18, 15, 47, 17, 19, 20, 23 and 52, spring No. 16) and 7 wells in Al-Burayhi and Hedran sub-basin (No. 67, 85, 70, 89, 69, 84 and 86)]. There are 7 samples out of 9 groundwater samples with water type of Na-SO4 have a high values of fluoride's concentration, 6 wells located in the Al-Hawban [(wells No. 39, 33, 4, 46, 3 and 35) and one located in Al-Burayhi and Hedran sub-basin (well No. 66)]. All samples with water type both of Ca-SO4, Mg-Cl, Ca-Cl and Mg-SO4 have abnormal fluoride's concentration as shown in **Table 5**. Abnormal concentration of fluoride was more prevalent with groundwater samples with Mg-Cl water type in Al-Hawban sub-basin (well No. 41 with

| Water type | Normal concentration N (%) | Abnormal concentration N (%) | P-value |
|---|---|---|---|
| Mg-HCO3 | 5 (100%) | NIL | 1 |
| Ca-HCO3 | 5 (62.5%) | 3 (37.5%) | 0.3 |
| Mg-SO4 | Nil | 1 (100%) | 0.10 |
| Na-HCO3 | 7 (26.9%) | 19 (73.1%) | 0.01 |
| Na-SO4 | 2 (22.22%) | 7 (77.78%) | 0.02 |
| Na-Cl | 8 (23.53%) | 26 (76.47%) | 0.01 |
| Ca-SO4 | Nil | 2 (100.0%) | 0.05 |
| Mg-Cl | Nil | 4 (100%) | 0.02 |
| Ca-Cl | Nil | 4 (100%) | 0.02 |

**Table 5.**
*Water type, normal and abnormal of F- mg/L and number of wells.*

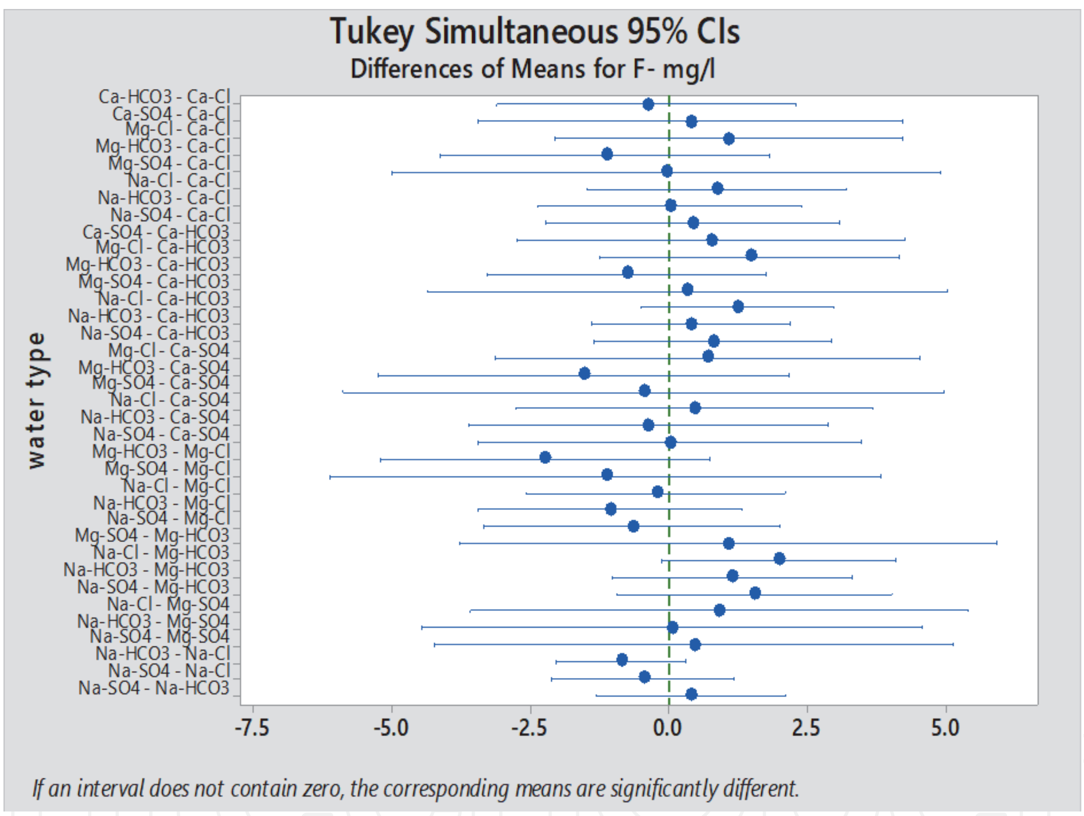


**Figure 20.**
*The difference of means for F- mg/L with 95% Cl.*

4.87 mg/L, No. 26 with 1.58 mg/L and well No. 10 with 3.33 mg/L) and Al-Burayhi and Hedran (source No. 81 with 2.66 mg/L); and with water type both of Ca-SO4 (wells No. 38 and 8 in Al-Hawban sub-basin), Ca-Cl (wells No. 71, 73 and 91 in the Al-Burayhi and Hedran sub-basin and well No. 31 in Al-Hawban sub-basin) and Mg-SO4 (well No. 7 in Al-Hawban sub-basin). **Figure 20** illustrated that there are no significant different in the fluoride concentration between the sources of groundwater samples according to the water type.

### *3.2.4 The spatial distribution both of water type and F- concentration according to pH*

The distribution type of groundwater according to pH showed that, from Mg-So4 type through a Na-HCO3, Na-So4 and Na-Cl type groundwater to Mg-Cl and

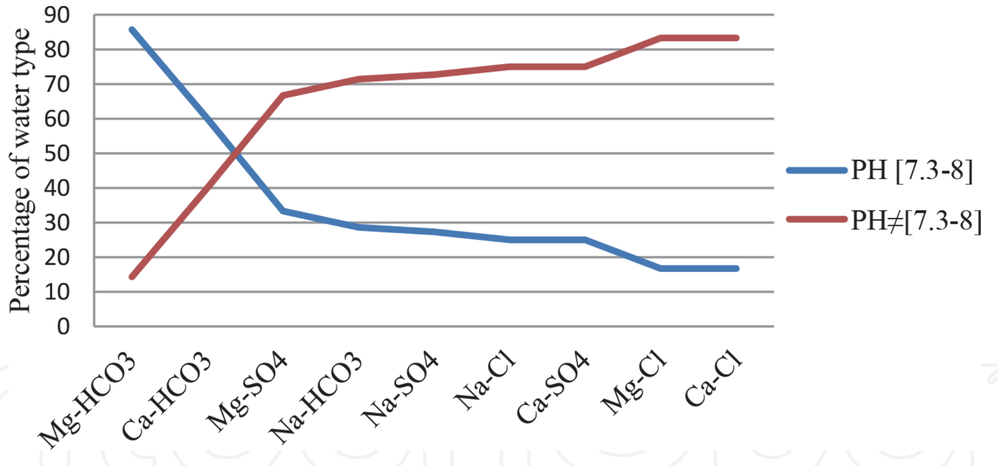


**Figure 21.**
*Distribution of water type according to pH.*

| | ORcrude | CI for 95% | p-value | ORa | CI for 95% | p-value |
|---|---|---|---|---|---|---|
| pH [7.3–8] | 0.417 | 0.164–1.062 | 0.067 | 0.373 | 0.139–0.99 | 0.050 |
| Water type | 1.755 | 1.295–2.378 | 0.000 | 1.711 | 1.261–2.322 | 0.001 |
| Sub-basin | 0.389 | 0.194–0.778 | 0.008 | 0.366 | 0.176–0.760 | 0.007 |

*ORa: odds ratio adjusted. pH ≠ [7.3–8]: reference. Mg-HCO3 water type: reference. Al-Hawban sub-basin: reference.*

**Table 6.**
*Logistic regression univariate and multivariate model for fluoride variation.*

ultimately Ca-Cl when the pH range between 7.3 and 8 was more lower than pH ≠ [7.3–8] (**Figure 21**) and the comparison of the groups "pH [7.3–8]" and "pH ≠ [7.3–8]" showed a significant difference in fluoride concentration ($p < 0.05$).

Results of the multivariate analysis are shown in **Table 6**. In the two logistic regression model, after adjusting for pH, water type and sub-basin (ORa = 0.366; CI: 1.76–0.76), the water type (ORa = 1.71; CI: 1.261–2.32) remained dependently associated with abnormal fluoride concentration (**Table 6**).

#### *3.2.5 The relationship between the concentration of fluoride and type of sources of samples*

The results statistic analysis show that the different of the fluoride concentration between the different sources of water samples (dug well, bore well and spring) in the study area is not significantly different. Fluoride concentration decreases not significantly according to well's type $F(2) = 2.19$, $p = 0.121$.

Fluoride concentration is positively and not significantly related to depth of the groundwater ($r = 0.046$, $p > 0.05$).

#### *3.2.6 The comparison of the abnormal and normal fluoride concentration according to TDS*

The comparison of the abnormal and normal fluoride concentration according to TDS (total dissolved solids) in the three sub-basins showed a significant differences between the three sub-basins ($p < 0.0001$) and positive relationship between the fluoride concentration and TDS ($r = 0.5$; $p < 0.0001$). A multiple comparison of median concentration among these sub-basins in fluoride shows that Al-Hawban and Al-Burayhi and Hedran sub-basins reach higher fluoride content which is more

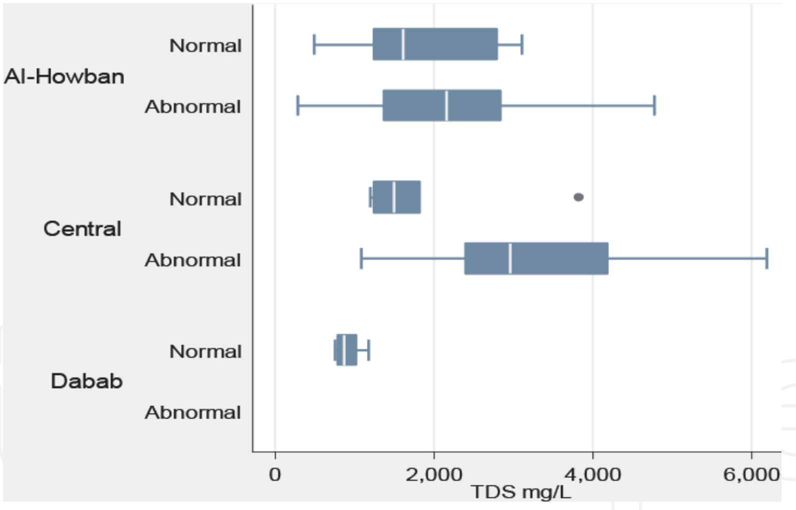


**Figure 22.**
*Box plot for the maxi, min and average of the fluoride content in groundwater according to TDS of three sub-basins.*

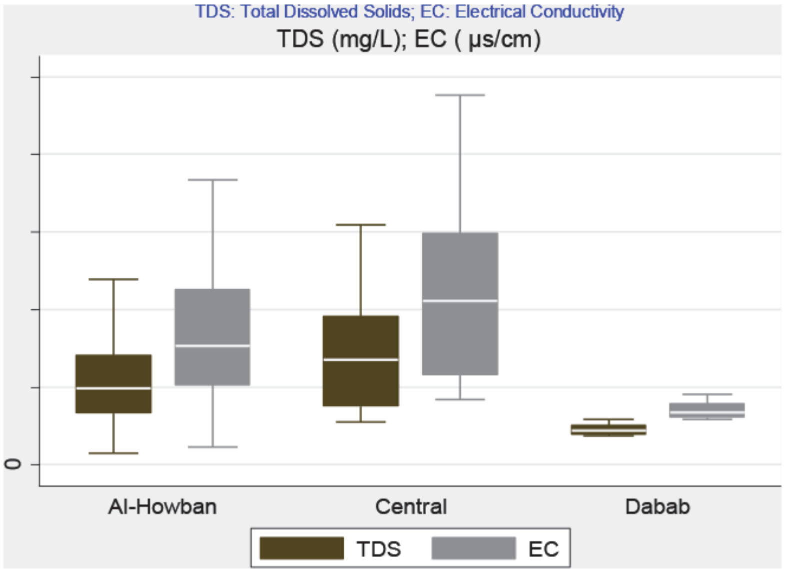


**Figure 23.**
*Box plot for the max, min and average of electrical conductivity and total dissolved solids according to study sub-basins.*

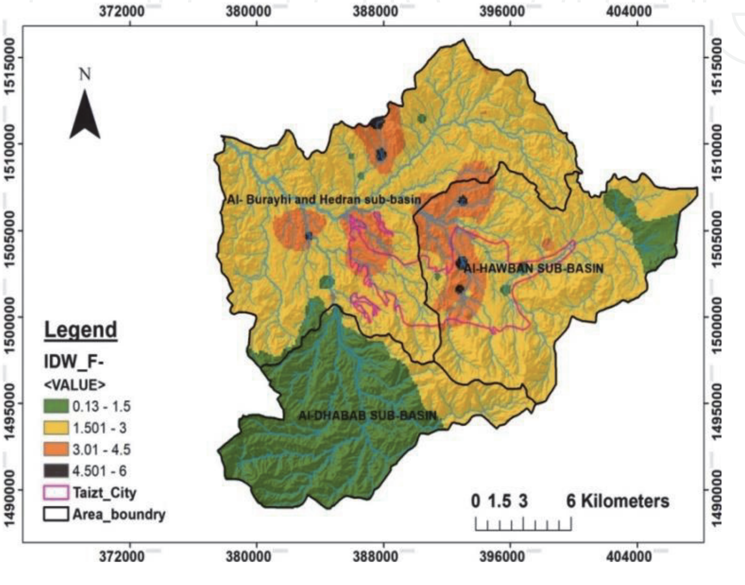


**Figure 24.**
*Spatial distribution of fluoride concentration in the study area.*

than 1.5 mg/L and similar but significantly higher than the Al-Dhabab sub-basin; Al-Hawban-Al-Burayhi and Hedran: ($p > 0.072$); Al-Hawban-Al-Dhabab: ($p < 0.003$); Al-Dhabab-Al-Burayhi and Hedran: ($p < 0.0001$). Moreover, this increase in TDS has been found only at two sub-basins when the fluoride is abnormal content (**Figure 22**). The results of the study samples of electrical conductivity and TDS according to study sub-basins are given in **Figure 23**.

*3.2.7 Spatial distribution of fluoride*

In order to enable sustainable development of groundwater resources, it is necessary to delineate the safe and unsafe zones with reference of fluoride content (1.5 mg/L); hence spatial distribution of fluoride's concentration was mapped in the three sub-basins of the study area (**Figure 24**).

Based on the Kruskal-Wallis test for the various sub-basins, the level of significance was ($p < 0.05$). This result illustrated that there were a significant differences between three sun-basins with regard to the concentration of fluoride in groundwater. The differences of means for fluoride concentration in groundwater for the three sub-basins show the mean's fluoride in Al-Burayhi and Hedran ($F^-$) > Al-Hawban ($F^-$) > Al-Dhabab ($F^-$). A multiple comparison of mean concentration of fluoride among these sub-basins shows that there is no a significant difference between the Al-Hawban and Al-Burayhi and Hedran sub-basins P-value 0.277, there is a significant difference between the Al-Hawban and Al-Dhabab sub-basins P-value 0.017 and there is a significant difference between the Al-Burayhi and Hedran and Al-Dhabab sub-basins P-value 0.001.

## 4. Discussion

Fluoride concentration variation is widely in the study area from 0.1 mg/L (in well No.93 in Al-Burayhi and Hedran sub-basin) to 6 mg/L [in Well No. 83, of the same sub-basin (Al-Burayhi and Hedran sub-basin)]. We observed that the concentration of fluoride in the Al-Dhabab sub-basin is the optimal concentration according to the WHO drinking water guidelines value of 1.5 mg/L.

Waters with high fluoride concentrations occur in large and extensive geographical belts associated with (a) sediments of marine origin in mountainous areas, (b) volcanic rocks and (c) granitic and gneissic rocks [21], and the high concentration of fluoride widely accepted that most of the F are derived mainly from acidic volcanic rocks such as pumice, obsidians, pyroclastic deposits, ignimbrites and rhyolite, and the main minerals for F are fluorite, fluorapatite, micas and hornblende [22]. Because the geology of study mainly constituent from the acid and basic volcanic and grants rocks, the level of fluoride concentration in the Al-Dhabab sub-basin can be explained by the nature on aquiver in this study area (Cretaceous Tawilah Sandstone), while the groundwater in the other sub-basin is produced either from Tertiary fractured volcanic (that have F- bearing mineral and the groundwater in this aquiver have long-time contact with aquiver, which adjudge the important factors leading to the high fluoride concentration result of interaction between the groundwater and the aquiver) or from the Quaternary alluvium aquiver, where the Wadi sediments deposited are derived from the alteration of volcanic ash and tufa mainly of (Tr1); this quiver depends on their recharge mainly on the wastewater of the urban and industrial activates; this aquiver exposed to over exploration of their groundwater and finally the dry and semi-dry condition plays an important role in the degradation of groundwater in this aquiver.

It is clearly observed that the Al-Burayhi and Hedran and Al-Hawban sub-basins have the highest concentration of fluoride ion in the chemistry of water. Highest concentrations were found to be 6 mg/L from Al-Burayhi and Hedran sub-basin, 5.81 mg/L from Al-Hawban unlike the Al-Dhabab sub-basin which remains unaffected by the contamination fluoride of groundwater. According to the report of [23], the dental fluorosis is the widely fluoride disease observed in the affected areas, and there is a positive relationship between fluoride in water and the occurrence of dental fluorosis in Taiz region.

In order to understand the vertical distribution of the fluoride ion concentration from the water of the study area, the type of the sample water (dug well, bore well and spring) evaluated separately. There was no significant difference between the three well types, dug well sample, springs and bore wells. It can be concluded that shallow aquifers do not reflect higher fluoride contamination than deeper aquifers. It is observed that most of the water samples showed enhanced concentrations with generally increasing trends to the low elevated area (Al-Burayhi and Hedran sub-basin), while the high elevation shows low concentration of fluoride (Al-Dhabab sub-basin). All the water samples collected from the uphill zones of Al-Dhabab sub-basin were exhibited low fluoride concentration.

Compared with Na-HCO3 type groundwater, Ca-HCO3 type groundwater is known to generally contain lower fluoride [24]. Its hydrochemistry is characterized by increased Ca2+ ion concentration with increasing total dissolved solid due to the gradual dissolution of carbonate minerals or Ca2+ bearing plagioclase in aquifer materials [25, 26]. The Na-HCO3 type groundwater is generally enriched in fluoride and sodium ions, due to the dissolution of silicates as well as the removal of Ca2+ by calcite precipitation and cation exchange [27, 28]. The solubility limits for fluorite and calcite provide a natural control on water composition in a view that calcium, fluoride and carbonate activities are interdependent [29, 30]. In addition to the effect of those areas by different liquid waste by runoff and sewage disposal, the heavy pumping of well water is also contributed because of the scarcity of water which leads to the increase of the concentration of salt in the water. TDS levels ranged widely from 291 to 6188 mg/L with most station levels above 400 mg/L and many of the samples studied were higher than the permissible limit of 1500 mg/L according to WHO (2003). This wide variation in TDS values indicates that the area hydrochemistry is influenced by diverse processes such as water-rock interaction and anthropogenic pollution. Fluoride concentrations frequently are proportional to the degree of water-rock interaction because fluoride primarily originates from the geology [9, 31–34]. Due to the high rainfall, rugged topography, factories, lack of total coverage per sewerage network, population density and faults in the study areas could also explain this high fluoride content by runoff and infiltration of chemical fertilizers in agricultural areas, septic and sewage treatment system discharges with fluoridated water supplies and liquid waste from industrial sources. The topography of the study areas varies from level plain to steep slopes. Study area ranges in elevation between 900 and 3000 m above sea level. Taiz plain receives about 500 mm/year of rainfall and significant recharge form runoff of surrounding mountains [35]. In addition to this groundwater fluoride pollution that can affect human health, there have been indications that uptake of fluoride from other sources like food, dust and beverages may be many times higher than that of water [36]. About the fluorosis in selected villages of Taiz Governorate, the percentage of children with fluorosis was very high. Not only because of drinking water, various food habits (like drinking black tea and Chewing Qat) indicated a high contribution of fluoride to food. In AL-Hawban sub-basin, some of children, especially from Jabal Sabir area, used to chew Qat daily, and the Qat are cultivated in the man-made terraces of Jabal Sabir alkali granite, where it expected to be the main source of F- reach minerals like fluorite [23].

On the other hand, the use of fluoridated water for cooking increases the fluoride content significantly especially in dry foods like maize flour which absorbs much water during cooking. It has been reported that fluoride availability may be influenced by simultaneous intake of food and fluoride containing compounds in a positive or negative manner depending on the food type, mode of administration and type of fluoride compound [37].

## 5. Conclusion

Much of the fluoride entering the body is from water and the high concentration of fluoride in water's sources is therefore a major concern. The fluoride is found in the atmosphere, soil and water. It enters the soil through weathering of rocks, precipitation or waste runoff. Understanding of the fluoride occurrence is important in the management of the fluoride related epidemiological problems. Al-Hawban and Al-Burayhi and Hedran are the worst sub-basins affected by fluoride contamination in drinking water. 71% of samples (66 samples out of 93 samples) in the study area have F- concentration (mg/L) above the permissible limit and alternate water sources will be difficult. Therefore, defluoridation of drinking water is the only practicable option to overcome the problem of excessive fluoride in drinking water in these areas. More refined studies however need to be done before any long-term intervention efforts can be planned. In the meantime, there is a critical need to educate young Yemenis about fluorosis and simple intervention measures to avoid long-term health problems. Other studies in the region are urged studying the cause and effect relationship between the abnormal content fluoride and population health.

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