A REVIEW OF GROUNDWATER FLUORIDE CONTAMINATION IN PAKISTAN AND AN ASSESSMENT OF THE RISK OF FLUOROSIS

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ABSTRACT: The fluoride ion (F) is an important anion and a major pollutant of groundwater, affecting millions of people around the globe. Groundwater contaminated with F is the main source of F exposure for the development of fluorosis in humans. Various natural and anthropogenic activities are responsible for the F contamination of groundwater sources. At concentrations greater than the permissible limits, F has adverse impacts on human health with various manifestations of fluorosis, especially in children. In Pakistan, the F content in groundwater sources varies considerably from the World Health Organization (WHO) and national standard value of 1.5 mg/L. In addition to the climatic conditions of an area, the factors controlling the F concentration in groundwater sources include the weathering and leaching of F-bearing minerals and rocks. F contamination of groundwater sources in Pakistan is widespread and is often intense with the highest mean concentration being 28.24 mg/L in the Chachro and Diplo sub-districts in Tharparkar. The lowest value was 0.29 mg/L in Peshawar. High mean values were found for the Estimated Daily Intake (EDI) and the Hazard Index (HI) [$HI=EDI_{water}/RfD$] in both children and adults (EDI: 0.406 mg and 0.098 F/kg bw/day; HI: 6.77 and 1.638, for children and adults, respectively). Children in Pakistan are at a higher risk than adults for developing fluorosis due to F contamination of ground water. The determination of the F status in all the drinking water sources in Pakistan is urgently required.

Keywords: Contamination; Estimated daily intake; Fluoride; Groundwater; Health; Hazard index; Risk assessment.

INTRODUCTION

Fluorine, one of the most reactive, light, and electronegative elements of the periodic table, is ranked 13th in terms of abundance on planet earth.[1] Fluorine does not, therefore, usually occur in elemental form in the environment but rather can form a variety of complexes and exists as the fluoride ion (F) in groundwater.[2-4] In nature, F exists in the form of different mineral complexes including calcium fluoride [CaF_2], sellaite [MgF_2], fluorapatite [$Ca_5(PO_4)_3F$], cryolite [Na_3AlF_6], villiaumite [NaF)] topaz [$Al_2(SiO_4)F_2$], tourmaline, muscovite, biotite, hornblende, and villianmite.[1,3] Other minerals which contain F include mica and amphibole, where a hydroxyl ion (OH^-) is replaced in the structural formula.[5,6]

F is one of the most significant groundwater contaminants.[7] Globally, more than 50% of the population uses groundwater for drinking purposes.[8] Therefore, groundwater F pollution is a widespread and serious concern in both developed and developing countries. Elevated F concentrations in drinking water of >1.5 mg/L are

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frequently reported in many parts of the world, including Pakistan, and jeopardize the health and wellbeing of millions of people.[3,9-13] Although, based on the development of F toxicity, a maximum allowable concentration of F in drinking water has been determined by the Pakistan Environmental Protection Agency (PAK-EPA) and the World Health Organization (WHO) of 1.5 mg/L,[14,15] the Chinese drinking water standard is 1.0 mg/L.[16] Similarly, based on the prevailing climate in Pakistan, a lower permissible F concentration in drinking water has been calculated of 0.7 mg/L, with an optimal range of 0.6–0.8 mg/L.[17]

When setting F standards, many factors need due consideration such as the levels and patterns of F-contaminated water consumption, climatic conditions, and exposure to other sources of F contamination.[3,15] F contamination arises from both natural and anthropogenic activities.[2,18] Natural sources include geological and geochemical sources such as volcanic gases and F-bearing minerals, in igneous (including volcanic), sedimentary, and metamorphic rocks.[2,19-21] There are also anthropogenic sources arising from activities such as the mining of phosphate rocks and various industrial activities, e.g., aluminum smelters, hydrogen fluoride manufacturing,[22] uranium enrichment facilities, steel mills, zinc smelters, the production of glass, tiles, ceramics, and bricks, combustion of F-rich coal in power plants, petroleum refineries,[23-25] the manufacture of fluorinated plastics, cosmetics, calcium carbonate, chalk, and talcum powder, and the production of fluorinated hydrocarbons such refrigerants and aerosol propellants. In addition, some agricultural activities are also associated with F pollution, such as the use of fertilizers, pesticides, and irrigation water,[22] as well as direct human exposure through water fluoridation, F supplements, and the use of fluoridated toothpastes and mouth rinses.[2,3,26,27]

F is a natural constituent of drinking water[28] and although it has been used to prevent dental caries, both topically and by being added to drinking water at a level of 0.7–1.2 mg/L (water fluoridation), it is neither an essential trace element for human health nor necessary for the development of healthy teeth and bones.[29-32] However, F at a concentration of more than 1.5 mg/L may adversely affect human health and wellbeing, causing dental, skeletal, and nonskeletal fluorosis,[29,31] especially in rural parts of developing countries.[2,3] The toxic manifestations of fluorosis may include deformed limbs, calcification of ligaments, rheumatic pain, stiffness, and rigidity of joints.[33] The long term intake of water with a high F concentration may also adversely affect the gastrointestinal tract and liver, renal function, the nervous system, muscles, the reproductive and immune systems,[34,35] DNA-structure,[36] the development of the infant brain, and bones with the development of osteosclerosis.[37] Permanent disability may occur.[2] Young children are especially vulnerable to fluorosis because of F accumulation in the tissues of the growing body.[27,38-40]

EXPOSURE PATHWAYS

Once released into the environment, F may enter the human body through the consumption of potable water and other contaminated sources like food, toothpaste and air.[41] However, with a few exceptions[42,43] potable water is typically the major source contributing to the human intake of F [44,45] and is a determinant of the health problems.[13,46] According to the United States National Research Council, human exposure due to airborne F is small.[27] Usually, food products contribute little to F exposure.[22] After intake, human tissues partially absorb F, and the remaining portion is excreted in urine. Accumulation of F in the human body is due to the regular exposure to various sources of F that release a small amount of F slowly.[2] Several research studies indicate that F contamination in groundwater sources is strongly associated with the mineral composition of the bedrock which contributes higher concentrations of F to underground water reservoirs.[20,47-50]

FACTORS AFFECTING THE F CONCENTRATION IN GROUNDWATER

The weathering and leaching of bedrocks releases F, which finds its way into groundwater sources.[41] Natural sources determine the higher concentrations of F in ground water, and F is closely linked to areas of volcanic activity.[51,52] Apart from natural causes of higher F levels in groundwater, industry is also a major cause of F pollution.[53] The dissolution and solubility of F in groundwater is dependent on different factors such as the calcium and $NaHCO_3$ concentrations in the groundwater,[21] climatic conditions of the area, ground water retention time in an aquifer, pH, depth and temperature of groundwater, recharge area distance from the source, interaction of water with soil and rocks,[44,54,55] and evapotranspiration.[25] In acidic waters of pH<5, F ions interact with metal ions to form complexes. However, at high pH values, the F ion prevails freely in water.[2]

Various studies have been conducted to determine the F concentration in groundwater sources of Pakistan,[56-59] but no review has so far been conducted to evaluate the extent and magnitude of F contamination in the country. In this review, groundwater F contamination reported by various studies from different parts of Pakistan have been compiled and are compared. A health risk assessment was also carried out for F contamination of the groundwater sources in different parts of Pakistan.

F CONTAMINATION IN PAKISTAN

In Pakistan, various studies have revealed higher than permissible concentrations of F in many groundwater sources; making it unsafe for drinking while a few studies have reported F concentrations in groundwater below the PAK-EPA and WHO upper limit guideline of 1.5 mg/L. The reported data for groundwater F concentrations for different regions of Pakistan are shown in Figure 1 and Table 1.

Generally, a high variation exists in the F concentrations in different groundwater sources, ranging from very low levels of 0.05 mg/L in Peshawar, to extremely high and toxic levels of 49.3 mg/L in Tharparkar (Figure 1 and Table 1). A high variation may exist even in different water sources of the same area.[60] Both natural processes and anthropogenic activities contribute to F contamination of groundwater in Pakistan[26,61] but the impact of natural processes on groundwater F contamination is significant.[50,62] F contamination of drinking water is not easy to remedy, and the solution lies in both the management and the monitoring of the contamination hotspots. Areas with high F levels of F should be defluorinated and but, as F is not an essential trace element,[32] there is no need to add F in areas with low F levels.[28]

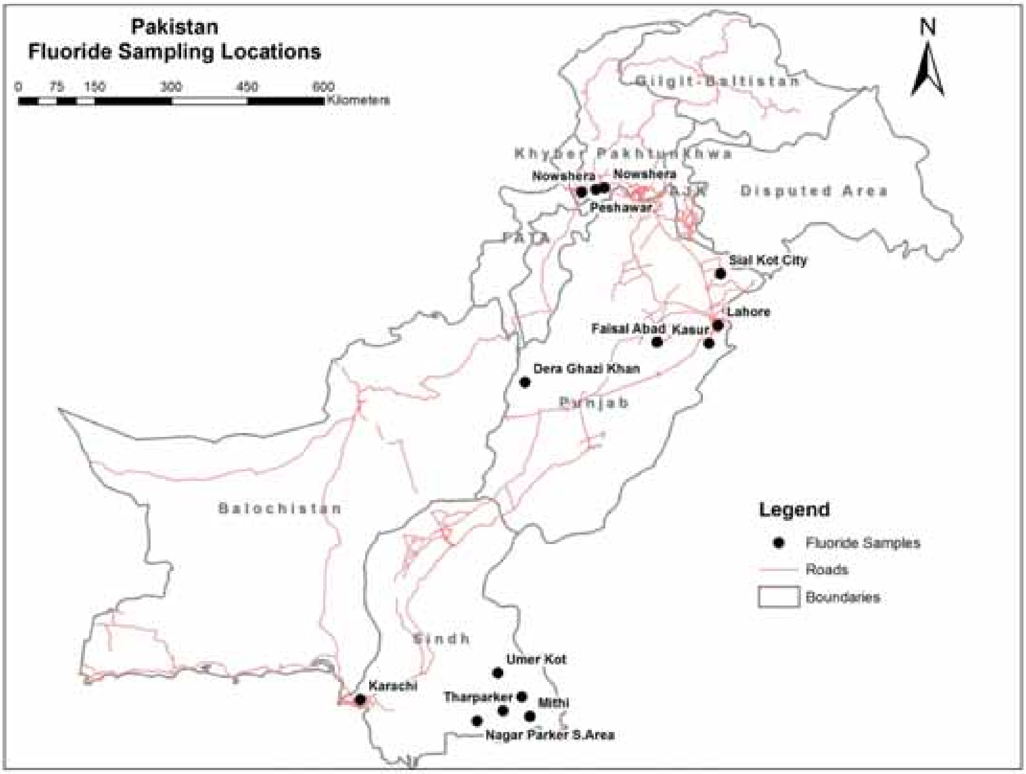

Figure 1. Fluoride sampling locations

Table 1. Fluoride concentration range and mean value (mg/L) in groundwater sources of Pakistan

Location No	Location and number of sources sampled	Range (mg/L)	Mean (mg/L)
1	Chachro and Diplo sub-districts of Tharparkar (n=120) [56]	1.27–43.11	28.24
2	Peshawar (n=38) [73]	0.05–1.10	0.29
3	Umarkot sub-district, Thar Desert, (n=152) [59]	0.06–44.4	5.22
4	Nagar Parkar, Thar Desert, (n=32) [13]	1.13–7.85	3.3
5	Ganderi Union Council, Nowshera (n=48) [56]	0.36–4.8	1.86
6	Dera Ghazi Khan (n=32) [72]	0.25–1.5	0.96
7	Areas of Lahore (n=29) [58]	0.27–7.6	3.07
8	Naranji village and surrounding areas, Nowshera (n=7) [62]	1.08–13.51	8.15
9	Mithi and Nangarparkar sub-districts of Tharparkar (n=24) [70]	13.8–49.3	26.93
10	Kalalanwala area, Lahore and Kasur districts (n=24) [26]	0.38–21.1	8.18
11	Nine different localities in Faisalabad city (n=40) [71]	0.38–1.15	0.76
12	Karachi (n=106) [61]	0.12–6.3	1.16
13	Sialkot city (n=25) [74]	0.41–0.99	0.68
14	Nagar Parkar, area Sindh (n=32) [50]	1.13–7.85	3.33

EXPOSURE DOSE DETERMINATION

The F exposure dose is measured in terms of the Estimated Daily Intake (EDI) of F from groundwater. The EDI values were determined using equation 1 derived from United States Environmental Protection Agency (US EPA).[63]

$$EDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad \text{...................... equation 1}$$

where:
EDI=estimated daily intake of fluoride from groundwater
C=mean fluoride (F) concentration in ground water sources (mg/L)
IR=daily water intake rate (L/day)
EF=exposure frequency (days/yr)
ED=exposure duration (yr)
BW=average body weight (kg)
AV=averaging time for fluorosis

The values of the different variables used in equation1 for the estimation of F exposure dose are given in Table 2.

Table 2. Values of the different variables used for the estimation of the fluoride (F) exposure dose in mg/kg body weight/day based on US EPA 1992,[63] US EPA 2011,[64] and US DOE 2011[65]

Variable	Description of variable	Value
C (mg/L)	Mean F concentration in groundwater sources	Values calculated in Table 1
IR (L/day)	Daily water intake rate	1 for children, 2 for adults
EF (days/yr)	Exposure frequency	365
ED (yr)	Exposure duration	6 for children, 30 for adults
BW (kg)	Average body weight	16.2 for children, 61.8 for adults
Lt (yr)	Life time	65
AT (days)	Average time for fluorosis	ED×365 for children, Lt×365 for adults

The mean F concentration values calculated in this study for the different groundwater sources (Table 1) were used to calculate the EDI for both children and adults (Table 3).

The effects on an individual of F ingestion through contaminated water can be best predicted by the F exposure dose (i.e., mg/kg body weight/day), age, exposure duration, and quantity of water consumed (L/day), including exposure through other routes.[3] For instance, high F concentrations are found in tea leaves and brewed tea may contain F in range of 1–6 mg/.L[3,66,67]

On the other hand, most of the published epidemiological reports have revealed that the health risk for teeth and bone is relatively high from drinking water with concentrations of F of 1 mg/L or above, compared to the exposure from all the other sources of F. Human exposure to F contamination can be effectively determined in by the drinking water F level in mg/L, subject to the conditions that water is the predominant F source and that its consumption is relatively constant in the population under consideration. Furthermore, the consumption of different volumes of water having the same levels of F will expose that population to different doses of F on a daily basis[3]. Moreover, certain factors like diet, humidity, temperature, overall health status, and certain physical activities affect the level of water intake of an individual.

RISK ASSESSMENT

F exposure dose (EDI) values were used to carry out the risk assessment for exposed children and adults following the procedure of Brahman et al. with slight modification.[38] Briefly, EDI values were compared with the F Reference Dose (RfD) and given in equation 2 as a hazard index (HI), which is the ratio of EDI to the reference dose (RfD).

$$HI = \frac{EDI_{water}}{RfD} \qquad \text{.........................equation 2}$$

where:
EDI_{water}=estimated daily intake of fluoride from groundwater
HI=hazard index
RfD=reference dose for fluoride (oral toxicity reference) with the value of 0.06 mg/kg bw/day

According to the US EPA, a HI value of greater than 1 shows a high risk of health effects, and the probability of adverse effects increases as the HI value increases.[68] Therefore, there is a significant chance of some of the various manifestations of fluorosis occurring with a HI value of more than 1, whereas when the HI value is less than 1 significant signs or symptoms of fluorosis may not develop. In the current review study, the EDI and HI values were used to assess the health risk from the intake of F-contaminated groundwater for both children and adults (Table 3).

The EDI values from the different groundwater sources of Pakistan indicate that children have high EDI levels compared to adults. The mean EDIs of F for children and adults were 0.406 and 0.098 mg/kg bw/day, respectively. These results were consistent with the findings of a study conducted previously in the southern region of Pakistan.[38] HI values higher than 1 were recorded for both children and adults with the mean HI value for children being much higher (6.770) than that for adults (1.638) (Table 3). This indicates that children are at high risk of developing fluorosis compared to adults. Only limited data are available on the effects of groundwater F contamination on the exposed population in Pakistan. However, a study carried out in 2004 reported a high prevalence, 66%, of fluorosis in children, aged 12–15 yr, in the Kheshki area of District Nowshera, Khyber Pakhtunkhwa Province.[69] Studies of the population in certain areas of Lahore, where the ground water is highly polluted with F, also found a high prevalence of various manifestations of endemic fluorosis.[58]

Table 3. Fluoride (F) exposure dose (mg/kg body weight/day) (EDI=estimated daily intake) and risk assessment (HI=hazard index) for children and adults

Location	Group			
	Children		Adults	
	EDI (mg/kg bw/day)	HI	EDI (mg/kg bw/day)	HI
Chachro and Diplo (n=120)	1.743	29.051	0.422	7.03
Peshawar (n=38)	0.018	0.298	0.004	0.072
Thar Desert, Umarkot (n=152)	0.322	5.37	0.078	1.299
Nagar Parkar, Thar Desert (n=32)	0.204	3.395	0.049	0.822
Ganderi, Nowshera (n=48)	0.115	1.914	0.028	0.463
Dera Ghazi Khan (n=32)	0.059	0.988	0.014	0.239
Areas of Lahore (n=29)	0.19	3.158	0.046	0.764
Naranji, Nowshera (n=7)	0.503	8.385	0.122	2.029
Mithi and Nangarparkar (n=24)	1.662	27.706	0.402	6.704
Kalalanwala, Lahore and Kasur districts (n=24)	0.505	8.416	0.122	2.036
Localities in Faisalabad (n=40)	0.047	0.782	0.011	0.189
Karachi (n=106)	0.072	1.193	0.017	0.289
Sialkot city (n=25)	0.042	0.7	0.01	0.169
Nagar Parkar, Sindh (n=32)	0.206	3.426	0.05	0.829
Mean	0.406	6.77	0.098	1.638

CONCLUSIONS

As in many other parts of the world, groundwater contamination with F has become a serious concern in Pakistan. Although the major F sources are geological and geochemical processes releasing F into the groundwater, anthropogenic pollution sources, such as industrial wastes, also contribute significantly to the problem. Groundwater is the major drinking water source in Pakistan. The F concentration in groundwater sources is not uniform and varies considerably with the source and location depending on many factors such as climate, rock weathering, and ion exchange. Most groundwater sources are highly polluted with F and are not suitable for drinking purposes.

The elevated F content in the groundwater sources of Pakistan poses a significant health hazard to the exposed population, especially to children. Due to the high EDI of F and the HI for F, immediate attention is needed to mitigate this risk of F-induced toxicity in children. Extensive monitoring is recommended, to determine the status of

F contamination in all drinking water sources of Pakistan. The government should adopt sustainable techniques to maintain safe F levels in drinking water sources, as well as raising awareness among the public regarding the health issues associated with F in groundwater.

ACKNOWLEDGMENT

This study was conducted with the financial support of the Higher Education Commission of Pakistan, and the University of Peshawar, Pakistan. We greatly acknowledge with deep gratitude this financial support.

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