Ground water toxicity due to fluoride contamination in Southwestern Lahore, Punjab, Pakistan

Abdullah Yasar, Tariq Javed, Firdaus Kausar, Jaweria Shamshad, Muhammad Umar Hayat Khan and Rashid Iqbal

ABSTRACT

The prevalence of dental/bone deformities provides motivation for studying the distribution, severity and sources of the Fluoride ($F^-$). The ground water samples ($n = 77$) were collected, from the districts of Lahore and Kasur of approximately 750 km$^2$ area. The water was analyzed for fluoride ($F^-$), pH, electric conductivity (EC), alkalinity and hardness. The results revealed $F^-$ concentration ranges from 0.25–21.3 mg/L. An inverse relation between depth and fluoride concentration was observed. On the basis of cluster analysis three zones were identified. Highly toxic zone was a strip of 15 km wide and 3 km long, along Multan Road from Sunder to Phool Nagar bypass, with fluoride concentration (08–21.3 mg/L). The highly toxic zone inhabited a number of industrial units, disposing off their wastewater through soaking pits. These units contribute pollution to the shallow water, which further penetrates to the surroundings. Hence the shallow water (depth of 45–50 feet) was the most contaminated. The intensity of toxic effects decreases from highly to mild toxic zone. It was concluded that the problem was actually associated with the industrial wastewater. Therefore, to overcome the issue, measures of supplying fresh drinking water from the deep aquifer as well as treatment of industrial water is suggested.

Key words | bone deformities, Lahore, teeth fluorosis, toxicity, water pollution

HIGHLIGHT

- Industry was actually responsible for fluoride toxicity in the region rather than natural sources.

INTRODUCTION

Fluoride is found in plants, soil, animals and water in trace amount. It helps in mineralization of teeth and bones and formation of enamel in teeth (Singh & Mukherjee 2015). Fluoride is required in an optimum concentration to the human body for normal physiological activities (Narsimha 2018; Kumar 2020). Consumption of water with fluoride contents above or below a certain limit may cause dental and skeletal fluorosis (Ghrefat et al. 2014; Narsimha 2018).

Fluoride contents less than (0.6 mg/L) leads to dental fluorosis mottled enamel, and above (3.0 mg/L) of fluoride results in skeletal fluorosis (Dar et al. 2011) other associated health issues include, thyroxine changes, kidney damage (Machenider et al. 2014). A very high concentration of fluoride may even induce cancer (Edmunds & Smedley 2016).

As per the World Health Organization, the range of fluoride contents should be 0.6 to 1.5 mg/L (Brindha & Elango 2011). Its impacts on the human body are irreversible (Jadhav et al. 2015). The sternness of toxic effects depends upon total dose gulped and period of exposure. The severity of toxic effects also depends upon the body response which varies...
person to person, depending upon their health status (Amalraj & Pius 2013).

Fluoride is introduced in water through natural as well as through anthropogenic sources. Most of the fluoride in ground water is natural in origin. Naturally, a trace quantity of fluoride can occur in soils, water, plants, animals and all kinds of vegetables (Narsimha & Rajitha 2018; Adimalla 2020). All over the world, fluoride levels beyond the safe limit in groundwater was due to the presence of fluoride bearing rocks and its mobility in ground water increased the fluoride contents above the safe limit, which has so far affected over 200 million people belonging to 25 nations (Ayoob & Gupta 2006; Adimalla 2020).

Its sources consist of dissolution through weathering of fluoride bearing rocks and emission from volcanic eruptions as well as from marine aerosols (Fawell et al. 2006; Banerjee 2015; Rahman et al. 2018). Primary human activities responsible for fluoride release in the environment are processing of phosphate rocks through mining. Coal is another major source of fluoride, as the coal-fired brick kilns are stimulating fluoride in the air (Ando et al. 2001). Another form of fluoride extensively used in industry is Hydrofluoric acid. It has expanding utilization in metal industry for de-rusting the metals, glass engraving, electronics engineering (Genuino et al. 2012), semiconductors, pottery varnishing, plastics, in aluminum brighteners and also in the cleaning of air conditioning equipment (Bajraktarova-Valjakova et al. 2018). The seepage of wastewater from these industries may cause toxicity of the aquifer due to accumulation.

In Pakistan, fluoride toxicity has been reported from Quetta (Blochistan), Gujrat and Kalalan wala (Punjab province), Dera Ismail Khan (Khyber Pakhtoonkhw), Thar Desert, Sindh, Nagarparkar, Dera Ismail Khan (Khyber Pakhtoonkhw) respectively (Farooqi 2013; Panezai 2016; Adimalla 2020). Khan et al. (2002) studied 1,011 samples from different parts of Pakistan but the fluoride contamination was reported in only 3.5% samples including Kasur district. All samples collected from Lahore were fit for consumption.

In western parts of the twin districts Lahore and Kasur (Punjab province), around 17 villages (1.51 million population) were reported with bone deformities. Most of the affected people were teenagers (Farooqi et al. 2007). In 2007, the issue was scrutinized for the last time and it was reported that phosphate fertilizer and brick kilns were responsible for fluoride introduction. It needs to be interrogated comprehensively to identify the real culprit as brick kilns and phosphate fertilizer is used throughout the Punjab. In addition, the paradigm shift of the issue also needs to be investigated. The real objective of the study was to identify the actual source of fluoride and its relationship with other factors. Secondly, it was to mark the boundary of fluoride contamination in the area.

**Study area**

The area under study is situated in the Punjab, the most populous province of Pakistan. The focus of the study was the northwest districts of Kasur and Lahore (being affected with bone and teeth deformities). The populations of the Lahore and Kasur districts is about 11,126,285 and 3,454,996 with areas of 772 and 4,796 km², respectively. The area under study is mainly lined with fertile sity plains of the River Indus and its tributaries. The study area is located at the left bank of River Ravi and at the right bank of River Sutlej. The ground water recharged mainly through these rivers and canals. Two layers of water exist underground. The shallow aquifer is the main source of water for the population. The deeper layer found at >400 feet. More than 80% of the population consume water from shallow aquifers through home installed hand pumps, motor pumps, etc. at the depth of 70–200 feet. The climate of the area is extreme with cold foggy winters followed by spring starting from mid-February; spring continues until mid-April, followed by a very hot and long summer, extending to September. Heavy rains, also called monsoon, occur from mid-July to mid-September. The annual temperature ranges from −2 to 45 °C. Map of the study area is presented in Figure 1. Despite of its tropical climatic conditions, the whole Punjab is under intense cultivation because irrigated agriculture is predominant. Overall, Punjab’s share in agriculture production is 56.1% to 61.5%. Here, the agriculture sector engages about 45% of labor and contributes 21.4% to the total GDP of the country. Most of the people are farmers but the study area has numerous industrial units, therefore people work in industry as well. The industrial sector contributes to 24% of the GDP of the Punjab.
MATERIALS AND METHODS

Sampling strategy

A total of 77 ground water samples were collected in pre-cleaned, high density polyethylene bottles directly from sources, i.e. hand pumps, motor pumps and tube wells. The samples were collected after purging for 5 min from a running water source. As the previous studies showed, there are two aquifers in the area, i.e. shallow and deep separated by a less permeable layer (Farooqi et al. 2009). Most of the community uses water from shallow aquifer. Therefore, almost 90% of samples were collected from first aquifer layer (hand pumps or/and motor pump) and 10% from the second kind of aquifers (tube wells/deep wells). The soil samples were collected in plastic bags, grinded,
and, after drying, were passed through 2 mm mesh sieve and then a suspension was prepared by mixing soil in 1:2.5 (g: mL) ratio with deionized water. Later, the supernatant was tested after shaking for 15 min (Battaleb-Looie et al. 2012). The chemical analysis was carried out following the American Public Health Association standard methods (APHA, AWWA & WEF 2005). Fluoride ion was electrochemically analyzed using ion selective electrode (ELE International Model 488–010), calibrated using standards solution (1,000 mg/L) of Merk, with concentrations, i.e. 0.1, 1, 5 and 10 mg/L, etc. covering the ranges of fluoride found in water. The pH was measured in the field by pH meter (HANNA HI98107), electric conductivity (EC) was measured through TDS meter. The fluoride, pH, total dissolved solids (TDS), total alkalinity (TA), total hardness (TH) and calcium ion concentration (Ca\(^{2+}\)) were analyzed by the APHA method 4500-F C, 4500- H + B, 2540-C, 2520 B, 2340-C and 3500-Ca-B respectively. The statistical analysis was carried out by the Statistica 10.2 software. The latitude and longitude of the sampling points were marked using a global positioning system (GPS) device (GARMIN eTrax 20). The map of the study area was prepared by GIS 10.2 software using inverse distance weighting (IDW) interpolation technique (Arif et al. 2015; Aravinthasamy et al. 2020).

**Quality assurance and quality control**

In order to maintain the meticulousness and accuracy of the results, all of blank, standard, and samples were tested in replicates. The data was rejected if standard deviations were more than 10%. Recovery ratios of the results were calculated for the determination of accuracy. Experimental instruments were calibrated before each sample testing.

**RESULTS AND DISCUSSION**

The basic statistical analysis of water quality data analyzed is presented in Table 1. The fluoride contents ranged from 0.25 to 21.3 mg/L. The pH value of the samples ranged between 7.7 to 8.5 with mean value 8.11 showing the alkaline nature of ground water as usual, which was in accordance with literature where the high pH values were cited in the fluoride contaminated areas (Battaleb-Looie et al. 2012). In the current study, the highest pH value was observed in the areas where the maximum concentration of fluoride was also observed. The maximum EC value of 3,280 \(\mu\)S/m was observed. It was also in accordance with the literature. The waters with EC values more than 1,750 \(\mu\)S/m normally has the highest concentration of fluoride (Dutta & Baruah 2013). The dissolution rate of fluoride in water. The pH was measured in the field by pH meter (HANNA HI98107), electric conductivity (EC) was measured through TDS meter. The fluoride, pH, total dissolved solids (TDS), total alkalinity (TA), total hardness (TH) and calcium ion concentration (Ca\(^{2+}\)) were analyzed by the APHA method 4500-F C, 4500- H + B, 2540-C, 2520 B, 2340-C and 3500-Ca-B respectively. The statistical analysis was carried out by the Statistica 10.2 software. The latitude and longitude of the sampling points were marked using a global positioning system (GPS) device (GARMIN eTrax 20). The map of the study area was prepared by GIS 10.2 software using inverse distance weighting (IDW) interpolation technique (Arif et al. 2015; Aravinthasamy et al. 2020).

| Serial # | Mean   | Min   | Max    | Std. Dev. |
|---------|--------|-------|--------|-----------|
| Depth in feet | 123.89 | 75.00 | 600.00 | 86.02     |
| Fluoride (mg/L) | 5.06  | 0.25  | 21.30  | 4.33      |
| pH     | 8.11  | 7.70  | 8.50   | 0.21      |
| Total alkalinity (mg/L) | 552.24 | 90.00 | 940.00 | 229.68    |
| Calcium (mg/L) | 24.88 | 6.500 | 101.00 | 14.8      |
| Total hardness (mg/L) | 192.24 | 80.00 | 298.00 | 64.42     |
| Total dissolved solids (mg/L) | 1,133.00 | 101.00 | 2,198.00 | 498.10 |

Fluoride contents above the permissible limits may cause various acute health issues. For example, greater than 4 mg/L induce dental and skeletal fluorosis (Adimalla et al. 2018; Dinka 2009) and 10 mg/L may cause chronic osteoporosis (fragile bones) in women, due to the replacement of calcium in bones by fluoride (Fawell et al. 2006). A brief classification of fluoride and associated health risk is presented in the Table 2. In the study area, almost 41.5% of water samples collected fall under the WHO safety limits and 59% of the water samples exceeds the WHO guideline value and thus have imposed a medium to high health risk to the population, whereas 9% of the sample falls in the category of the highest risk. In addition, a previous study conducted about dental fluorosis by Rizwan et al. (2010) in University of Lahore revealed that 12% of patients having dental fluorosis (39%) showed moderate, and 19% showed extreme dental fluorosis in the study area and females were more affected compared to males (Rizwan et al. 2010). From the Punjab province, maximum level of fluoride was reported from District Mailsi 29.6 mg/L (Rasool et al. 2015), while 0.29–0.43 mg/L, 0.1–0.36 mg/L, 0.15–1.2 mg/L was reported from Islamabad, Rawalpindi, and Bahawalpur, respectively.
Table 2 | The categorization of fluoride level, of its health impacts and percentage of the samples fall in these categories

| Category        | F (mg/L) | The number of samples | %age | Impact on human health                  | References               |
|-----------------|----------|-----------------------|------|----------------------------------------|--------------------------|
| Safe            | <1.5     | 32                    | 41.5 | Healthy                                | Yari et al. (2016)       |
| Mild risk       | 1.5–4    | 16                    | 20.7 | Dental fluorosis                       | Dissanayake (1991)       |
| Medium risk     | >4       | 22                    | 28.57| Dental fluorosis and osteoporosis      | Adimalla et al. (2018)   |
| High risk       | >10      | 7                     | 9.09 | Swear fluorosis and carcinogenesis     | Ozsvath (2009)           |

(Arshad & Imran 2017). Raza et al. (2016) reported 0.3–6.4 mg/L from Gujrat. From Kasur district Arshad & Imran (2017) reported the concentration of 0.6–8.6 mg/L. However, from Sindh province Nagarparkar exhibited 18.5–35.4 mg/L of the fluoride (Brahman et al. 2013). The comparison of the current study with the studies conducted in Pakistan and in the region is presented in the Table 3.

In order to discover the linkage between the fluoride with other parameters, the scatter plots were shown in Figure 2(a)–2(f). The scatter plot of F⁻ versus pH

Table 3 | Comparison of selected parameters with previous studies from the developing countries

| Location                                   | F⁻ (mg/L) | pH     | Ca²⁺ (mg/L) | TDS (mg/L) | References               |
|--------------------------------------------|-----------|--------|-------------|------------|--------------------------|
| Kalalan wala, Punjab, Pakistan             | 0.25–21.3 | 7.7–8.5| 8–102       | 101–2,198  | Present study            |
| Kalalan wala, Punjab, Pakistan             | 0.11–22.8 | 7.3–8.8| 2–140       |            | Farooqi et al. (2007)    |
| Kasur, Punjab, Pakistan                    | 0.6–8.6   | 7.3–9  | 253–1,581   |            | Arshad & Imran (2017)    |
| Nagarparkar Sindh, Pakistan                | 18.5–35.4 | 7.6–8.7|            |            | Brahman et al. (2015)    |
| Nagarparkar Sindh, Pakistan                | 1.13–7.85 | 7.1–8.4|            | 449–15,933 | Rafique et al. (2009)    |
| Tharparkar Sindh Pakistan                  | 0.96–2.74 | 7.38–8.59| 24–220    | 792–3,782  | Hussian et al. (2012)    |
| Dera Ismail Khan area, Pakistan            | 0.75–1.21 | 7.3–7.6| 61–139      | 904–1,400  | Ahmad & Qadir (2011)     |
| Mailsi, Punjab, Pakistan                   | 5.5–29.6  | 6.84–8.76| 17.1–96.6 | 421–1,323  | Rasool et al. (2005)     |
| Gujrat, Punjab, Pakistan                   | 0.3–6.4   | 7–8.9  | 1.12–256    | 87–2,238   | Raza et al. (2016)       |
| Sialkot, Punjab, Pakistan                  | 0.41–0.99 | 6.72–7.98| 135–581   |            | Ullah et al. (2009)      |
| Quetta, Balochistan, Pakistan              | 0.3–3     | 7–8.5  | 333–1,200   |            | Panezai et al. (2008)    |
| Alleppey, Southern India                   | 0.68–2.88 | 6.65–10.43| 14–71.8   |            | Raj & Shaji (2017)       |
| Kuhbanan basin, Central Iran                | 0.05–10.8 | 6.6–8.68| 16.2–528    | 138–9,100  | Puzand (2016)            |
| Shahai in the Hetao basin, Inner Mongolia   | 0.30–2.57 |         |            |            | Guo et al. (2012)        |
| Palghat District, Kerala, India             | 0.2–5.75  | 7.21–8.5| 12–212      |            | Shaji et al. (2007)      |
| Nalgonda district, Andhra Pradesh, India    | 0.07–8.8 mg/L | |         |            | Brindha & Elango (2013) |
| Gaya Region of Bihar, India                | 0.19–14.4 |         |            |            | Yasin et al. (2011)      |
| Andhra Pradesh, India                      | 0.4 to 5.8 mg/L | 7.18 to 9.32| 290–2,640  |            | Adimalla et al. (2019)   |
| Gujarat, Western India                     | 0.4–4.8   | 7–8.2  | 12–176      |            | Kumar et al. (2017)      |
| Western India                              | 0.1–6.6   | 7.4–8.6| 449–5,300   |            | Singh & Mukherjee (2015) |
| Tamilnadu, India                           | 0.3–3     | 6.3–9.2| 4–1,600     | 194–23,699 | Srinivasamoorthy et al. (2012) |
| Central India                              | 1.3–3.8   | 6.8–7.9| 20–503.6    | 302–997    | Naaz (2015)              |
| Northwestern Saudi Arabia                  | 0.98–2.1  | 7.38–9.63| 144–1,869  | 545–7,027  | Ghrefat et al. (2014)    |
| Dambulla, Kakirawa, Northwestern Sri Lanka | 0.04–3.16 | 6.1–9.4| 0.78–77     |            | Young et al. (2011)      |
| Yuncheng Basin, Northern China             | 0.5–14.1  | 7.11–8.55| 274–9,597  |            | Li et al. (2019)         |
| Sri Lanka                                  | 0.01–5    | 5.2–8.5| 0.88–300    |            | Rubasinghe et al. (2015) |
(Figure 2(a)) showed a strong linear association \( r = 0.813 \) of the \( F^- \) with pH as reported in the literature (Brindha & Elango 2011). This is because the ionic radii of \( F^- \) and \( OH^- \) have same ionic strength and they often substitute each other within minerals, that is why \( F^- \) is found in equilibrium with hydroxide, i.e. at pH greater than 7.0 (Rafique et al. 2019). Clay minerals, such as kaolin has the ability to grasp \( F^- \) ions on its surfaces, but when the pH increases, the \( OH^- \) ions displace the \( F^- \) ions, discharging it to groundwater (Pazand 2016). Moreover, the \( F^- \) contents were found to be highest in those areas where pH and alkalinity values were high, i.e. Manga Mandi, Chah kalalanwala, Talab saraey, Nath-e-Khalsa localities (Figure 3(b)). The highest ranges of \( F^- \) values were found to be in coexistence with...
high alkalinity values (Figure 2(b)), i.e. 12–21.3 mg/L at 610–940 mg/L alkalinity. The map of the study area representing relationship of pH, depth and fluoride concentration is presented in Figure 3(a)–3(c), whereas the F⁻ versus alkalinity scatter plot has shown moderately positive correlation (r = 0.564). Normally high alkalinity is observed where F⁻ ion concentration is high (Manikandan et al. 2014; Narsimha & Sudarshan 2016). It has been already established that the higher alkalinity of groundwater stimulates the leaching process of F⁻ hence increasing its amount in the groundwater (Tiwari et al. 2012; Rao 2013). The alkalinity of groundwater is mainly caused by bicarbonate. Thus, a high positive correlation (r = 0.82–0.90) was observed between F⁻ and bicarbonate by Rao (2013). The adsorption of F⁻ in soils increases from acidic soils to alkaline soils (Young et al. 2011). In contrast, an inverse relationship between the F⁻ ion and Ca^{2+} (−0.264) was observed (Figure 2(c)), which was in accordance with literature, as reported by Das et al. (2003), and Kumar et al. (2017) reported r = −0.34, −0.391. Furthermore, the water rich in F⁻ has low calcium contents because when F⁻ increased and attained an equilibrium, calcite was removed by precipitation, ultimately decreasing the calcium contents of water (Annadurai et al. 2014). A weak negative correlation of fluoride with Ca^{2+} and Mg^{2+} −0.22, −0.25 respectively were reported by Narsimha & Sudarshan (2016) and Dinka (2019). In contrast, a positive correlation of F⁻ and calcium r = 0.62 was also detected by Alabulaaly et al. (2013).

During the present study, the Ca^{2+} contents were found at lowest level, i.e. 11 mg/L in response to high levels of alkalinity (940 mg/L) and F⁻ (21.3 mg/L) in ground water at the same spot. The high alkaline nature of ground water indicates the poor nature of calcium and magnesium ions (Masuda et al. 2010; Dinka 2013). The scatter plot of F⁻ versus depth (Figure 2(f)) showed negative loading which means that the F⁻ concentration in ground water decreases as the depth increases. The high level of F⁻ contamination was present in the shallow water aquifer and its concentration decreased with depth which did not comply with the study of Kumar et al. (2017) and Karro & Uppin (2013). However, these results comply with the findings of Brindha & Elango (2013) who computed maximum concentration of F⁻ at 15.3 to 30 feet. The moderately positive correlation of TDS with F⁻ was r = 0.422 observed (Figure 2(e)); a higher concentration of dissolved salts upsurges the ionic strength, leading to an intensification of F⁻ in groundwater (Rafique et al. 2009).

The factor analysis was used for plotting graph between first two varifactors VF1 and VF2. The two principal components were extracted by varimax normalized rotation. It extracted maximum variation of data which was plotted against each other (Figure 4). Two groups were identified, i.e. 1st group has pH and F⁻ demonstrating their inter-dependence, while 2nd group contain total alkalinity (TA), total hardness (TH), EC and TDS which demonstrate their close relationship with each other.
The F\(^-\) concentrations were subjected to the cluster analysis and three clusters were obtained (Figure 5). Where highly toxic zone included the areas having maximum F\(^-\) concentration up to 8–21.3 mg/L F\(^-\). This zone roofed an oval area with 15 km width and 3 km length parallel to Lahore Multan Road. Manga Mandi was discovered as the epicenter of this abuse. The toxicity zones are highlighted using GIS technique in Figure 3. The level of toxicity and its spatial distribution in the area has been shown by different colors. Dark orange color represents areas with maximum and blue with minimum F\(^-\) contents.

The community of highly toxic zone was suffering from different types of bone and dental fluorosis especially in young. The maximum concentration of fluoride was observed in Talab Saraey village having F\(^-\) (21.3 mg/L) located at 03 km Manga Raiwind Road. Previously, Farooqi et al. (2007) computed 22.8 mg/L, 4.2 mg/L, and 17.1 mg/L from Chah Kalalan wala,
Manga Mandi and Shamkey Bhattian sampling site. In contrast, the current study revealed that Chah Kalalan wala, Manga Mandi and Shamkey Bhattian have 13.9 mg/L, 12.8 mg/L, and 9.95 mg/L of F$^-$/C0 respectively. Farooq et al. (2016) reported maximum 3.45 mg/L of fluoride, while in present study it was 2.7 mg/L from Thokar Niaz Baig. It was also observed that fluoride contamination was not equally spread in affected areas and it varies from village to village at same depth. The maximum fluoride value was observed at depth of 50 feet from Talab Saraey village and, at the same time just 1.5 km away, it was found 1.25 mg/L at same location and depth. Similarly, the contaminant level varies from depth to depth at the same site, for example in Kamas village and its vicinity the value was 9.3 mg/L at 150 feet depth and it was 0.314 mg/L at 100 feet depth and 0.475 mg/L at 300 feet depth, in the same area. Similar findings were reported by Farooq et al. (2016) from Thokar Niaz Baig, stating that the samples collected from shallow water (80–200 feet) were mostly contaminated with fluoride; in contrast, samples collected from the depth of 450 feet had 0.7 mg/L of fluoride. Lahore city’s 392 tube wells investigated in 2007, at a depth of 500–800 feet, had no fluoride contamination (Farooq et al. 2016).

The medium toxicity zone consists of areas having F$^-$/C0 contents between 4 to ≤8 mg/L in shallow ground water. In these areas, dental diseases were prevailing on a large scale among the residents having yellowish and porous teeth. The situation was even worse in Phool Nagar city where arthritis, periodontics, and stiffness of muscles was evident in most of the population. Kaminsky (1990) showed that residents exposed to 4–8 mg/L of F$^-$/C0 range may suffer from fluorosis in teeth and osteoporosis.

The mild toxic zone was a strip of 5–10 km in width along Lahore-Raiwind Road, covering Kot Radha Kishan-Phool Nagar road and surroundings, where F$^-$ ranges between 1.5–4.0 mg/L. Dental caries were more evident here. The 40% of children at the age of 6–12 years were suffering from dental caries. It was observed that in the highly toxic zone and in the mild toxic zone, industrial units including sugar, plastic, polymers, chemicals, etc. were found disposing their waste into soaking pits, contaminating the ground water, while in the medium toxic zone, industrial units were disposing their waste in rohi nullah.

Source identification

Principal component analysis (PCA) is an independent technique for capturing the variability of the data, it recognizes the pattern of variation in a large data set of inter correlated variables and transforms them to a smaller uncorrelated set. The analysis recognizes the most meaningful parameters. PCA based on factor analysis was applied on the data of all three zones separately to assess the possible sources of the pollution and considerable factors were recognized. For each zone, unrotated principal component with factor loading >0.7 were considered (Table 4). For each zone, PCA with eigen value more than one was considered important.

In the highly toxic zone, the VF1 showed 38.05% of total variance and had a strong positive loading with EC ($r = 0.842$), F ($r = 0.745$) and TDS ($r = 0.854$) and negative loading for Ca$^{2+}$ ($r = -0.626$) which showed variation in the concentration of the F$^-$ and increase in the TDS and EC of the water along with decrease in calcium contents, which indicated that the F$^-$ has inverse relation with calcium as discussed earlier. A higher concentration of dissolved solids enhances the solubility of F$^-$ ions (Rafique et al. 2009). In this zone, F$^-$ as well as the ionic strength is continuously increasing ($r = 0.745$); mean salts are added to the shallow water from some unknown sources. Previously, Farooqi et al. (2007) argued that the brick production and coal combustion introduce F$^-$/C0 into air and its deposition to soil; along with phosphate fertilizer, these were the main sources of F$^-$ in the area, but the whole Punjab province of Pakistan is using the same fertilizer and, throughout the Punjab, brick kilns are functional; the problem lies in a specified region while the PCA showed the addition of TDS along with F$^-$, indicating a continuous source of F$^-$ in the region which might be the industry.

In highly affected areas, investigation from the local community and concerned departments, i.e. Environment Protection Agency Punjab, etc., it was found that no drainage system exists in the area and about all industrial units of the region have been disposing their wastewater into ground water through soaking pits. The major types of industry found in this area were wire manufacturing industry, fertilizers, pharmaceuticals, metal works, textiles, auto industry, brick kilns, etc. Their wastewater was directly added to the aquifer, continuously adding TDS and F$^-$ in...
the area verifying the perception. The VF2 showed a total variance of 22.7% of the same zone; this explains a negative loading ($r = -0.727$) of the hardness meaning the hardness in the region is decreasing.

In the medium toxic zone, VF1 showed 38.24% of the total variance with negative loading of EC, total alkalinity and TDS ($r = -0.900, -0.844, -0.899$) while $F^-$ also had weak negative loading $r = -0.417$, indicating all these parameters have been decreasing in the region. VF2 of the same region explained 17% of the total variance with only strong negative loading of the $Ca^{2+}$ ($r = -0.722$), indicating a sharp decrease in calcium contents in the region, indicating the source of the problem was in the highly toxic zone.

The VF1 of the mild toxic zone explained a total variance of the 34.4% with negative loading of EC, total alkalinity and TDS ($r = -0.900, -0.844, -0.899$) while the VF2 had 16.24% of the total variance with negative loading of the $F^-$ ($r = -0.526$), indicating a decreasing trend and strengthened our findings that $F^-$ and other dissolved solids were introduced through the highly toxic zone.

### Natural sources of fluoride

In most of the studies in the world, it was evident that the most of $F^-$ is introduced into the environment through natural sources. In order to investigate the natural contribution, six soil samples were collected from the highly toxic zone to test for $F^-$ contents and the results were found in the range of 0.03–1.6 mg/kg. Previously, a detailed study of the soil of the same area was conducted by Farooqi et al. (2013) who had reported $F^-$ in surface soil in the range of 0.1–5.2 mg/kg; with mean value of 1.9 mg/kg and for deep soil samples 0.1–2.1 mg/kg; with mean value of 0.8 mg/kg except one sample containing 16 mg/kg collected from the surface soil near the industrial zone having numerous units, including chemical plants. In contrast, the studies from the other areas of the world showed very high concentration of the $F^-$ in soil where $F^-$ is detected in the ground water. A comparison of the current study with the other studies is presented in the Table 5.

The adsorption and desorption processes directly affect $F^-$ migration and exchange from soil to water and water to soil (Wang et al. 2002). In most of the cases in the world, the main reason of elevated concentration of $F^-$, in soil and water, was its natural intrusion from dissolution of bed rocks containing $F^-$ minerals. In the bed rock, fluoride is as abundant as 625 mg/kg which was because of fumarolic gasses, geography and volcanic activity (Rasool et al. 2015). Liu et al. (2014) reported the $F^-$ concentration in the range 20–500 mg/kg in soil. Young et al. (2011) argued that the $F^-$

### Table 4 | Factor loadings of significant principal components in different zones

| Variables                  | Highly toxic zone | Medium toxic zone | Mild toxic zone |
|---------------------------|-------------------|-------------------|-----------------|
|                           | VF 1              | VF 2              | VF 1            | VF 2              | VF 1              | VF 2              |
| Depth in feet             | -0.023            | -0.632            | 0.126           | 0.501             | -0.076           | 0.673            |
| pH                        | 0.489             | 0.206             | -0.444          | 0.188             | -0.417           | -0.517           |
| EC $\mu$s/m               | 0.842             | -0.330            | -0.900          | 0.264             | -0.892           | 0.247            |
| $F$ (mg/L)                | 0.745             | 0.619             | -0.417          | -0.506            | -0.550           | -0.526           |
| Total alkalinity (mg/L)   | 0.634             | -0.437            | -0.844          | 0.147             | -0.802           | -0.089           |
| $Ca^{2+}$ (mg/L)          | -0.626            | -0.246            | -0.583          | -0.722            | 0.228            | -0.387           |
| Total hardness (mg/L)     | -0.137            | -0.727            | 0.051           | -0.310            | 0.091            | 0.154            |
| TDS (mg/L)                | 0.854             | -0.322            | -0.899          | 0.260             | -0.891           | 0.247            |
| Expl. Var                 | 3.045             | 1.817             | 3.059           | 1.319             | 2.754            | 1.299            |
| Prp. Totl                 | 0.381             | 0.227             | 0.382           | 0.165             | 0.344            | 0.162            |
| Eigen value               | 3.045             | 1.817             | 3.059           | 1.319             | 2.754            | 1.299            |
| % Total                   | 38.057            | 22.714            | 38.243          | 16.483            | 34.422           | 16.243           |
| Cumulative                | 38.057            | 60.771            | 38.243          | 54.726            | 34.422           | 50.665           |
| Source                    | Industry          | Industry          | Intrusion       | Intrusion         | Intrusion        | Intrusion        |
contaminated ground water has most often been found in crystalline basement aquifers and from arid sedimentary basins. Ghrefat et al. (2014) reported from Saudi Arabia, the F\textsuperscript{-} concentration in the soil was in range of 250–520 mg/kg. The total fluoride ranges from 100 to 400 mg/kg in Silurian and Ordovician carbonate rocks while clayey dolomite contain up to 1,100 mg/kg. The maximum fluoride found in K-bentonite, 2,800–4,500 mg/kg. The fluoride leached into water varies from 4–10 mg/kg in case limestone and dolomite and 25–51 mg/kg in K-bentonite (Karro & Uppin 2013). In the light of all these findings the possibility of natural contribution was ruled out.

Another possibility of introduction was canals and drains. So, six water samples were collected from hand pumps installed at the bank of drains and canals. Results presented in Table 6 were within the WHO permissible limits. While Farooqi et al. (2007) reported 1.7–2.28 mg/L of F\textsuperscript{-} in canal water with a mean value of the 2 mg/L from the same area, Kausar et al. (2013) reported 0.15–1.02 mg/L from River Chenab (irrigating the study area). On the other hand, the water samples collected from Jhugian village located at the left bank of River Ravi had fluoride up to 0.5 mg/L. Normally F\textsuperscript{-} concentrations in surface water are usually low 0.01–0.5 mg/L (Susheela et al. 1999; Msonda et al. 2007). Therefore, the possibility of surface water contribution towards the contamination of the F\textsuperscript{-} in the area was also ruled out. So the only culprit of the contamination seemed to be the industrial wastewater intrusion through soaking pits in the area.

Further investigation of the fact may be carried out through sampling of wastewater of the industry, but the main hurdle was the attitude of industrialists, not allowing sampling of their effluents.

**CONCLUSIONS**

Fluoride contamination in ground water of Southwestern Lahore, Punjab, Pakistan was evaluated for identifying the source of contamination. Overall, 59% of the sample falls in the category of medium risk while 9% falls in the highest risk category. The contaminated area was categorized into three zones, i.e., high, mid and low toxicity zones. The shallow aquifer (80–200 feet) was the most contaminated with F\textsuperscript{-} up to the 100 feet depth. In contrast, deep water was fit for consumption. Most of the highly contaminated areas run along main grand trunk road, i.e. Multan Road, which holds heavy industry having no drainage system. The low concentration of F around the canal and River Ravi indicates

| Table 5 | Fluoride concentration in soil and water samples from the region |
|---------|---------------------------------------------------------------|
| Region                          | Depth (cm) | Fluoride conc. in soil (mg/kg) | Fluoride conc. in water (mg/L) | References         |
| West Lahore and Kasur, Punjab, Pakistan | 0–30       | 0.03–1.6                        | 0.25–21.3                        | Present study                      |
| West Lahore and Kasur, Punjab, Pakistan | 0          | 0.1–5.2                          | 0.11–21.8                        | Farooqi et al. (2009)               |
| West Lahore and Kasur, Punjab, Pakistan | 30         | 0.1–2.1                          |                                     | Farooqi et al. (2009)               |
| Saudi Arabia                     | 250–520    | 0.98–2.1                         | 0.51–21.3                        | Ghrefat et al. (2014)               |
| Mysore District, Karnataka, India | 5–20       | 3–11.2                           | 1.5–25.5                          | Begum (2012)                      |
| Maharashtra, India               | 1–30       | 2.63                             | 1.63                             | Naik et al. (2017)                  |

| Table 6 | Fluoride toxicity near canals or drains |
|---------|----------------------------------------|
| Serial # | Source | Depth feet | pH | F (mg/L) | T. Alk. (mg/L) | Ca (mg/L) | T.H mg/L | TDS mg/L |
| 1.       | H P    | 100        | 7.8 | 0.506    | 480           | 29        | 120      | 1,400     |
| 2.       | H P    | 70         | 7.8 | 1.250    | 460           | 17.5      | 188      | 907       |
| 3.       | H P    | 80         | 7.9 | 0.962    | 360           | 27        | 140      | 930       |
| 4.       | H P    | 70         | 8.0 | 0.912    | 160           | 38        | 288      | 225       |
| 5.       | H P    | 140        | 8.0 | 1.150    | 440           | 30        | 120      | 3,276     |
| 6.       | H P    | 100        | 8.0 | 0.234    | 380           | 28        | 120      | 770       |
dilution of the water with water having low F contents. Whereas the soil samples analysis indicated that soil had very low concentration of fluoride as compared to the rest of the world, indicating that the bed rock gave slight contribution. The old residents interviewed indicated that no such disease history prevailed in past. Therefore, fluoride contamination of ground water in the study area was due to industrial waste water intrusion.

Further verification was possible with the industrial wastewater analysis but access was denied. Recently reported bone deformities and dental caries can be linked with the increased F toxicity in the area and needs remedial actions such as treatment of the wastewater before disposal through law enforcement and deep-water utilization for drinking rather than treatment of water before drinking.

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This article does not contain any studies involving animals performed by any of the authors.

CONSENT TO PARTICIPATE
This article does not contain any studies involving human participants performed by any of the authors.

AUTHOR CONTRIBUTIONS
Dr Yasar Abdullah conceived the idea, managed overall article development, Mr Tariq Javed collected field data (interview the public) and water samples, performed experimental work with the help of Firdaus Kausar. Abdullah Yasar facilitated the experimental work and gave supervisory help at every phase of research. Firdaus Kausar and Jaweria Shamshad organized the write up and performed data analysis as well as offered technical writing assistance. Muhammad Umar Hayat Khan provided specialized support in GIS mapping. Dr Rashid Iqbal has reviewed the whole work done. All authors read and approved the final manuscript.

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All relevant data are included in the paper or its Supplementary Information.

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