*Pak. J. Bot.*, 47(SI): 205-209, 2015.

# EFFECT OF FLUORIDES ON AIR, WATER, SOIL AND VEGETATION IN PERIPHERAL AREAS OF BRICK KILN OF RAWALPINDI

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**Abstract**

Coal burning in brick kilns releases high fluoride concentration that is major cause of fluorosis in living beings and necrosis in plants. The present study was conducted to assess fluoride concentration in air, soil, water and natural vegetation *Euphorbia helioscopia* (Deodal), *Acacia nilotica* (Kikar) and *Cenchrus ciliaris* (grass) and staple crop that is wheat (*Triticum aestivum*) in the vicinity of brick kilns of Dhoke Syedaan, Rawalpindi in different densities of brick kilns and controlled sites. In ambient air fluoride concentration was below the detection limit of detector tube that is 0.1ppm (0.08mg/m$^3$) while high concentration of hydrogen fluoride was observed at coal burning site. High density of brick kilns resulted in increased levels of fluoride concentration in vegetation and soil samples on site. Average fluoride content of vegetation ranged between 25.78mg/kg and 9.21 mg/kg. Only fluoride concentration of *Euphorbia helioscopia* in highly dense brick kiln area exceeded the limit of Canadian guideline for fluoride in vegetation that is 30mg/kg. The BCF values of *Euphorbia helioscopia* (Deodal), *Acacia nilotica* (Kikar), *Triticum aestivum* (wheat), *Cenchrus ciliaris* (grass) were 32.02, 29.50, 22.67, 19.29 and 17.79 respectively. Water samples had no significant difference in fluoride concentrations of different directions. Few health impacts were observed in brick kiln workers and other residents of nearby localities due to fluoride in the surrounding environment of brick kilns. The study concludes high impact of fluorides on living biota due to burning of coal.

**Keywords:** Brick Kilns, *Triticum aestivum, Euphorbia helioscopia*, *Acacia nilotica*, Bio Concentration Factor

## Introduction

Brick kiln is the unorganized industry, especially in the developing countries, operating in the vicinity of urban and peri urban areas (Le & Oanh, 2010). Worldwide about 300,000 brick kilns are present out of which 8% are concentrated in Pakistan. Major source of fuel in these brick kilns are low quality and cheap fuel, such as coal, wasted oil, oily sludge, rubber tyres, wood and bagass (Baum, 2010). Brick making is highly energy consumptive and consumes about 1.2-3MJ/kg of energy which is usually fulfilled by coal burning. Coal and rubber tyre burning results in the release of fine dust particles, hydrocarbons, CO, $F^-$, $SO_2$, $NO_x$, particulate matter and small amount of carcinogenic dioxins (Joshi & Dudani, 2008; Laghari *et al.,* 2015).

Various soils naturally contain about 20-1000 µg/g of fluoride (Telesinski *et al*., 2011) and different areas of Pakistan such as Kasur are more prone to fluorosis due to the naturally occuring fluoride (Farooqi *et al*., 2009). Soil near the emission source contains thousands of µg/g of fluoride deposits. After oxidants such as $O_3$ and $SO_3$, fluoride especially in the form of hydrogen fluoride is the third most damaging environmental pollutant to vegetation (Telesinski *et al*., 2011). Coal burning in different industries is the major source of fluoride pollution. Due to baking of bricks in kilns at high temperature of 950-1150$^o$C fluoride is released in gaseous and particulate form like hydrogen fluoride, silicon fluoride and particulate calcium fluoride (Suttie, 1980). Fluoride is also released in small concentration as $CF_4$, $F_2$ in gaseous form and cryolite ($Ca_3AlF_6$), $NH_3F$, $AlF_6$, CaSiF, NaF and $Na_2SiF_6$ in particulate form. Aerosol fluoride can be transported through wind to long distances and deposited through dry and wet deposition on soil and plants (Stein, 1971).

There is generally less availability of fluoride to plants through uptake by roots however uptake of fluoride by plants increases at low pH and in presence of clay (Anonymous, 2002). Most of the fluoride is usually entered into plant via stomata from where it is transferred to margins of broad leaves and tips of monocotyledonous leaves causing necrosis in plant. It also blocks stomatal opening, affecting plant transpiration and exchange of gases (Jha, *et al*., 2008; Shi *et al*., 2015). Ahmad *et al*., (2012) have reported the damages of gaseous fluoride to different fruit trees in the vicinity of Peshawar brick kilns, Pakistan.
Fluoride present in drinking water obtained from ground is considered more toxic to animals and humans than ingestion of fluoride contaminated food. Drinking water containing fluoride above 1.5mg/l is highly toxic causing fluorosis of teeth and bones in humans and animals (Groth, 1975).

**Study area:** The area selected for study was a semi urban area, Chak Jalal Din Shown in Fig. 1, union council of Rawalpindi having population about 21000 (Anonymous, 2010). Soil composition of the area is clayey which is used as raw material for 35 brick kiln unit concentrated in about 3km area. During the operational period of brick kilns, the wind direction is usually towards south west and south east which is highly populated and emission can pose threat to the health of residents. The land surrounding the brick kilns is also used for agriculture purposes for growing different crops like wheat, oat and brassica etc. Natural vegetation found in the area included *Euphorbia helioscopia* and *Silybum marianum* and grass species including *Dactyloctenium aegyptium* (L.), *Cynodon dactylon* (L.) and *Cenchrus ciliaris*. Common trees found in the area were *Dalbergia sissoo* and *Acacia modesta*. While aquatic weeds like *Pistia stratiotes* was also found (Khan *et al.,* 2014).

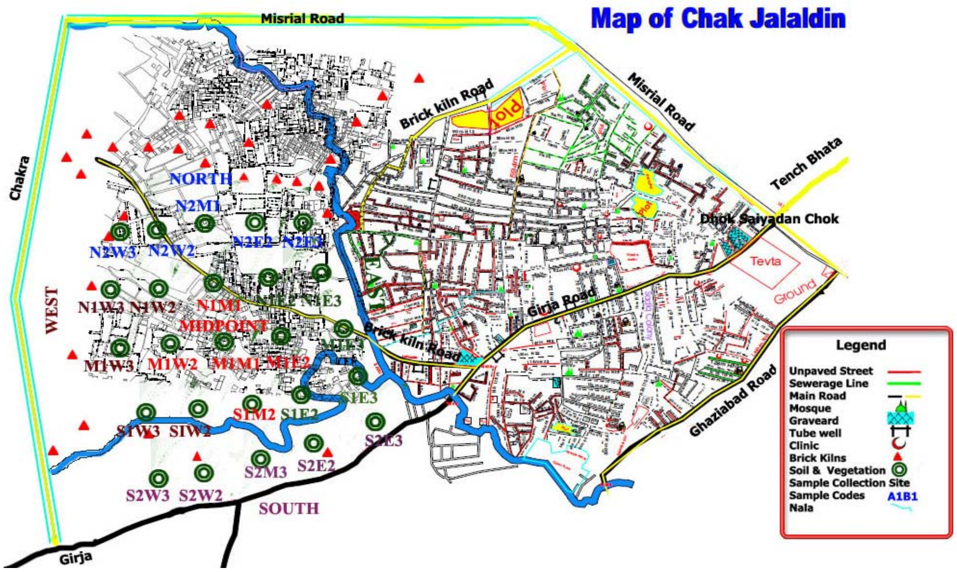


Fig. 1. Map of Chak Jalal Din (Anon., 2010).

**Table 1. Location of area and weather conditions of sampling area (Anon., 2012).**

| | |
|---|---|
| **Coordinates** | 33°34’45”North<br>73°1’24”East |
| **Temperature** | $39^oC$ |
| **Pressure** | 760mmHg |
| **Humidity** | 12% |
| **Wind** | 30km/hrs from NW |

Table 1 indicates the location of area and weather conditions during air monitoring.

## Materials and Methods

Vegetation and soil samples were collected during first week of April while water samples were collected during month of July. Air was directly analysed by monitoring the study area for hydrogen fluoride. 25 samples each for soil and vegetation were collected from 1-2km area at distance of $400x200m^2$ from each sample. Soil samples were taken through the depth of 10cm and vegetation samples were harvested up to 75-80cm. 25 drinking water samples were collected randomly from different areas.

**Pre-treatment of vegetation samples:** Leaves separated from each plant were washed and rinsed with distilled water and air dried for one day. Samples were then oven dried for 24hours and ground with mortar and pestle. These were then sieved through 100 mesh sieve. 0.5g of each sample was taken in a beaker and $5cm^3$of conc. $HNO_3$ was added in it. The resulting mixture was heated on hot plate at $150^oC$ until dry and $NO_2$ gas was released. The solution was cooled after it and distilled water was added up to the mark of $100cm^3$ volumetric flask.

**Pre-treatment of soil samples:** Soil samples collected were first air dried and then oven dried at $110^oC$ for three days and grounded with the help of mortar and pestle and sieved through 100 mesh sieves to remove coarser particles. 10g each of sieved soil samples were taken in sealed bottles and $20cm^3$of distilled water was added in it and stirred and placed in it for 6 hours. Each soil sample was filtered in $100cm^3$ volumetric flasks and the remaining residue was leached in beakers containing the filtrate by distilled water for two hours. This solution was diluted up to the mark by using distilled water.

**Spectroscopic Fluoride analysis:** Pre-treated samples were analysed using spectroscopic method used by Paul *et al*., (2011).

**Air monitoring:** Hydrogen fluoride in air was monitored by using Gastec detector tube system GV-100S No.17. For this purpose, inserted detector tube in the Gastec pump was directed towards the point of measurement handle which was pulled and allowed air to enter in the detector tube. Color change due to the contaminated air with fluoride was noted (Safetech, 2006).

### Questionnaire survey

Questionnaire survey was conducted to get information about the production capacity of brick kilns, type, source and quantity of fuel used in brick kilns, awareness about environmental damages from brick kilns and understanding of health impact resulting from the emissions of brick kilns. For this purpose random samples of 50 respondents were selected consisting of 25 brick kiln workers and 25 residents of near localities having ages between 18- 45. Some of questions asked from respondents were.

Q1. What is the most preferred fuel used for brick production?
Q2. What quantity of fuel is used in these brick kilns for brick production?
Q3. What is the annual time period for brick kiln operation?

Q5. How much agriculture area do you possess?
Q6. Do you feel any economic loss due to any plant disease in that area?
Q7. What do you think would be the cause for that loss?
Q8. Do you think that the brick kilns operating in the area have any contribution for the crop damage?
Q9. What strategies you adopted to overcome the decreased crop yield?
Q10. Does your crop yield increase by using these strategies?
Q11. Are you satisfied with the presence of brick kilns in that area?
Q12. Do you have any idea about fluoride and its damages to health?

## Results and Discussion

**Hydrogen fluoride concentrations in air:** Hydrogen fluoride concentration was below detection limit of gas detector tubes that is 0.08mg/$m^3$ while its concentration at coal burning sites ranged from 0.454mg/$m^3$ to 16.36mg/$m^3$. The possible reason for no hydrogen fluoride determined in ambient air in the present study could be due to small sampling time (45 second per stroke) and below detection limit (0.1ppm or 0.08mg/$m^3$ for 7 strokes) of the instrument (Gastec, 2006). In the vicinity of emission source, hydrogen fluoride concentration usually ranges from 0.002-0.003mg/$m^3$ (Guigard *et al.*, 2006; Weinstein *et al.*, 1998) and it does not exceed 0.0027ppm (0.0022mg/$m^3$) for 24hours (Anon., 2006). Hydrogen fluoride detector tubes detection limit was also lower than the air quality objectives of Canadian Council of Ministers of the Environment (CCME) for hydrogen fluoride that is 1.1µg/$m^3$ (0.0011mg/$m^3$) for 24 hours (Anon., 1996; Guigard *et al.*, 2006). There could be other reasons for hydrogen fluoride not determined in the ambient air and that could be low humidity at the day of measurement as at higher humidity, hydrogen fluoride concentration are generally higher (Sikora & Chappelka, 2004)

**Fluoride analysis in vegetation:** A comparison of fluoride content between *Euphorbia helioscopia, Acacia nilotica* (Kikar), *Cenchrus ciliaris* (grass) that were representative of natural vegetation of the study area and staple crop *Triticum aestivum* (wheat) showed that fluoride concentration in natural vegetation was greater as compared to the cultivated staple crop in the study area. This was due to greater BCF value that were 32.02, 29.50, 22.67, 19.29 and 17.79 for *Euphorbia helioscopia, Acacia nilotica, Cenchrus ciliaris* and *Triticum aestivum,* respectively. The reason could be BCF value varies in different vegetation and wheat has usually low affinity for accumulation of fluoride (Jha *et al*., 2011; Gheorghe *et al.*, 2011). All plant species had more fluoride concentration in the brick kiln area as compared to controlled site (Fig. 2). Average fluoride concentration in all wheat samples was below the limit of fluoride accumulation in vegetation that is 30mg/kg presented by Canadian Council of Ministers of the Environment. Fluoride concentration in samples of *Euphorbia helioscopia* near brick kilns (north) that is 37.05±8.00mg/kg was above the limit of Canadian guidelines (Anon., 1996; Guigard *et al*., 2006). All vegetation showed fluoride concentration in order of north> west>south>midpoint>east. 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). This trend was also presented in a study showing that fluoride concentration decreased with increasing distance from brick kilns (Ahmed *et al*., 2012). Fluoride concentration of wheat in the present study was consistent with that of Jha *et al*., (2011) who analysed fluoride concentration in the range 15.3mg/kg to 7.7mg/kg for brick kiln and controlled area.

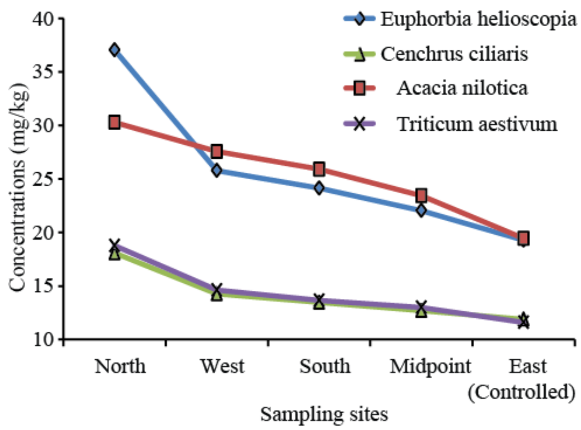


Fig. 2. Fluoride concentration of vegetations at different sites.

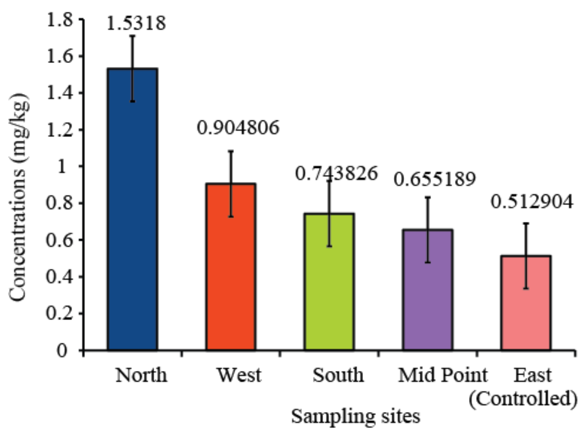


Fig. 3. Soil leachable fluoride concentration at different sites.

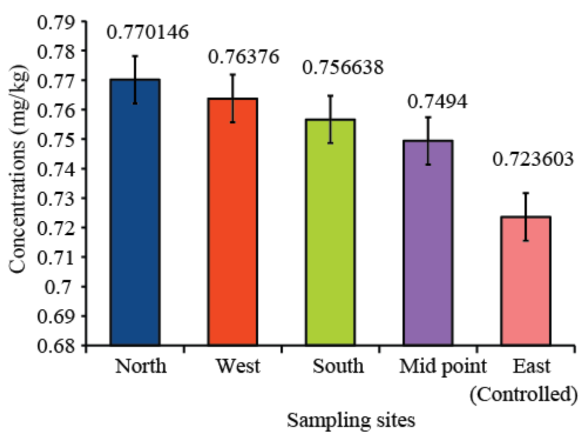


Fig. 4. Fluoride concentration of water at different sites.

**Fluoride analysis in soil:** Fig. 3 depicts high concentration of fluoride observed in north direction, more closer to brick kilns, while low concentration was analysed in east direction (controlled site) as it was about 2km farthest from the brick kilns. The possible reason for low fluoride concentration could be due to absence of brick kiln in that area. Overall less difference was found in its concentrations at all sites indicating less accumulation of fluoride released from brick kilns in soil. The possible reason could be alkaline pH of all soil samples as fluoride accumulation in acidic and alkaline soil varies and soil retention capacity of fluoride decreases in alkaline soil due to increase in unfavourable electrostatic potential (Brewer, 1965). The results of the present study for fluoride analysis of soil were consistent with Jha *et al*., (2011).

**Fluoride analysis in water:** Fluoride concentration in all water samples was below the permissible value set by WHO that is 1.5mg/l (Anon., 2004). This low concentration can be due to its natural occurrence rather than its emissions from brick kilns (Brindha *et al*., 2011). Another factor may be low exposure of ground water to fluoride dry deposition as well as low concentration present in soil. In the presence of alkaline soils, fluoride does not retain on soil particles and can be easily transferred to water during precipitation resulting in the leaching of fluoride to ground water, so lesser the concentration of fluoride in soil lesser will be concentration in water (Brewer, 1965). Fluoride concentrations detected in water samples at different sites are shown in Fig. 4.

**Paired t-test:** Paired t-test at confidence interval of 95% ($p<0.05$) for soil, each vegetation and water samples showed significance difference between fluoride concentration of polluted and controlled area as explained in Table 2.

**Questionnaire survey:** Brick kiln emissions had little effect on the health of residents of nearby localities but brick kiln workers were more prone to diseases showing some health problems arising that are generally due to emissions from brick kilns. Those workers who were working near coal burning sites were facing more health problems than other worker which is indicative of brick kiln pollution as cause of diseases in workers.

Fewer farmers were facing loss due to brick kilns which indicates no marked effect of brick kilns on the staple crops of the study area. Those crops were more affected form brick kiln pollution which were grown near the brick kilns. No necrosis effect was observed in the staple crop of study area and this could be attributed to the less affinity of staple crops towards fluoride accumulation (Jha *et al*., 2011).

**Table 2. Paired t-test of soil, vegetation and water samples.**

| Samples | n | df | t value | p value |
|---|---|---|---|---|
| Soil | 4 | 3 | 3.19 | 0.0497 |
| *Euphorbia helioscopia* | 4 | 3 | 4.42 | 0.0215 |
| *Acacia nilotica* | 4 | 3 | 13.00 | 0.000 |
| *Cenchrus ciliaris* | 4 | 3 | 6.64 | 0.003 |
| *Triticum aestivum* | 4 | 3 | 3.20 | 0.0493 |
| Water | 4 | 3 | 14.95 | 0.0006 |

## Conclusion

From the present study it is concluded that fluoride pollution exists in the brick kiln area of Chak Jalal Din, Rawalpindi as fluoride concentration in soil, water, and vegetations decreased with the increasing distance from the source. Coal was the major fuel used in these brick kilns that’s why hydrogen fluoride emission was greatest at coal burning site but in ambient air it was below detection limit of instrument. Significant difference in fluoride concentration of both vegetation and soil in polluted and controlled area was observed which indicated brick kilns as main source of fluoride. Fluoride released from the brick kilns had least effect on the ground water due to no direct exposure to brick kilns pollution. From the questionnaire survey it was found that brick kiln workers were facing more health problems as compared to other residents of nearby locality due to their more exposure than the residents. Whole community was unaware of fluoride pollution from brick kilns and its effect on human health and environment. It is suggested that Environmental Impact Assessment and Initial Environmental Examination should be done while establishing new brick kilns in the area and fluoride concentration should be regularly monitored in vegetation in the brick kilns area especially in staple crops.

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(Received for publication 26 August 2014)