An assessment of fluoride accumulation in the air, soil, water and vegetation around brick kilns at Tarnol, Islamabad, Pakistan.

Khalıd S.[1], Bıbı N.[1], Asf I.[1], Ahmad M. N.[2] And Shah R. [3]

1: Environmental Sciences Department, Fatima Jinnah Women University, Rawalpindi, Pakistan

2: Department of Agricultural Chemistry, Agriculture University, Peshawar, Pakistan

3: National Institute of Health Islamabad, Pakistan

Corresponding author

email: sofiarahim@hotmail.com

Abstract

Fluoride has been reported as an emerging pollutant espacially around brick kilns in South Asia. The current study was conducted to determine the inorganic fluoride concentration in air, water, soil and vegetation in the vicinity of brick kilns at Tarnol, Islamabad Pakistan. All samples were tested highly positive for fluoride contents in air, soil, water and vegetation near the brick kilns as compared to sites further away. The soil leachable concentration ranged from 2.57mg/kg to 4.08mg/kg, water fluoride level ranged from 0.5mg/L to 1.85mg/L and vegetation fluoride content ranged from 48.29 mg/kg to 20.3 mg/kg. The results from the present study suggest that due to the increase in population of the capital city of Pakistan i.e. Islamabad, the brick kilns numbers will also be increased that will jeopardize the environmental condition for both plants as well as humans.

Keywords: Fluoride, Environment, Brick Kilns, Pakistan

Introduction

Greater urbanization in the major cities of South Asia have resulted in the brick manufacturing as the fastest growing industrial sector (Skinder *et al*., 2014). There have been increased number and outpt of brick kilns in the vicinity of these cities (Ahmad *et al*. 2014). There are about 11000 brick kilns currently operating in Pakistan (Barrows, 2010), out of these 5000 are reported to be functional in Punjab province (Bales,2012). In Pakistan mostly the wood, waste oil, tyres, oily sludge and coal is used to fire the brick kilns (EPA, 2004).These brick kilns are considered to be an important source of Fluoride emissions that affect the quality of surrounding environment (Saleem *et al*. 2015). Fluoride is emitted from bricks kilns at about 900^{o}C-1150^{o}C in the form of HF, SiF_4 and CaF_2 (CATF, 2010). Coal burning in the manufacturing of bricks is a potential source of fluoride pollution in the environment (Churchill *et al*., 1948). Stein *et al*. (1971) have reported the fall out of particulate fluoride as well as gaseous fluorides in the rain and snow to be the main sources of soil fluoride accumulation in the vicinity of brick kilns.

Pakistan is amongst those 24 countries that are prone to fluorosis (Shengji *et al*., 2004). The extensive problem of fluoride pollution has been determined in three major cities of Pakistan which are Kasur, Quetta and Loralai. Furthermore, fluoride contaminated drinking water has been reported in different parts of the country like Bahawalpur, Faisalabad, Karachi and Ziarat. The brick kilns contribute to the ground water contamination of fluoride (Farooqi, 2015). The fluoride emitted in the form of particulate matter is removed from the atmosphere during wet deposition (rain), which leads to the contamination of ground water (Joshi and Dudani, 2008).

Gaseous fluoride usually hydrogen fluoride (HF) has been reported to be very harmful to different fruit orchards as well as to some cereal crops in Peshawar, North Western Pakistan. The source of HF reported in these studies was the large number of brick kilns operating in the peri urban regions of Peshawar city (Ahmad *et al*., 2012 and 2014). Wahid *et al*.(2014) have also reported severe impacts to mango trees due to HF in the vicinity of functional brick kilns in Southern Pakistan. Gladiolus is an ornamental plant and was used as biomonitor for Flouride pollution around brick kilns in Northern Punjab region of Pakistan and Fluoride accumulation was found to be directly proportional to the injury in plant (Ullah *et al*. 2016).
Fluoride is considered to be 1-3 times more damaging to the vegetation as compared to other pollutants (Rey-Asensio and Carballeira, 2007). The fluoride emitted from the brick kilns enters inside the mesophyll cells of the leaf through stomata that affects normal photosynthetic rate (Jha *et al*., 2008). In addition, fluoride depositions on leaf surface in wet and dry form can block stomatal openings and can hence affects the plant growth rate (Gheorghe and Ion, 2011). Fluoride accumulation in leaves is exhibited by foliar injuries (Ahmad *et al*, 2012, Wahid *et al*. 2014). Even in the absence of foliar injuries, there may be changes in the activities of some enzymes as well as changes in the levels of various metabolites that result in decreased plant productivity (Mccune and Weinstein, 2002).

Increased Fluoride levels in soil and vegetation around brick kilns of Rawalpndi, Pakistan have also been reported (Khalid and Mansab, 2015).

Study Area

The area chosen for the present study was Benazir Chowk near village Bhadana Kalan at Tarnol, Islamabad. The study was carried out in 2012. This

There were 15 brick kilns present in the area of about $3km^2$. The sampling was carried out starting from the central location near to the source and the other four directions, i-e North, East, West and South away from the source, within the 2-3km area of the brick kilns.

Material and Methods

Total 25 samples were collected for each plant. The samples were collected at the distance of 200m length wise and at the distance of 200m width wise. The total distance between any two sampling points was $200x200m^2$. *Triticum aestivum* (wheat), *Calotropis procera (Aak)*, *Acacia nilotica* (Kikar) and *Cenchrus ciliaris* (grass) were collected from polluted and controlled area to determine the concentrations of Fluoride. About 25 soil samples were also collected from the area at 10-15cm. Soil sampling was done at the distance of $200x200m^2$ between different sampling points. The samples were stored in polyethylene bags. Ground water was used through bore holes for drinking and other purposes so 20 water samples were collected in plastic bottles through taps of residents near brick kilns following WHO guidelines. All the collected samples were then transferred to the Environmental Sciences laboratory at FJWU for analysis.

Pretreatment of plant samples

The plant samples collected were washed with distilled water and then dried at 105^oC for 24 hours. These dried plant samples were then ground with the help of mortar pestle (Ishaq *et al.*, 2010). 5ml of concentrated HNO_3 was added to the 0.5g of the powdered vegetation sample in a beaker. It was heated to near dryness at 150^oC for 6 minutes so that NO_2 was expelled out. The resulting solution was then allowed to cool and dissolved in a small proportion of distilled water and made up to the mark in a $100cm^3$ volumetric flask (Paul *et al.*, 2011).

Pretreatment of soil samples

The soil samples were oven dried at 110^oC for 24 hours and then they were sieved through 2mm sieve to remove coarser particles. The samples were then ground and stored (Ishaq *et al.*, 2010). $20cm^3$ of distilled water was added to 10g soil sample. The mixture was stirred and then kept for about 6 hours and then filtered to $100cm^3$ volumetric flasks (Paul *et al.*, 2011).

Spectrometric fluoride analysis

After pretreatment of all the samples, spectrometric analysis was carried out by the method of Paul *et al.* (2011) to determine the fluoride concentrations in the samples.

Air monitoring

Air monitoring of HF was conducted using GV 100 Gastec tubes of No 17 (Safetec, 2006). Detector tubes are glass tubes with measurement scales printed on these and contain detecting reagents that are sensitive to HF. These were inserted in the pump that was pulled and directed towards the point of measurement to allow air sample to be collected. Colour change of the inserted sample showed the presence of hydrogen fluoride.

Results and Discussion

Fluoride analysis of plants

The highest concentration in *Acacia nilotica* (Kikar) shown in figure 1, may due to the higher BCF of *Acacia nilotica* (Kikar) as compared to other vegetations (Jha *et al.*, 2011). The BCF values of *Acacia nilotica* (Kikar), *Triticum aestivum* (wheat), *Cenchrus ciliaris* (grass) and *Calotropis procera (Aak)* were 15.3, 13.03, 12.39 and 10.33 respectively. The fluoride concentration in all vegetations was greater than that of soil samples. Similar results were reported by Jha *et al.*, (2011). The reason for higher fluoride contents in vegetations may be due to the direct stomata absorption of gaseous fluoride emitted from brick kilns which is reported by Jha *et al.*, (2011; 2008). Highest concentration of fluoride was found near the source which was coded as the midpoint as shown in figure 2. The fluoride contents in all plants were different in different directions. This difference could be due to the difference in density of brick kilns in different directions. This was also consistent with the findings of Ahmed *et al.*, (2012).

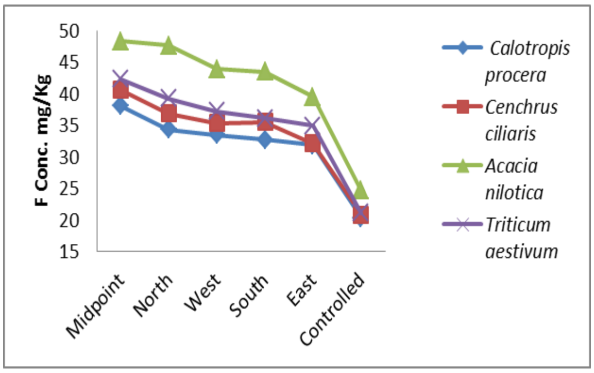

Fig 1. Mean Fluoride contents of plants at different sampling sites.

Soil leachable fluoride

It was found that the soil leachable fluoride at all sampling sites was below the fluoride contents present in plant samples (Figure 2). These results were in agreement with the previous studies of Jha *et al.*, (2011; 2008). The fluoride content of soil at brick kiln site was significantly greater (t_{crit}=2.13,p=0.003) than controlled site which was 35 Km away from brick kiln site. This could be due to difference in pH of soil at both sites. This difference could also be attributed to the presence and absence of brick kilns at both sites (Jha *et al.*, 2011).

Water level of fluoride

The polluted site had significantly higher water fluoride content as compared to the controlled site (Figure 3). This difference could be attributed to the presence and absence of brick kilns at both sites. As polluted area had alkaline soil so there was a chance that the fluoride content of the soil leached down and contaminated the ground water (Farooqi *et al.*, 2009).

F in ambient air

The results of air monitoring showed that maximum fluoride was detected at coal burning points. The fluoride at coal burning points ranged between <0.1972 mg/m^3 - > 15.776 mg/m^3. However, the concentration of fluoride in ambient air was below the detection limit (<0.1ppm or <0.0817mg/m^3) of the HF Gastec tubes. Ahmed *et al.*, (2012) also reported in their study that HF in ambient air at one site was below the detection limit. The less fluoride in air may be due to the wet deposition of HF particles on land (Jha *et al*., 2008). Another reason for below detection limit may be due to the impacts of different environmental

Vegetation	Pairs	n	df	t value	p value
Calotropis procera	Polluted-Controlled	5	4	4.44	0.113
Cenchrus ciliaris	Polluted-Controlled	5	4	6.64	0.0030
Acacia nilotica	Polluted-Controlled	5	4	13.00	0.0002
Triticum aestivum	Polluted-Controlled	5	4	7.81	0.014

factors like humidity level and temperature. Sikora and Chappelka, (2004) reported that HF concentration might be below detection limit in ambient air due to low humidity as at low humidity level HF concentration is low.

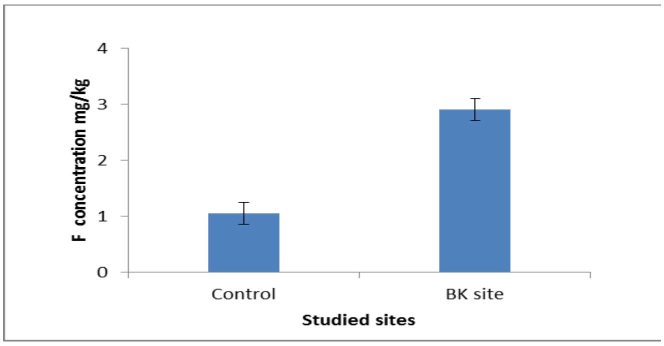

Fig 2 Soil leachable content of fluoride at different sampling sites.

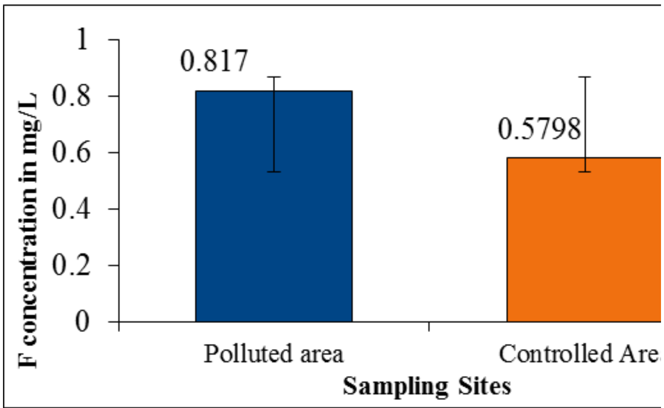

Fig 3 Water fluoride level at polluted and controlled site.

Paired p test

Paired t test at 95% confidence interval ($p<0.05$) indicate significant difference for all comparisons of vegetation among polluted and controlled site except for *Calotropis procera* (Aak).

Table 1 Comparisons of means of plant samples at polluted and controlled site.

Conclusion

From the present study it was concluded that the brick kilns could be responsible for the fluoride emissions in the vicinity of the area where they are operating. The results of air monitoring showed that the HF concentration at coal burning points was higher. The fluoride concentration of vegetation in comparison with the controlled site was higher indicating that brick kilns in the area are possible source of increased fluoride. Similarly the mean soil leachable fluoride content and fluoride content of water was below the permissible limit but higher in comparison with the controlled site indicating that the HF emissions from brick kilns are contributing toward the fluoride in the area. The complete data of fluoride content of every plant growing near the brick kilns should be developed to provide the clear information about the deleterious effects produced to ecosystem.

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