



Appraisal of Fluoride Contamination in Groundwater Using Statistical Approach in Rural Areas of Quetta, Balochistan

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Abstract

Fluoride is a significant parameter of water quality and its consumption less or more than the permissible limits in drinking water is detrimental to human health. Therefore, an analysis of groundwater sources in rural areas of Quetta was carried out. Altogether 32 samples were collected from Borewells and Tubewells from Kuchlak, Mariabad, Hazarganji, and Hanna Valley. Samples were subjected to the examination of physicochemical parameters using standard procedures. All the samples were transparent; pH was in the range of 6.4-11.2, Electrical Conductivity (EC) varied from 342-784 $\mu\text{S}/\text{cm}$, Total Dissolved Solids (TDS) ranged between 219-502 mg/L Total Hardness (TH) varied from 140-680 mg/L and F^- ranged from 0.17-3.2 mg/L. The comparison of estimated values showed that all the samples were exceeding the limits prescribed by WHO. Correlation studies showed that pH and EC were positively correlated with F^- . Fluoride showed a strong positive correlation with TDS and a negative correlation with TH. This research study indicates that 75% of groundwater samples had F^- concentration greater than the allowable limits of WHO. A reliable monitoring program is needed to manage the drinking water quality and health of the population.

Keywords: Groundwater, Physicochemical Parameters, Fluoride, Correlation.

Introduction

Groundwater is regarded as the key source for drinking water and other domestic practices. However, threats to groundwater have been increasing because of the rise of the population. Anthropogenic activities and natural processes may be accountable for the deterioration of groundwater. Fluorine is the 13th utmost plentiful and the most electronegative of all the elements in the crust of earth. The natural abundance fluoride ion in the crust of earth is 0.06 to 0.09% [1, 2]. Fluoride possesses no color, smell or taste when it is dissolved in water, so the chemical analysis is used to determine the concentration of fluoride in samples of groundwater. Fluoride is one of the imperative elements of

life. It is crucial for the bones for usual mineralization and for dental enamel formation [3]. Entrance of fluoride in human body occurs through various ways, such as food uptake, breathing, and drinking water. The key source of fluoride contact with human body is through water uptake [4]. Around 95% fluoride of the entire human body is present in human teeth and bones. WHO (1984) has set the fluoride range from 1-1.5 mg/L in potable water as appropriate intake of humans. Intake of fluoride through water either less or more than the desirable limits is detrimental to the health of humans. The fluoride concentration in groundwaters is mainly overseen through the climate, host rock arrangement, and the

hydrogeology. Regions that have crystalline rocks, alkaline soils, and semi-arid climate are principally effected by fluoride contamination [5].

Fluoride is found naturally in groundwater because of the weathering of the rocks that are enriched in fluoride. Water with elevated fluoride content is generally found in marine origin sediments and at the foot of mountain ranges. Generally, the natural fluoride content influenced by the chemical, geological, and physical features of the aquifer, the permeability, and soil and rock, the adjacent temperature, the action of other chemical elements, weathering strength, and depth of the aquifer [6]. Fluoride is a beneficial element for human health; stimulates bone mineralization, dental enamel formation, and fertility maintenance is comprehended when its ingestion does not surpass optimum levels, its higher concentrations causes dental fluorosis, skeletal fluorosis, weight loss, anorexia, anemia, and cachexia. Unceasing absorption of a non-fatal quantity of fluoride can cause permanent inhibition of growth [7]. Projected that more than 200 million people worldwide are ingesting water with fluoride content higher than the permissible amount of 1.5 mg/L. Pakistan Council of Research in Water Resources (PCRWR) established a National Water Quality Monitoring Program from 2001 to 2006 in 23 major cities of Pakistan showing prevalence of fluoride (5%), nitrate (13%), arsenic (24%) and bacterial contamination (68%) in the surface and groundwater sources of Pakistan [8]. The assessment of water quality can be calculated by finding correlation coefficient. Correlation is the degree of association between two variables when such correlation exists among different parameters; water quality can be easily evaluated [9].

The main aim of this research study is evaluation of fluoride in groundwater of

selected rural areas of Quetta using statistical approach.

Materials and Methods

Study Area

Quetta, the principal city of Balochistan, Pakistan, located at $30^{\circ} 10' 59.7720''$ N and $66^{\circ} 59' 47.2272''$ E (Fig. 1). Quetta is positioned over 1,650 m above sea level that makes it the only high-altitude main city of Pakistan. Quetta is surrounded by four imposing mountains named Chiltan, Takatu, Murdar, and Zarghoon [10]. It has a population of 1,001,205 as of 2017. The total area of Quetta is 3,501 km². The climate of Quetta is semi-arid having a great disparity in summer and winter temperatures.

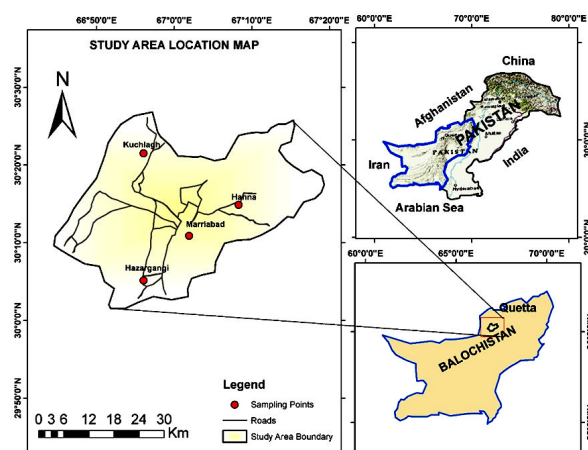


Figure 1. Map of sampling locations

Collection of Groundwater Samples

A total of 32 groundwater samples were gathered in May and June from the peripheral areas of Quetta. Sampling sites included Kuchlak, Hazarganji, Hanna Valley and Mariabad. Samples were collected randomly from each sampling site in such a way that it represents the quality of water of the entire area. 8 samples were gathered from Kuchlak, 6 from Hazarganji, 10 from Hanna Valley and 8 from Mariabad. The sources of

sampling were limited to bore wells and tube wells. Water samples were collected in clean bottles of polyethylene of 500 mL capacity. Each polyethylene bottle was carefully cleaned and washed with the water that is being sampled. All the samples were collected according to a standard procedure. Sampling date, location, and sample number were marked on the polythene bottles and water samples were carried to the laboratory for further examination [11, 12].

Water Quality Analysis

Samples of groundwater were analyzed for its physicochemical parameters; color, odor, and taste was measured by organoleptic method. pH was measured on the spot by using Milwaukee potable pre-calibrated pH meter. EC and TDS was measured in the lab through the Hanna's Portable EC/TDS meter. Total hardness was measured by Complexometric titration using EDTA and Eriochrome Black-T indicator. The concentration of fluoride in samples of groundwater was determined by colorimetric method using 2 mL SPADNS (2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonate) Fluoride Reagent solution that contain sodium arsenate and deionized water. Its values were also stated in mg/L [11, 12].

Results and Discussion

The obtained analytical results of physicochemical parameters in groundwater samples showed that all the samples whether collected from borewells and tube wells were colorless, odorless and tasteless. In the current study, 32 samples of groundwater had minimum pH of 6.4 and a maximum of 11.2 (Table 1). pH is one of the most vital water quality parameters. However, values of pH between 6.5 and 8.5 generally show good quality of water and this range is

characteristic of the drainage basins of the world. It is not measured to be essential to propose a health-based guideline value for pH. A PH >8.5 may indicate that water is hard. Although hard water does not cause health problems, it causes aesthetic problems such as transferring alkaline taste to the water, the formation of scales in vessels. High pH is more common than low pH [12,13].

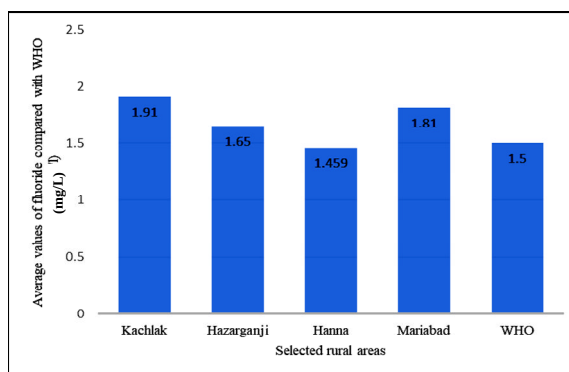
The EC of water is a measurement of its capability to transmit an electric current; the greater dissolved ionic solutes in water, the more its EC. The EC essentially measures the ionic phenomenon of a solution that allows conducting an electric current. The lowest EC observed was 342 $\mu\text{S}/\text{cm}$ in borewells water sample of Hazarganji and highest 784 $\mu\text{S}/\text{cm}$ was in the borewell water sample of Hanna Valley. In the current study, the values of conductivity were below the endorsed values and the water can securely be utilized for domestic purposes. The overall mass of dissolved constituents is called TDS concentration. TDS in supplies of water instigate from natural sources, urban run-off, sewage and wastewater from industries [14]. The water delectableness with a level of TDS less than around 600 mg/L is usually measured to be good. Drinking water is considered highly unpalatable when the TDS level is greater than approximately 1000 mg/L. In the present study, TDS values were well below guidelines recommended by WHO. Low levels of TDS are said to be a feature of mountains. The maximum value for TDS was 502 mg/L and the minimum value was 219 mg/L (Table 1). Total hardness (TH) is used to define the dissolved minerals' effect (Ca and Mg), determining water appropriateness for diverse purposes such as domestic, industrial and drinking [15]. The maximum value of TH that was 680 mg/L and lowest was 140 mg/L (Table 1).

Table 1. Basic statistics for the physicochemical parameters of groundwater samples of Quetta.

Parameter	Min	Max	Mean	Median	Mode	Standard Deviation	Variance
pH	6.4	11.2	7.38	7.3	7.6	0.79	0.63
EC ($\mu\text{S}/\text{cm}$)	342	784	513.53	446.5	657	142.91	20424.64
TDS (mg/L)	219	502	328.59	286	420	91.37	8348.89
TH (mg/L)	140	680	361.25	345	350	99.01	9804.83
F ⁻ (mg/L)	0.17	3.2	1.69	1.68	3.2	0.59	0.34

TH in water is activated by dissolved minerals, principally divalent cations. In natural water systems, calcium and magnesium are the key contributing ions for TH. Zinc (Zn), iron (Fe), strontium (Sr), aluminum (Al), and manganese (Mn) may also increase water hardness; though, they are mostly present in very low amount. TH in freshwater typically ranged from 15 to 375 mg/L as CaCO_3 . Concentrations of calcium beyond 100 mg/L are frequent in natural sources of water, principally groundwater [16]. The maximum average value of fluoride was 1.9 mg/L and highest value was 3.2 mg/L both were observed in bore well of Kuchlak (Fig. 2, Table 1) and the lowermost was 0.17 mg/l in Hanna tube well (Table 1). The permitted limit of fluoride set by WHO is 1 to 1.5 mg/L (Fig. 2). The level of fluoride concentration was found higher than the allowable guidelines in thirty samples out of thirty-two samples and lower in two samples only (Fig. 2). Natural sources of water are associated with numerous categories of rocks and volcanic activity. Fluoride is a significant parameter of water quality and has beneficial impacts on teeth in fewer amounts in drinking water; however, extreme fluoride exposure in potable water can give rise to a number of adverse effects, which may range from minor dental fluorosis to severe skeletal fluorosis as the level and exposure period rises [17]. Anions of fluoride risk health of humans at amounts more and less than the limit, and this is the major issue in many parts of the world

now. Usually, maximum sources of groundwater have more fluoride content than being present in the surface water. As groundwater infiltrates through the weathered rock into the aquifers, it dissolves minerals containing fluoride, later liberating fluoride into the solution. In groundwater, the natural content of fluoride depends on the chemical, geological and physical features of the aquifer, acidity of the soil and rocks, porosity, depth and the temperature of source. Several minerals such as cryolite, fluorite, villiaumite, and fluorapatite, etc. hold soluble fluoride and when groundwater passes over such fluoride containing rock structures, the water possibly will become polluted with fluoride [18]. Fluoride is toxic at amounts more than 1.5 mg/L and is related to dental fluorosis. Fluoride content within 3.0 to 6.0 mg/L in drinking water may cause skeletal fluorosis and when a concentration of 10 mg/L is exceeded crippling fluorosis could arise fluoride can also be a reason for respiratory failure, decrease of blood pressure and paralysis [19, 20]. The average concentration of fluoride in selected regions of Quetta District is given in (Fig. 2) which clearly indicates that except Hanna Valley all other areas have fluoride in excess. The use of wells of different depths, viable water products, water purifiers at home, and systems of purification upsurge the changeability fluoride in drinking water and obscure approximations of consumption [21, 22].

**Figure 2.** Average Distribution of Fluoride in rural areas of Quetta

Basic Statistical Analysis

Basic statistical data for the fluoride and other significant physicochemical parameters of the groundwater that was taken from tube-wells and bore wells are displayed in Table 1, in terms of minimum, maximum, mean, median, mode, standard deviation, and variance. The pH of groundwater samples varied from 6.4 to 11.2 with mean value standing at 7.3, median at 7.3, the mode at 7 while standard deviation and variance at 0.795 and 0.632, respectively (Table 1). This shows an alkaline condition that favors the dissolution of fluoride-containing minerals in groundwater. The resemblance between the ionic size of fluoride and hydroxyl ion substitute each other at high pH that can also result in the elevated concentration of fluoride in the water [23]. The minimum conductivity was 342 $\mu\text{S}/\text{cm}$ and the maximum was 784 $\mu\text{S}/\text{cm}$. The mean value of conductivity of groundwater was documented to be 513.53. Median and mode were recorded to be 446.5 and 657, respectively. The standard deviation of EC was recorded to be 142.914 while variance was 20424.64 (Table 1). The minimum value of TDS was measured to be 219 mg/L and the maximum was 502 mg/L with a mean value of 328.59. The median was measured to be 286 and mode was 420 while standard deviation and variance were measured to be 91.37 and 8348.89, respectively (Table 1). The mean value of TH of groundwater samples was 361.25 with a median of 345 and mode 350, having a minimum value of TH of 140 mg/L and a maximum of 680mg/L. While standard deviation was calculated to be 99.019 and variance was 9804.8387 (Table 1).

The fluoride values varied from 0.17 to 3.2 mg/L with a mean value of 1.69 which shows that fluoride level is beyond the WHO permissible guidelines. However, if the concentration of fluoride in water is less than

1 and more than 1.5 mg/L, the water is considered to be inappropriate for purposes of drinking [24]. The median value was 1.68 and mode value was 3.2 with a standard deviation of 0.590 and variance of 0.348 (Table 1).

Correlation Coefficient

The correlation coefficient is defined as the measure of the degree of association that occurs in two variables, one is taken as the dependent variable. Correlation is the communal affiliation among the two variables. The direct or positive correlation occurs when a rise or fall in the value of one parameter is related to a conforming increase or decline in the value of another parameter [25]. The controlling mechanism of the concentration of fluoride in samples of groundwater can be studied from the correlation coefficient of fluoride with pH, EC, TDS, and TH. The relation between fluoride and pH showed $r=0.355$ (Fig. 3). Hence, there exists a direct association between pH and fluoride, but it is not significant enough. Usually, fluoride concentration increases due to leakage of minerals of fluoride in the development of rock under basic situations. The amount of fluoride minerals is low in the area of study that leads to a weak correlation between these two parameters. When pH is greater than 8, the concentration of fluoride generally exceeds 1.0 mg/L [26, 27]. However, in the current study, the pH in many samples of groundwater was not greater than 8 that may be the cause of the weak correlation between pH and fluoride. The pH of groundwater increases with the rise in fluoride content which designates that content of fluoride in groundwater will differ because of the variations in alkalinity, i.e. the content of carbonate and bicarbonate, so maybe sources of carbonate and bicarbonate content are not present in the study area. Nagaraju *et al.*, [18] found that there was a substantial inverse association of fluoride with pH in their study.

Correlation analysis of another study conducted in Iran indicates that there is no important relationship between the fluoride concentrations of water with pH. A weak relationship between pH and fluoride has also shown in the study led by [15]. The correlation between EC and fluoride was $r = 0.44$ (Fig. 4) which shows a moderate link between the two parameters. The weak association between EC and fluoride has been reported and shown that EC had good correlation with fluoride [28, 29].

The values of TDS and fluoride shows a strong correlation where $r = 0.659$ (Fig. 5). Many studies exhibited that there is a momentous and direct association between TDS and fluoride. The primary ion causing TDS are carbonate and bicarbonate, sulfates, fluorides, chlorides, calcium and magnesium, nitrates, potassium, and sodium. Where TDS and fluoride are high, the probability of replacement by fluoride is less [29].

The relation between TH and fluoride is negatively correlated ($r = -0.249$) as shown in Fig. 6. The process of a reduction in the concentration of hardness causing greater fluoride content can be accredited to calcium complexing effect. Complexes of fluoride are created more rapidly in mineralized water as compared to dilute water [29]. Lesser calcium content gives rise to the solubility of CaF_2 , with a surge in the number of fluorides in the groundwater. The reaction between Ca^{++} and F^- ions showed that the fluoride content was measured by fluorite equilibrium. When the water was soaked with fluorite, low calcium content causes greater fluoride concentration. More fluoride content was consequently anticipated in ground-water from the aquifers having little calcium content. The outcomes mostly displayed that rise in calcium was linked with a fall in the amount of fluoride and vice versa. However, their study showed an inverse relationship between fluoride and TH because of the existence of magnesium and

calcium carbonates and bicarbonates. The reduction in hardness, ensuing in greater fluoride content leads to calcium complexing effect [30]. The above-studied literature shows that an inverse association between fluoride and TH may be due to a higher amount of magnesium and calcium ions occur in the study area.

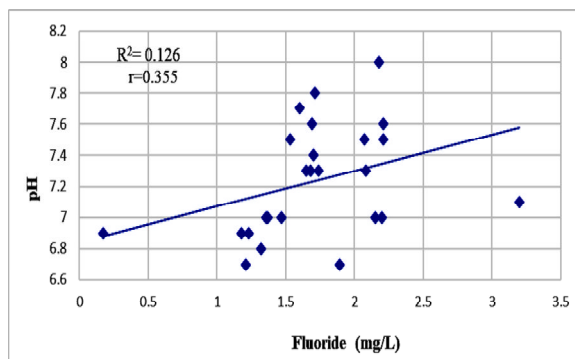


Figure 3. Correlation between pH and fluoride

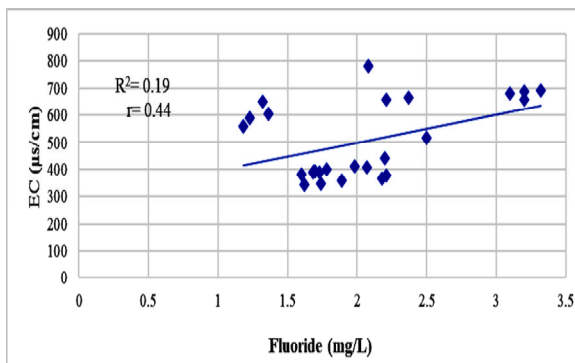


Figure 4. Correlation between EC and fluoride

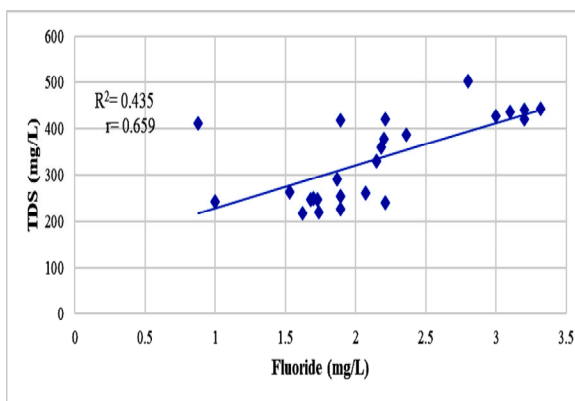


Figure 5. Correlation between TDS and fluoride

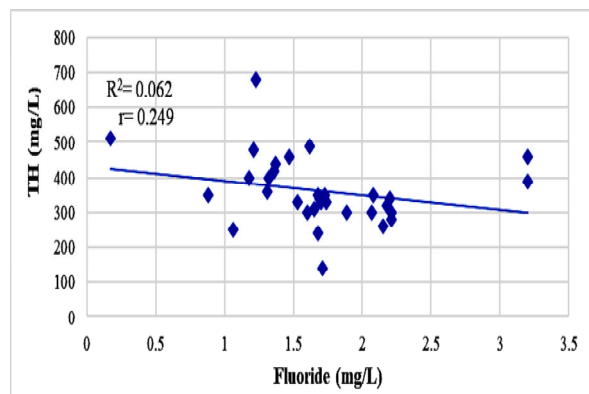


Figure 6. Correlation between total hardness and fluoride

Conclusion

The current status of groundwater in selected rural areas of Quetta was assessed in this paper. pH is in the range 6.4-11.2 while the acceptable range is 6.5-8.5 Fluoride concentration in groundwater varied from 0.17-3.2 mg/L. The TH, TDS, and EC of all the water samples were within the permissible limits. Weathering of rocks and extensive agricultural activities are may be the major reasons for higher level of fluoride in groundwater samples. The descriptive analysis of water quality parameters provided a wide range of variation in mean, median, mode, standard deviation, and coefficient of variation. Linear relationship of fluoride with other parameters through correlation coefficient show that fluoride has a strong correlation with TDS and EC, a positive relation with pH and negative correlation with TH, and we conclude that all the parameters are more or less correlated with each other. Correlation coefficient is an appropriate method to get a fair idea of groundwater quality, by analyzing some of the water quality parameters. Hence it is recommended that a continuous and reliable monitoring program is needed to manage the drinking water quality and health of the environment. The research could be more improved in future by further elaborating the groundwater quality.

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