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Fluoride Accumulation in Soil and Vegetation in the Vicinity of Brick Fields

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Abstract Fluoride in the soil and vegetation in the vicinity of brick field in the suburb of Lucknow, India was estimated. The water soluble fluoride (1:1) in the surface soil ranged from 0.59 ppm to 2.74 ppm where as $CaCl_2$ extractable fluoride ranged from 0.69 ppm to 3.18 ppm. The mean total fluoride concentration in surface soil varied from 322 µg g^{-1} to 456 µg g^{-1}. The local vegetations grown in the area found to accumulate air borne fluoride from the brick field. The fluoride accumulation in the vegetation followed the order *Mentha arvensis* > *Spinacea oleracea* > *Luffa cylindrical*.

Keywords Brick field · Soil · Vegetation · Fluoride

Brick kilns has been a considerable source of air pollution to fruits and vegetables due to its gaseous emission of sulphur and fluorine containing compounds. Fluorine is widely regarded as the third most important air pollutant after SO_3 and O_3. Brick kiln industries utilize burning of coal which is a potential source of fluoride emission. Coal contains between 40 and 295 ppm of fluoride (Churchill et al. 1948). Clay is used in the manufacture of bricks which contains several hundreds ppm of fluoride. It has been established that the normal operation of a high temperature kiln used in the manufacture of bricks, results in the aerial emission of fluoride which are generally in the form of gaseous hydrogen fluoride and /or silicon fluoride and particulate calcium fluoride (Suttie 1980). In the vicinity of brick kiln, the fluorides are brought to the soil surface by fall out of particulate fluorides, and, through absorption of gaseous fluorides in rain and snow (Hluchan et al. 1964). The air borne gaseous fluorides enter the leaf through the stomata, and then it dissolves in the water permeating the cell wall, thus has consequences on the plant growth, and, may find way in the food chain. Most of the added fluorides to the soil is either effectively fixed by the soil compound (Clay, Ca, and P) or readily removed from the light soil by water, thus making less available to plants. Limited information is available on the effect of brick kilns fluoride emission on the soil and vegetation hence, a study was conducted to evaluate fluoride accumulation in soil and fresh vegetations grown in brick kiln affected area.

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Materials and Methods

The study area is located in the northern periphery of the Lucknow, one of the oldest urban agglomeration in India. The area bordered by National highway No 28 in the south and Chinhat canal in the east and Kursi road in the west (Fig. 1). The climate is semi-arid-subtropical, characterized by hot summers and a cool winter, with mean annual rainfall of 950 mm most of which occurs during June–September. The typical soils sampled in the study area, were well drained, Typic Haplustalfs and Typic Ustochrepts (Soil Survey Staff 1998). Because of the proximity to the city, a large numbers of brick fields have come up in the area.

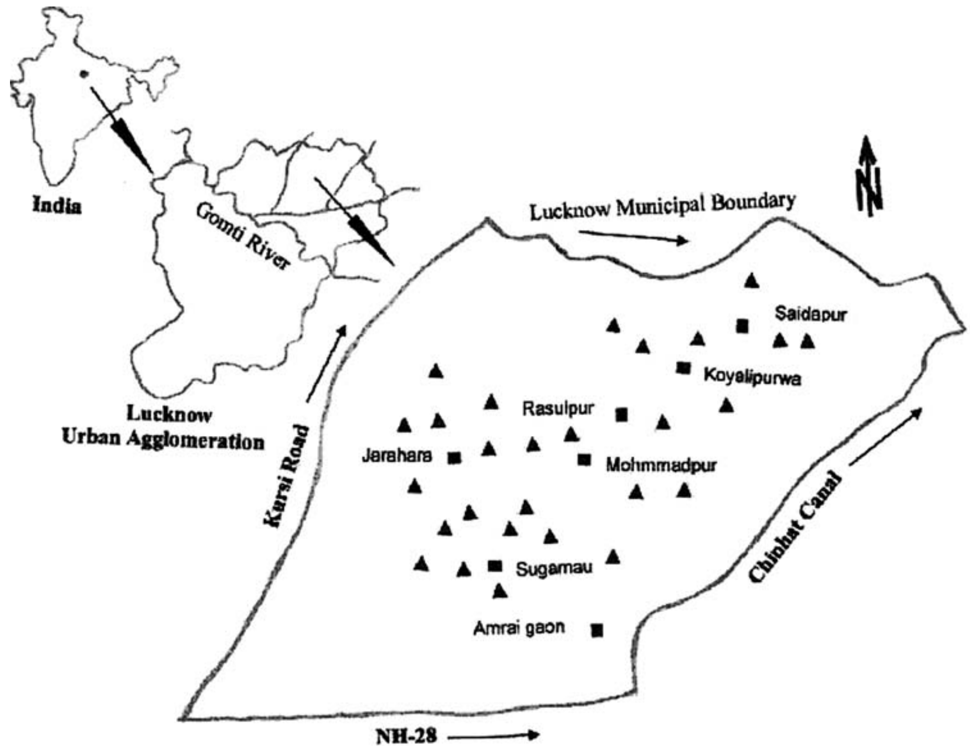

Fig. 1 Map showing the study area towards northern boundary of Lucknow Urban Agglomerates. ▲, brick fields and ■, the village sites around which samples were taken for fluoride concentration measurement

Locations of the soil samples are shown in the Fig. 1. The sampling points in each village were selected on the basis of flat terrain agricultural land and far from major roads. Soil samples from 44 locations were collected at the depth of 0–15 cm of the surface soil. The sampling sites fall within 10 km of the brickfields. All the soils were air dried, grounded and passed through 2 mm sieve prior to analysis.

Fresh common local vegetation samples *viz.* Mentha *(Mentha arvensis)* Spinach *(Spinacea oleracea)* Ridge gourd *(Luffa cylindrica)* were collected from the farmer's fields of different villages within the study area. They were immediately put into plastic bags sealed and transported to the laboratory for analysis, the same day. The samples were then washed thoroughly under running tap water to remove all the soils or any other foreign particles. Then they were rinsed with distilled water and let the water drain for 1 h on a clean surface. Half of the samples were then chopped off separately into small pieces. The chopped samples were fed into USHA LEXUS juicer cum mixer and the juices were extracted. Enough vegetables were used to get at least 50 mL of the vegetable juice. The other half of the samples were air dried followed by oven drying at 80°C till a constant weight was achieved. The samples were grounded and passed through 60 mesh sieve.

The total soil fluoride was determined by using alkali fusion-Ion selective technique (McQuaker and Gurney 1977). Approx. 0.5 g of the dried (105°C), grounded and sieved through 100 mesh sieve, was taken in a 130 mL nickel crucible and, the sample was moistened slightly with distilled water. Then 6 mL of 17 N NaOH was added to it. The crucible was tapped slightly to mix the content and placed in oven at 150°C for 1 h. After the sodium hydroxide solidified, it was placed in the muffle furnace at 300°C. The temperature was raised to 600°C and kept for 30 min. Then the crucible was removed from the furnace and cooled, 10 mL of distilled water was added and heated slightly to dissolve NaOH cake. After cooling, about 8 mL of conc. HCl was added slowly by stirring to adjust the pH 8–9. The content was then transferred to 100 mL volumetric flask, diluted to the volume and filtered through Whatman 40 filter paper. To the 5 mL of the above extract, 5 mL of TISAB (58 mL glacial acetic acid + 12 g Sodium Citrate dihydrate in 1 L distilled water adjusted at the pH 5.2 by using 6 N NaOH) was added and mixed, and the fluoride measurement was done by fluoride ion selective electrode using ORION 5 Star ion analyzer. The detection limit of method (LOD) was 0.05 mg/L.

For the determination of soluble fluoride in the soil, an extract was made (1:1) using distilled water (Brewer 1965). To 25 mL of the extract, 25 mL of the TISAB (4 g CDTA + 58 g NaCl and 57 mL glacial CH_3COOH in 1 litre of distilled water adjusted to pH 5–5.5 by 6 N NaOH) was added and the fluoride concentration in the extract was measured by fluoride ion selective electrode using ORION 5 Star ion analyzer. The detection limit of method (LOD) was 0.03 mg/L. Similarly calcium chloride extractable fluoride was determined by extracting the soluble fluoride with 0.01 M $CaCl_2$ following the method (Larsen and Widdowson 1971). The detection limit of method (LOD) was 0.02 mg/L.

All the soil fluoride was calculated on dry weight basis. The village-wise mean and standard deviations (SD) were computed. The pH of the soil was determined by taking 20 g of the soil sample into 40 mL of distilled water. Measurement was done by ORION 5 Star Analyser.

5 mL of aliquot of the vegetation juices was mixed with TISAB (4 g CDTA + 58 g NaCl and 57 mL glacial CH_3COOH in 1 litre of distilled water adjusted to pH 5–5.5 by 6 N NaOH) and the fluoride concentration was measured by fluoride ion selective electrode using ORION 5 Star ion analyzer and presented as water labile fluoride. In order to evaluate the validity of the procedure, the recovery analysis was performed. The recovery values ranged from 96% to 104%. The total fluoride was determined in the vegetation samples by Perchloric acid digestion method (Villa 1979). The average recoveries based on the spiked samples at two different levels of fluoride were 96 ± 8%, 98 ± 4% and 95 ± 6% for *Spinacea oleracea*, *Luffa cylindrical and Mentha arvensis*, respectively.

Results and Discussion

The result of the study revealed that 1:1 water soluble fluoride in the brick field area varied from 0.59 ppm at Amraigaon to 2.74 ppm at Sugamau. Similarly, the $CaCl_2$ extractable fluoride ranged between 0.69 ppm and 3.18 ppm, respectively. The distribution of brick kiln such as density and its proximity to the sampling points affected the soil water soluble fluoride contents. At all the places, the $CaCl_2$ extractable fluoride were significantly correlated (Fig. 2) and were higher than the 1:1 water extractable fluoride. This is in agreement with the earlier researcher who pointed out that $CaCl_2$ is generally more efficient than

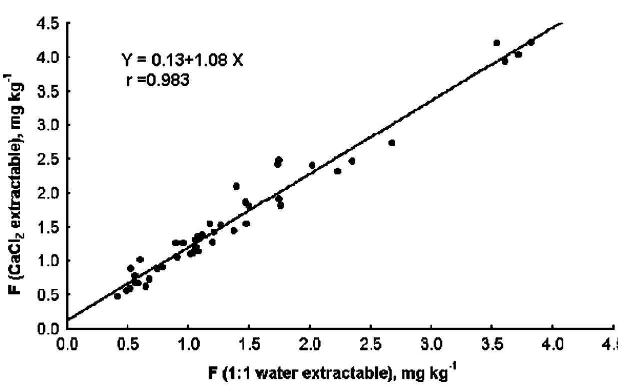

Fig. 2 Relationship between $CaCl_2$ extractable F and 1:1 water extractable F in soils of brick klin area of Lucknow Urban Agglomeration

water in extracting fluoride from soil exposed to brickwork effluents (Supharungsun and Wainwright 1982). While working in the contaminated soils in the vicinity of the alumina production plants, Haidouti 1991, reported the water extractable fraction of fluoride in the range of 2.4 and 238 μg g^{-1}. A wide variation in water-extractable fluoride concentration of soils has been reported by several authors (Polomski et al. 1982; Walton 1987). However, the data reported in the literature are not always comparable, since the extraction procedure varies widely. All the soluble fluoride values reported in this study are clearly in excess of the non polluted agricultural soils reported by investigator (Larsen and Widowson 1971). The range reported for $CaCl_2$ extractable fluoride was 0.05–1.5 ppm. Polomski et al. (1982) found that atmospheric F pollution during several decade may raise the level of water extractable F in soil. The soil pH of the brick field affected area is normal to alkaline, comparatively higher water soluble fluoride was observed in the soils with alkaline reaction than the neutral ones. The water solubility fluoride increases in the pH > 6 (Adriano 2001).

The result of the study showed that the mean total fluoride content of 0–15 cm surface soil ranged from 322 μg g^{-1} at Jarahra to 456 μg g^{-1} at Sugamau. The wide variations in the total fluoride may be attributed to the distance of sampling points from source of pollution and the wind direction etc. The total fluoride content in the study area was higher than the total fluoride contents in the normal soil reported, indicating the accumulation due to the air borne fluoride emission from the brick kiln. The average total fluoride content of the world wide soil is 320 ppm (Alina and Henryk 1984). The fluoride content in surface soil of the atmospheric fluoride contaminated site ranged from 1.5 to 950 μg g^{-1}. A wide variation of total fluoride concentration of soils has been reported by various authors (Sidhu 1979; Pickering 1985). There was no significant correlation of total fluoride with 1:1 water soluble fluoride ($r = 0.29$) and with $CaCl_2$ extractable fluoride ($r = 0.23$). Thus the total soil fluoride values tell us little about the amount of biologically available fluoride present. The soil may contain considerable fluorine but most of it is bound tightly in silicate and phosphates minerals and, therefore a small fraction of the total fluoride is soluble fluoride. In the study area, 1:1 water extractable fluoride constitute 0.18–0.60 per cent of total fluoride, where as $CaCl_2$ extractable fluoride constitute 0.20–0.69 per cent (Table 1). Normally the values of water soluble fluorine ranged between 0.3 and 0.5 ppm, whereas the total fluoride level fluctuates between 10 and 1000 ppm (Bear 1964). In normal soil, water soluble fluoride is only 0.05% of the total fluoride, in saline soil it rises to 0.78%, whereas in alkaline soil it is 1.24% of the total fluoride (Lavado and Reinaudi 1979).

Table 1 Different fluoride fraction and pH of brick kiln affected soil

Name of the village	Soluble fluoride, ppm		Total fluoride ($\mu g\ g^{-1}$)	pH (1:2)
	($CaCl_2$) extract	1:1 water extract		
Jarahra (N = 7)	1.52 ± 0.56	1.09 ± 0.42	322 ± 43	7.98 ± 0.12
Rasulpur (N = 6)	0.69 ± 0.22	0.62 ± 0.21	336 ± 38	7.18 ± 0.11
Saidapur (N = 8)	1.59 ± 0.41	1.31 ± 0.40	404 ± 47	7.29 ± 0.14
Sugamau (N = 7)	3.18 ± 1.18	2.74 ± 1.17	456 ± 39	8.41 ± 0.11
Mohamadpur (N = 5)	1.33 ± 0.31	1.23 ± 0.34	414 ± 21	8.00 ± 0.15
Koyali Purwa (N = 8)	1.66 ± 0.74	1.57 ± 0.75	438 ± 26	7.88 ± 0.09
Amaraigaon (N = 3)	0.69 ± 0.09	0.59 ± 0.05	335 ± 19	7.20 ± 0.16

N = No of samples

Table 2 The total and water labile fluoride in the local vegetations of brick kiln affected area

Name of the village	Mentha (*Mentha arvensis*)		Spinach (*Spinacea oleracea*)		Ridge gourd (*Luffa cylindrica*)	
	Labile (ppm)	Total ($\mu g\ g^{-1}$)	Labile (ppm)	Total ($\mu g\ g^{-1}$)	Labile (ppm)	Total ($\mu g\ g^{-1}$)
Jarahra	3.38 ± 0.28 (5)	82.9 ± 7.2 (5)	1.77 ± 0.14 (7)	42.3 ± 4.1 (7)	0.26 ± 0.08 (4)	12.8 ± 0.8 (4)
Rasulpur	3.97 ± 0.32 (4)	77.5 ± 2.3 (4)	1.44 ± 0.26 (4)	37.8 ± 2.3 (4)	0.38 ± 0.06 (6)	18.5 ± 1.0 (6)
Saidapur	3.46 ± 0.22 (4)	80.4 ± 5.1 (4)	2.05 ± 0.30 (6)	65.4 ± 3.7 (6)	0.57 ± 0.07 (7)	25.3 ± 1.3 (7)
Sugamau	–	–	1.27 ± 0.22 (5)	32.6 ± 1.3 (5)	0.39 ± 0.05 (5)	20.6 ± 1.2 (5)
Mohamadpur	3.29 ± 0.34 (6)	69.5 ± 3.3 (6)	1.52 ± 0.20 (5)	50.4 ± 2.3 (5)	0.30 ± 0.02 (8)	15.5 ± 1.2 (8)
Koyali Purwa	4.45 ± 0.26 (5)	102.3 ± 8.2 (5)	1.36 ± 0.28 (6)	34.6 ± 3.1 (6)	0.25 ± 0.04 (8)	18.5 ± 1.1 (8)
Amarai gaon	–	–	1.41 ± 0.32 (4)	29.8 ± 1.21 (4)	0.37 ± 0.06 (5)	22.2 ± 1.2 (5)

Sample no (N) is indicated in parenthesis, – not analysed

Fresh raw vegetables are known to be rich in vitamins and minerals. Fluoride, like other mineral is present in different proportion in the vegetable juice and become an issue of growing concern. The water labile ionic fluoride in the juices of raw vegetations (Mean ± SD) is given in the Table 2. Accumulation of fluoride was highest in *Mentha arvensis* and varied from 3.29 ppm to 4.45 ppm. The *Luffa cylindrica* had lowest fluoride concentration which ranged from 0.25 ppm to 0.57 ppm. The water labile fluoride in vegetations had no relationship with water soluble soil fluoride. This indicated that the direct absorption of the airborne fluoride by plant foliage directly affects the concentration in the juice and masks any soil uptake. Similar findings are reported by Vike and Habjorg 1995.

The total fluoride content in the three vegetations *viz. Mentha arvensis, Spinacea oleracea* and *Luffa cylindrica* (Mean ± SD) are given in the Table 2. The total fluoride content in the vegetations were found to be in the order *Mentha arvensis* > *Spinacea oleracea* > *Luffa cylindrica*. *Spinacea oleracea* one of the popular vegetable consumed through out the year in this region contains 29.8–65.4 $\mu g\ g^{-1}$ dry weight basis, and is higher than the permitted values. The permitted value of fluoride in vegetables is 1 $\mu g\ g^{-1}$ as prescribed in Chinese Food and Sanitation standard (Hou 2004). There was no significant correlation between the total fluoride content in vegetation with both water soluble and total fluoride content in soil. This indicated the atmospheric pollution from the brick industries besides soil, was the major contributing factor for such higher fluoride accumulation in the vegetation. In order to prevent the vegetables in the suburbs from being polluted, emissions should be severely restricted and factors such as lay out and management should be taken into account so that vegetables are grown far away from source of emission as far as possible.

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