

Assessment of Fluoride in drinking water and its correlation with different physicochemical parameters in the selected areas of Quetta, Pakistan

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Abstract. Fluoride is found naturally in water, soil, plants, and animals in trace amount. The level of fluoride in drinking water has to be controlled in order to get rid of dental and skeletal fluorosis. A study conducted on children of Quetta city aged 12-year from randomly selected areas showed that dental fluorosis has been found in 63% of children (the data is available) which is a very high percentage. Hence, the focus of this research is mainly to assess the contents of fluoride and its correlation with other physicochemical parameters of drinking water quality in Quetta city. By applying an even sampling plan with the samples distribution taken from tube wells of different sites of Quetta city, where the drinking water quality is known to have been deteriorated. The technique for the analysis of fluoride in groundwater sample is the colorimetric SPADNS method. The study shows that the Concentration of fluoride varies from 0.32 ppm to 3.0 ppm (Hazara town to the western by-pass area of Quetta) as compared with World Health Organization (WHO) guidelines of drinking water for fluoride (i.e., 1.5 ppm). A total number of 13 drinking water samples out of 20 were found unfit for human consumption due to increase in fluoride concentration. The statistical correlation results of drinking water show that solubility of fluoride depends on the level of pH. The salts of, K^+ , Na^+ , Ca^{2+} , SO_4^{2-} and Cl^- ions take a major role in attaining the favourable pH for the dissolution of fluoride-containing compounds in drinking water. However, fluoride correlation with other physicochemical parameters has not been studied in drinking water of Quetta city. Therefore, this aspect of research was studied accordingly. Furthermore, it is observed that the prevalence of fluoride-related health problems in the study area is due to high fluoride concentration in drinking water, which is expected from rocks with fluoride-bearing minerals of Quetta valley. On the account of the results, de-fluoridation of the identified sampling sites, and regular monitoring of drinking water is recommended at government level to avert further fluorosis risk.

Key words: Concentration, drinking water, defluoridation, fluoride level, fluorosis risk

1. Introduction

Our planet consists of 71% of water resources and among this only 1% of the water on the Earth's surface is available to be used by humans, and 99% of this usable quantity is located under groundwater [1]. Underground water contains some quantity of dissolved salts with different concentration of ions, which cause different health issues all over the world, besides other ions, fluoride is one of those ions which in high concentration causes health problem [2].



As in drinking water fluoride is present naturally due to geological composition of bedrock containing minerals like fluorapatite, fluorspar, cryolite, hornblende, fluorite, biotite and hydroxyapatite found in local rock and sediment [3]. Due to climatic factors, adsorption and leaching directly affect the migration and exchange of fluoride from soil to water [4]. Water is the convenient source of fluorides for everybody, so the importance of this element in the human body cannot be ignored, as it is mandatory for durable teeth and bones [5]. The preferred optimum level of fluoride which is recommended by WHO is $0.8\text{--}1.2\text{ mg L}^{-1}$, [6] as it supports public health and avoids any sort of tooth decay, as 1.5 mg L^{-1} is the guideline value for a nominal chance for dental fluorosis [7]. When the fluoride level exceeds 1.5 mg L^{-1} , the threat of dental fluorosis increases. People frequently exposed to fluoride, suffer from neurological symptoms including a headache, excessive tiredness, sleepiness, indisposition, and giddiness [5]. The concentration of fluoride in drinking water is assessed only through chemical analysis. The commonly used technique for the analysis of fluoride in water sample is colorimetric SPADNS (sodium 2(para sulfo phenyl azo)-1, 8-dihydroxy-3, 6-naphthalene disulfonate) method. Fluoride concentration can also be measured by ion chromatography. It can also be detected through portable Ion-selective electrodes, which is used either in the laboratory or in the field [2].

Reports of high concentration of fluoride in groundwater have been studied throughout the world such as USA, Africa, Russia, Middle East and Pakistan. [08] One such research was conducted in North America suggests that dental fluorosis ranges between 35% to 60% in fluoridated communities [9]. Different studies with regards to water quality have also been conducted in Pakistan. The water quality of Mastung, Mangocher, and Pringabad in Baluchistan have been studied with special focus on the concentration of fluoride and other water quality parameters [1]. A study shows that highest fluoride contamination (22%) has been detected in Balochistan province followed by 19% in Punjab province. [10] Another study conducted on 349 children aged 12-year from 14 schools of Quetta showed that dental caries was found in 81 children (23.2%) with mean DMFT 0.61. Boys had 1.6 times more chance to have dental caries than girls. Dental fluorosis was found in 63.6% of children with the majority of moderate degree (50.5%) [11]. The previous studies have also focused on fluoride toxicity, in a research conducted on drinking water samples of Quetta, 81 samples were collected from different sites and 14% were found with increased level of fluoride [8]. Another study conducted on the contamination of fluoride in drinking water and tea samples, in which the concentration of fluoride was detected between 0.61 to 2.55 ppm [12]. However, there has been no study on the statistical correlation of fluoride with other parameters of Quetta city, hence the study has focused on the fluoride correlation and their analysis of physio chemical parameters that distinguish it from other studies. The water samples collected from tube wells in selected areas of Quetta city, specifically those areas where the population was suffering from dental fluorosis have been examined. In this regard concentration of fluoride and other physicochemical parameters have been analyzed. Besides water analysis, a statistical correlation between fluoride and other physicochemical parameters were examined. The statistical correlation results in drinking water showed that the solubility of fluoride depends on the level of pH. The salts of K^+ , Na^+ , Ca^{2+} , SO_4^{2-} and Cl^- ions play a major role in attaining the favorable pH for the dissolution of fluoride-containing compounds in drinking water. The findings of this study explain that the correlation assessment of fluoride with various physicochemical parameters in water helps the population of mentioned areas to know the quality of water, especially the concentration of fluoride in their drinking water as shown in figure 1.

2. Materials and Methods

2.1 The Area of Study

The study area for this research is Quetta City. The selection of the sites was mostly based on the physical symptoms of dental fluorosis of the population of concerned area. The drinking water samples were collected by maintaining the distance of 5 to 10 km². EPA sampling procedure was followed throughout the sampling. A total of 20 samples were collected from selected sites of

groundwater source such as tube wells during November-December 2017. The water samples were kept at 4 ± 1 °C in sterilized polyethene bottles of 1.5-liter capacity properly washed by distilled water followed by sample water.

Analysis of the aesthetic and physicochemical parameters was according to standard methods applied to the analysis of drinking water quality. The pH of the water samples was detected by pH meter (Orion 720A). Total dissolved solids(TDS) were measured by Jenway 4320 TDS meter. The concentration of fluoride in these samples were estimated by SPADNS methods recommended by (APHA_AWWA_WEF,1992) due to its sensibility and efficiency [11]. Magnesium and Calcium ions were determined with the help of UV spectrophotometer. Potassium and sodium ions were estimated by using flame photometer (Model 360, Sherwood Scientific Ltd). Chloride of the samples was measured by the Argentometric method. Bicarbonate and sulphate ions were analyzed according to the standard (APHA_AWWA_WEF,1992) [12]. The results of the samples were compared with WHO and National water quality standards.

2.2 Statistical Analysis

In Statistics the relationship between two continuous variables is evaluated through correlation analysis. Statistical correlation analysis was performed to examine any potential relationship between fluoride and other physicochemical parameters of water samples by using IBM SPSS.

3. Results and Discussion

In total 20 samples of drinking water, 07 samples (35% of the total) were having the content of fluoride within the permissible limit of WHO (1.5mgL^{-1}). The remaining 13 samples (65% of the total) were not suitable for drinking purpose, as the amount of fluoride of these water samples were detected between 1.60 to 3.00 mg/L as shown in figure 1. A study conducted on drinking water samples of Quetta, the concentration of fluoride was ranged between 0.61 to 2.55 ppm [8].

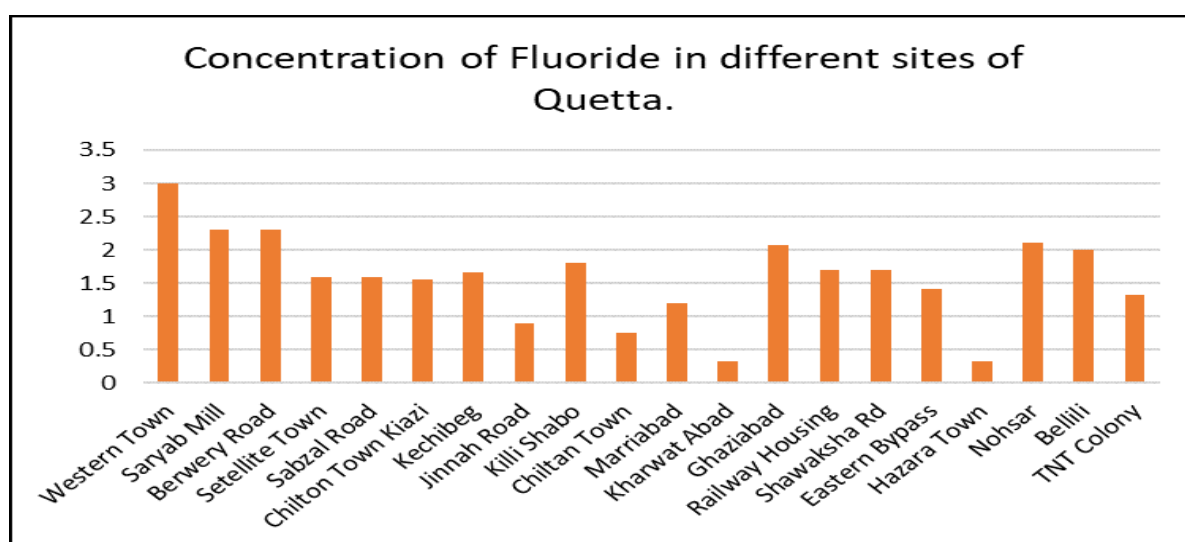


Figure 1. The concentration of fluoride in different sites of Quetta

The fluoride concentration in drinking water, which exceeded the permissible limit, caused adverse effects on health. The deteriorating dental health condition may vary from mild dental fluorosis to crippling skeletal fluorosis as the amount and intake of fluoride increases. Major symptoms other than dental and skeletal fluorosis are depression, weakness of muscles and nervousness may appear as a result of high fluoride intake.

The high content of fluoride in groundwater of Quetta valley is due to metamorphic and igneous rocks such as gneisses and granite [13]. The high amount of fluoride in this area is mainly due to the dissolution of large deposits of fluoride (the estimated total reserves is about 100,000 t) in Balochistan [14]. The fluoride contamination cannot be removed by simply boiling the water or passing through charcoal-based water filtration plants; therefore, reverse osmosis and distillation techniques are suggested for the elimination of drinking water with high fluoride contents.

A study conducted on tap water of Quetta and the results showed that pH of drinking water samples is within the range of WHO standards, which is 6.5-8.5. [15,16,17]. In present study, out of 20 samples the pH values ranged from 7.0 to 8.5, in which one sample acquired the higher acceptable pH value (8.5). For pH of drinking water, no health-based guidelines value has been estimated, as it does not impart any direct effect on human health. However, water samples with pH value near to upper or lower permissible limits are not acceptable. The relationship between fluoride and pH has been depicted in figure 3. In order to control and check the quality of water, it should be monitored periodically. TDS (total dissolved solids) of samples is the totality of Ca^{2+} , Na^+ , K^+ , and Mg^{2+} cations and CO_3^{2-} , SO_4^{2-} , Cl^- , NO_3^- , and HCO_3^- anions as the major inorganic constituents [17]. WHO has recommended 500 and 2000 mg L^{-1} as the upper and lower permissible levels, respectively. [18] The taste of drinking water is affected as follows: excellent, < 300 mg L^{-1} ; good, 300–600 mg L^{-1} ; fair, 600–900 mg L^{-1} ; poor, 900–1200 mg L^{-1} ; and unacceptable, > 1200 mg L^{-1} [19]. A research based on water quality of 16 different points of Quetta city showed that TDS and hardness of the tap water was within the range of WHO limit [15]. Whereas in this study, 19 samples of Quetta have the permissible TDS level (333–1200 mg L^{-1}) and 1 sample has the objectionable TDS >1200 mg L^{-1} .

Very little concentration of TDS makes water intolerable for drinking purpose, owing to lack of some useful minerals and flat taste. The lower acceptable limit may be 80 mg L^{-1} , as there is no lower recommended limit.

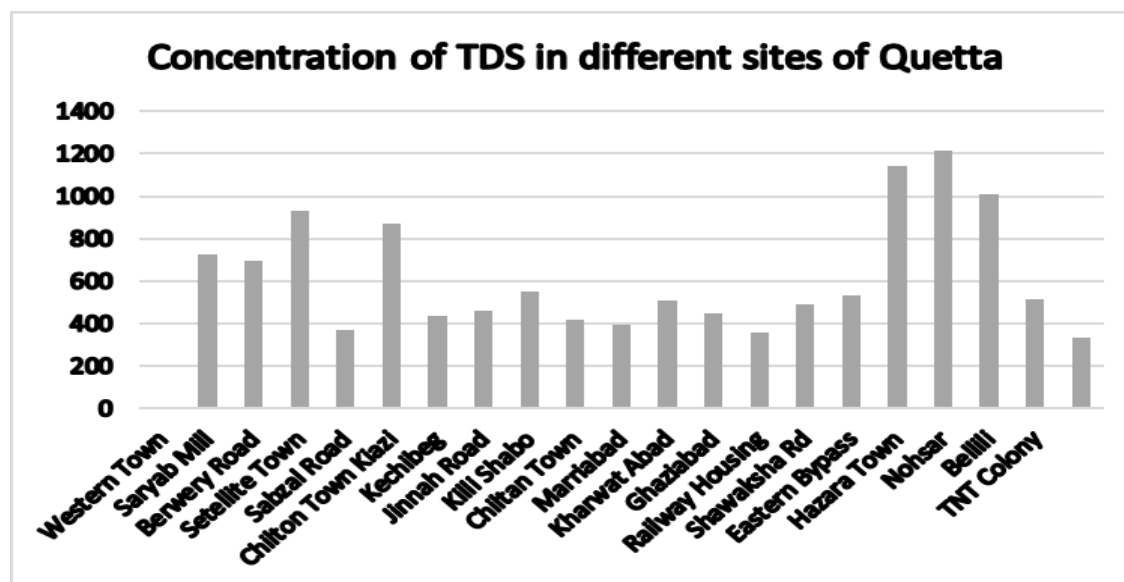


Figure 2. The concentration of TDS in different sites of Quetta.

Ground water with higher TDS value (>500 mg L^{-1}) may be unpleasant because it causes objectionable taste and layers of scales inside the water pipes, household appliances, boilers and heaters. TDS in different sites of Quetta City is shown in figure 2. The scales are caused by some constituents of TDS, like Ca^{2+} , CO_3^{2-} , Cl^- , SO_4^{2-} , Mg^{2+} ions.

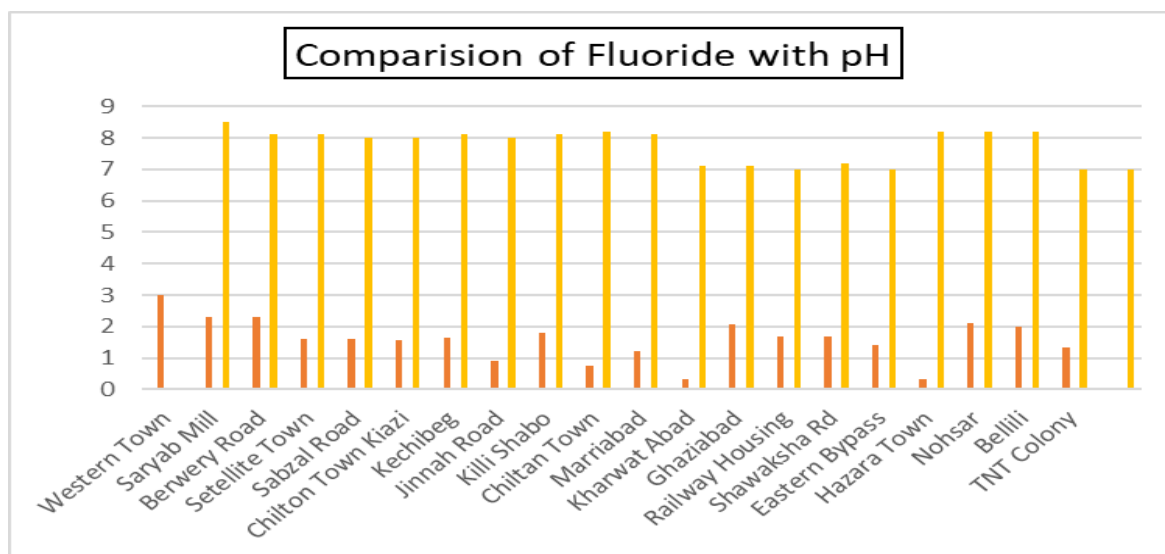


Figure 3. Comparison of fluoride with pH

Note: — pH — Fluoride

The hardness of water is caused by the higher concentration of Calcium and magnesium. The data obtained from analysis of water samples showed that only one sample exceeded the maximum permissible limit (75 mg L^{-1}), set by National Standards of Water Quality [16]. Figure 2 shows the concentration of TDS in different sites of Quetta City. The high amount of Ca^{2+} in water can be decreased with the help of treatments like, chemical softening, electro dialysis, ion exchange, and reverse osmosis [7]. Magnesium in drinking water is relatively non-hazardous to humans at low concentration but at high concentration, it causes diuretic and laxative effects on human. The results of the analysis showed that five samples acceded the maximum acceptable level of 50 mg L^{-1} [17]. The presence of higher concentration of Ca^{2+} and Mg^{2+} reflects the hardness of water and shows that this water is unfit for drinking.

High intake of sodium is harmful for the patients suffering from renal, cardiac and circulatory diseases. WHO has not recommended any maximum limit for Na^+ ; though, the possible objectionable limit for the taste is 200 mg L^{-1} . Only 02 drinking water samples were detected with a high concentration of sodium. Water can be purified by demineralization and Ion exchange process. It is evident that the presence of Ca^{2+} and Na^+ cations cause high TDS value in the studied area.

The major source of chloride (Cl^-) is sodium chloride (NaCl) added in the food while drinking water supplies comparatively less concentration. Chloride concentration is associated with Na^+ ions. If the concentration of chloride exceeds 250 mg L^{-1} then it can be detectable through its taste. The high intake of chloride causes kidney and heart diseases [16]. Another experimental work performed on drinking water of Quetta revealed that the concentration of chloride and sulphate ranged from 5.00 ppm to 80 ppm and 20 ppm to 90 ppm , respectively [20]. While, in current study only 1 sample was identified with a concentration of Chloride more than 250 mg L^{-1} .

On human health, no toxic effects have been studied for the concentration of SO_4^{2-} in drinking water. However, the concentration between 1000 – 1200 mg L^{-1} may give purgative effect, which may not lead to, diarrhoea, dehydration or weight loss. According to WHO, the lowermost taste detectable limit of SO_4^{2-} as a sodium salt is 250 mg L^{-1} [17]. The results showed that 4 samples were identified with a higher concentration of Sulphate ($>250 \text{ mg L}^{-1}$). The occurrence of high Sulphates may cause corrosion and gives taste to drink water. The contribution of Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) to the alkalinity of water have been reported [18]. The amount of HCO_3^- in water samples have been detected in the range of 110 to 320 mg L^{-1} .

3.1 Statistical Correlation analysis

The result of each area has been put under the statistical Pearson correlation analysis. The correlation between pH and TDS with fluoride is strongly positive providing 0.841 and 0.775 Pearson correlation coefficient respectively, which is the highly significant result with P value 0.000. This result indicates that the increase in pH and TDS causes to increase in the concentration of fluoride in drinking water samples. These results are formed from the correlation outputs as shown in table 1. It shows that high concentration of fluoride is found in samples which have more concentration of TDS and high pH value. So, the amount of F^- takes part in increasing the concentration of TDS. In the same way, K^+ , Na^+ , Ca^{2+} , Cl^- and SO_4^{2-} are recognized to have a positive correlation with the F^- .

Table 1. The Pearson correlation of pH and TDS with fluoride.

Parameters	Correlation		P-value	N
	pH	Fluoride		
pH	1	0.841	0.000	20
Fluoride	0.841	1	0.000	20
	Fluoride	TDS		
Fluoride	1	0.775	0.000	20
TDS	0.775	1	0.000	20

4. Conclusions

The results of the analysis showed that most inhabitants of the Quetta city utilize contaminated groundwater for drinking purpose. With the exception of 35 % of drinking water samples, other remaining samples were recognized as polluted and not fit for human drinking purpose. The risk of dental fluorosis and dental caries was found for the remaining 65% of the sites due to the higher concentration of fluoride. The increasing pH and TDS of the groundwater were due to the contribution of different salts of F^- , Cl^- , K^+ , Na^+ , and SO_4^{2-} . Statistical correlation between fluoride, pH and TDS is strongly positive and highly significant. From correlation analysis, it is found that fluoride concentration in drinking water depends on the level of pH and concentration of TDS. The salts of K^+ , Na^+ , Ca^{2+} , SO_4^{2-} and Cl^- play a major role in attaining the favourable pH for the dissolution of fluoride-containing compounds in drinking water. Hence it is concluded that rocks present in Quetta valley, are possibly the reason for the increased concentration of fluoride in groundwater. Moreover, the groundwater may come from the strata of the same surroundings. Nevertheless, there has been no inclusive health survey conducted for dental fluorosis to address the problems in the past and there is a very minor difference in the concentration of fluoride that imparts a beneficial or hazardous effect on human health, therefore, there should be regular monitoring of drinking water scheme to maintain the water quality. Hence, the results reveal that in the selected area of Quetta city the assessment of fluoride in drinking water and its correlation with various physicochemical parameter has been studied successfully. Furthermore, there is a need for remedial measures for the removal of fluoride in drinking water on governmental scale.

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