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Accumulation of Arsenic and Fluoride in Lichen *Pyxine cocoes* (Sw.) Nyl., Growing in the Vicinity of Coal-based Thermal Power Plant at Raebareli, India

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ABSTRACT: Levels of arsenic (As) and fluoride (F) were determined in an epiphytic lichen Pyxine cocoes (Sw.) Nyl., collected from the vicinity of coal based thermal power plant of Raebareli, India. Both the elements are abundant in lichen thallus, while their substratum contained negligible amount. The As ranged between 8.9±0.7 to 77.3±2.0 µg g-1 dry weight in thallus and 1.0±0.0 to 9.7±0.2 µg g-1 dry weight in substratum; whereas F ranged between 9.3±0.52 to 105.8±2.3 µg g-1 dry weight in thallus however, it not detected in the substratum. The quantities of As in thallus increased with decreasing distance from the power plant, but F showed an opposite trend. The distribution of As and F around the power plant showed positive correlation with distance in all directions with better dispersion in western side as indicated by the concentration coefficient (R2). The F accumulaiton patterns in lichens clearly indicate that the coal burning in power plant is the major contributor, and has its maximum levels on the down wind side. The analysis of variance and LSD indiacted that the As, F concentrations among lichen thallus is significant at p< 0.01% level.

Key words: Bioaccumulation, Arsenic, Fluoride, Lichen, Thermal Power Plant

Introduction

There are many traditional studies on atmospheric contamination but most of them have restrictions due to high cost involved in the project and their inability to carry out extensive sampling in short duration. There is thus, an ever increasing interest for using indirect monitoring methods such as analysis of organisms that are bioaccumulators (Fernandez and Carballeira 2000). The lichens are one such bioaccumulator with good accumulation abilities suitable for determining the heavy metal deposition in terrestrial ecosystem. Due to their peculiar morphological, anatomical and physiological characteristics lichens are one of the most valuable biomonitors of atmospheric pollution (Markert *et al.* 1999; Garty 2001; Kircher and Darllant 2002).

The coal based power generation is emerging as the biggest environmental problem in India as it emits fly ash, acid precursors, green house gases, non combustible hydrocarbons, heavy metals, metalloids and particulates. These pollutants can be carried to a long distance by wind and ultimately have a negative impact on both biotic and abiotic environment.

Arsenic (As) and fluoride (F) occurrence, mobilization takes place through a combination of natural process (e.g. weathering reactions, biological activity, volcanic emission etc.). Although natural As and F are the main source of pollution, whereas anthropogenic activities account for a widespread contamination arising from a varieties of processes such as mining, electrolytic, combustion of fossil fuels, wood preservation, urban wastes, medicinal use, sewage sludge, fertilizers, pigments, biocides, glass, alloys and it may accumulated in high concentation in plants and animanls (Smedley and Kinniburgh 2002).

Earlier studies carried out elsewhere has shown that As can also be present in air and a major source of threat to living organisms including man and it is classified as group I carcinogen (IARC, 2004). Its severe health effects have been observed in populations all over the world over long period (EPA, 2006). The permanent ingestion of water, air, food with high As and F concentration provokes the appearance of arsenicosis and fluorisis respectively, an illness with high incidence in Asia (Litter, *et al.* 2010).

Both the elements are mainly associated with water pollution but now a days these are also found in air (EPA, 2006). The areas in the neighborhood of the industrial complex, mining and vehicular activites exhibit significant increase in the concentration of As and F. Koch *et al.* (2000) recorded that fungi and lichens collected from Yellowknife Canada, an area affected by past mining activites, exhibited elevated arsenic levels. Perkins (1992) studied the F content and loss of lichen diversity near an aluminum works at United Kingdom while, Notcutt and Davies (1999), estimated fluoride in lichens growing around volcanic activites and found foliose lichen accumulated most of the F in thallus with compare to crustose lichen.

In india, As and F are most common problem in some states like West Bengal, Madhya Pradesh and part of Uttar Pradesh (Chakarbarti *et al.* 1998; Jha *et al.* 2008). The metal accumulaiton in lichens have been initiated recently and the As concentration in indian lichens are reported first time by Bajpai *et al.* (2009). The higher concentration of As was found in the lichen samples collected from area having past mining records followed by incineration of fossil fuel and vehicular exhaust at Madhya Pradesh. Fluoride though, is not recorded so far in the Indian lichens, however it was estimated in vegetation in the vicinity of brick field by Jha *et al.* (2008). The present study we utilize naturally growing lichen (*P. cocoes*) to indirectly analyze the As and F in air around thermal power plant and also provide their distribution pattern. The aim of the present study is to summarizes the new data about As and F accumulation in lichens and exploratory analysis may be used in determining the air quality around power plant and can be used for future biomonitoring studies.

Materials and Methods

Study area

Firoz Gandhi Unchahar National Thermal Power Plant Corporation (FGUNTPC) is situtated in Raebareli district of Uttar Pradesh, India (Fig. 1) between 25°49'N to 26°36'S and 100°41'E to 81°34'W at an altitude of 120.4 m. FGUNTPC has the stack height of 130 m with electricity production capicity of 5x210 MW coal are the main source for fuel. The climate of the region is tropical, with eight months of dry period and four months of rains (June to September) ranges from 110 to 485 mm. The area experiences temperature range between 12.2-14.6°C in winter and 42.2-45.8°C in summer.

Sample collection

The area around FGUNTPC was surveyed for collection of lichens during the months of February-March 2008. Lichen, *Pyxine cocoes* (Sw.) Nyl., which was growing abundantly on trees of *Mangifera indica* was collected from 12 different sites at 5, 10 and 15 km radious, on north (N), south (S), east (E) and west (W) directions from the FGUNTPC. It was widely distributed in this area and thus available at all sites for As and F accumulaiton studies.

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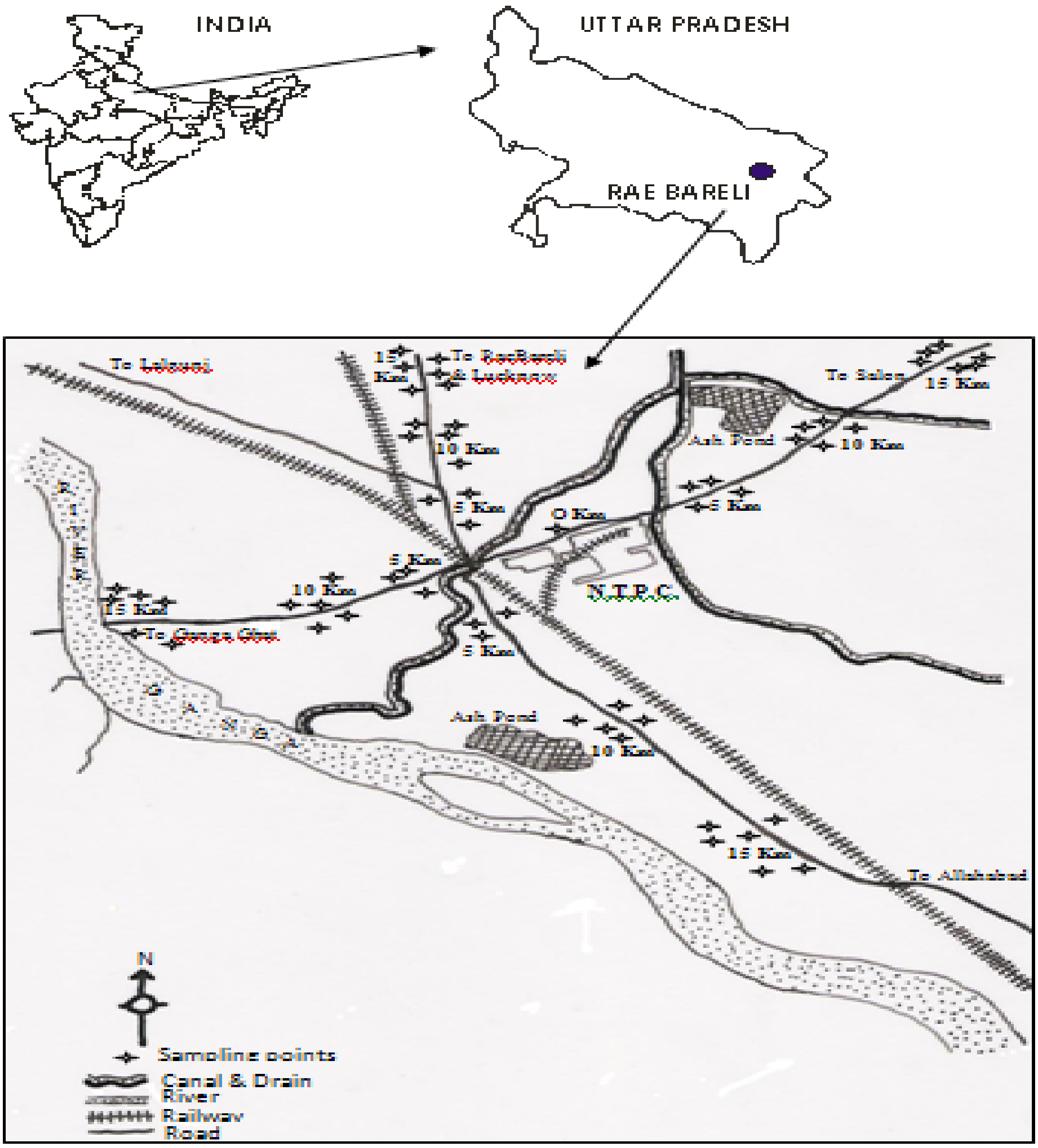
Fig. 1. Map of the study area with location of sampling sites



Five samples of lichen *P. cocoes* were collected from each site (5, 10, 15 km N, S, E and W) along with substratum. The lichen thallus were carefully removed from the substratum (tree bark) and mixed together (single site) to make cumulative samples from which triplicate (n=3) were drawn for As and F analysis, same pattern follow for substratum analysis. A set of voucher specimens of the lichen utilized in the present study were identified and preserved in herbarium of National Botanical Research Institute, Lucknow (LWG).

Asenic measurment

Lichen thallus as well as substrates were oven dried for 24 h at 60^{o}C temperature. The dried lichen samples and substrates were seprately grinded to powder (0.5 g) and digested with mixture of concentrated H_2SO_4:HNO_3:H_2O_2 (3:3:1) for 1-2 h. Residues were filtered through Whatman filter paper no. 42 and diluted to 5.0 ml with double distilled water. Analysis was done with flame atomic absorption spectrophotometer (Perkin Elmer, model A Analyst 300). Stock standards were used from Merck India and traceable to the National Institute of Standards Technolgy. Working standards were prepared from the stock using deionized water from dilution. The detection limit was 0.005mg/L.

Fluoride measurment

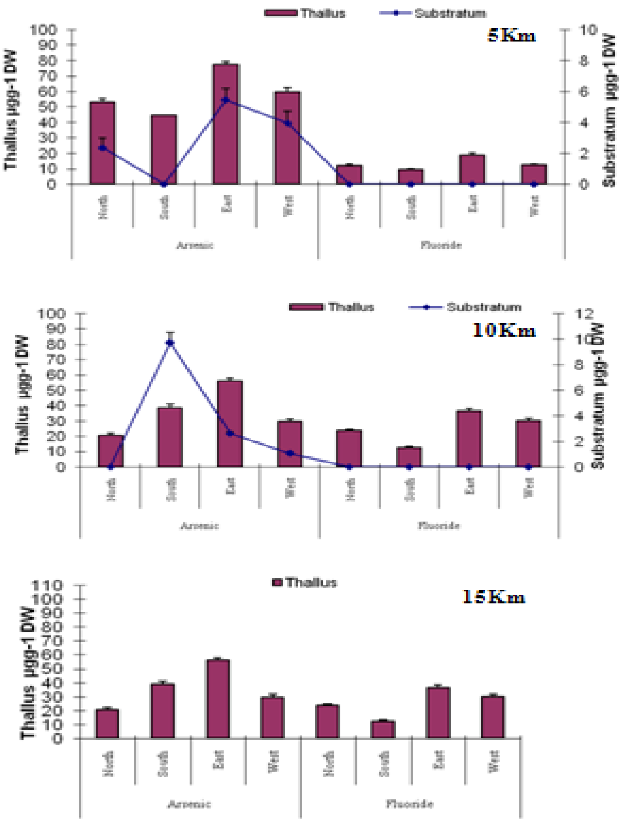
The total fluoride was determined by using alkali fusion-Ion selective technique (McQuaker and Gurney 1977). Approx. 0.5 g of the dried, grounded lichen thallus as well as substratum was taken in a 130 ml nickel crucible and the sample was moistened slightly with distilled water. Then 6 ml of 17N NaOH was added to it. The crucible was tapped slightly to mix the content and placed in oven at 150^{o}C for 1 h. After the NaOH solidified, it was placed in the muffle furnace at 300^{o}C. The temperature was raised to 600^{o}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 concnetrated HCL was added gradullely to adjust the pH between 8-9. The content was then transferred to 100 ml volumetric flask, diluted to the volume and filtered through Whatman no. 40 filter paper. The 5 ml of this extract, 5 ml of TISAB (Glacial acetic acid : Sodium citrate dihydrate : Distilled water; 14.5 ml: 3.0 g: 250 ml; pH 5.2) was added and mixed. The F measurment was done by fluoride ion selective electrode using ORION 5 Star ion analyzer. The detection limit was 0.05mg/L.

Results and Discussion

Accumulation of As and F in thalli of *P. cocoes* along with substratum were estimeted for all the directions at distances of 5, 10 and 15 km from the source of pollution (table 1). Among both the elements F was accumulated in higher amount in comparison to As. The concentration of F ranged from 9.3±0.5 to 105.8±2.3 µg g^{-1} dry weight in thallus while it is not detected in substratum. The accumulation of As ranged from 8.93±0.7 to 77.3±2.0 µg g^{-1} and 1.0±0.0 to 9.7±0.2 µg g^{-1} dry weight in thallus and substratum respectively. The samples collected at 5 km away from FGUNTPC accumulated highest concentration of As followed by the samples of 10 and 15 km. It is intresting to note that As concentration in lichen thallus exhibited an increasing trend with decreasing distances from the power plant. At 15 km no As was recorded in substraum at any directions (Fig. 2). Menard *et al.* (1987) stated that As in air is found in particulate forms as inorganic As and the dust of induastrial periphry contains huge amount of this element. In the present study, As has been found accumulated in higher concentration in lichen thallus and lesser in substratum. Accumulation of pollutants is a continous process for lichens, they accumulate pollutants cummulatively over the year with least possibilities of leaching out from the thallus. However, pollutants deposited on substratum can be washed out with rain water or blown off by wind. According to Deb *et al.* (2002), the concentrations of As in different areas shows the accumulation sequences as industrial>heavy traffic>commercial>residential. In the present study higher concentration of As was recorded near the vicinity of the power plant (upto 5 km), which is obviously due to industrial exhaustion and heavy traffic involved in disposal of coal waste.

Fluoride also turned out to be the element of greatest environmental concern. Concentration of this element were significantly high in the whole study area with values 9.3±0.5 to 105.8±2.3 µg g^{-1} dry weight in thallus, whereas not detected in subsratum. The area of most intense contamination were observsed at 15 and 10 km away from the power plant as shown in figure 2. There is no doubt that the coal combustion plant is the source of atmospheric F pollution. Wind and its direction are probable agents for dispersion of this element, away from the source. According to Garty (2001), dispersion of metals depends on the gravity of a particular metal alnog with speed and direction of wind. The element F is lighter in gravity than As and hence can be carried away to longer distance by wind and deposited on the vegetation. Notcutt and Davies (1999), used a foliose lichen *Parmelia perlata* (Huds.) Ach., around volcanic activites and estimated about 75 µg g^{-1} F in thallus and observed its increasing concentrations with distance from the sources. Correlation coeficient indicated the dispersion of As and F in all the directions, however poor towards south and east (Fig. 3 A, B). Prasad and Mondal (2006) concluded that coal fly ash disposed area with high quantities of As, F, Se and B determine the cocnentration of F, which may range between 0.4-610 µg g^{-1}, but also depends on the type of coal being burnt. Thus F in coal also a major factor for its increased concentration in environment. The presence of brick fields between 10 -15 km both at east and west may be another reason for high F content in these localites, as coal is the major firing substances used in brick industry. This may be a reason to support higher F content in samples collected at 15 and 10 km away from the thermal power plant. Davies and Notcutt (1988) reported accumulation of F (2-141 µg g^{-1} dry weight) in two lichen species *Xanthoria parietina* (L.) Beltr. and *Stereocaulon vesuvianum* (Flot. Ex Korb.) Poelt, in Volcanic vicinity of Mt. Etna, U.K. and observed no morphological damage in any lichen at this highest concentrations. Similarly, in the present study also, no morphological changes were observed in the lichen thallus of this locality. According to Perkins (1992), the loss of lichen (*Ramalina* sp.) was closely correlated with F content in them. Thalli contaning 300, 200, and 100 µg g^{-1} F would be expected to have losses of cover of 46, 38 and 24% per year respectivelly, which means more concentration is alarming and causes destruction of lichen diversity. Jha *et al.* (2008), estimated the F content in some vegetation around a brick field of Lucknow City, and reported that vegetation accumulated air borne F from brick field up to the 69.5±3.3 to 102.3±8.2 in *Mentha,* followed by 29.8±1.2 to 65.4±3.7 and 12.8±0.8 to 25.3±1.3 µg g^{-1} dry weight in *Spinach* and *Luffa* respectively. The result indicated that the atmospheric pollution from burning of coal in brick industries is the major contributing factor for such higher F accumulaiton in vegetation.

Fig. 2. Comparison between As and F accumulation at various distance from FGUNTPC for all the directions



LeBlanc and Sloover (1970), described the effects of pollution on lichen in the vicinity of an aluminium smelter using lichen *Parmelia sulcata* Taylor, for 12 months of exposure at 15 km distance from the source. The colour of thallus was changed with higher concentrations of F and algal cells displayed varying degree of plasmolysis and loss of chlorophyll. Even control site at 40 km apparently contained as much as 70 mg F kg^{-1}.

Fig. 3. Dispersion of (A) arsenic and (B) fluoride in the vicinity of FGUNTPC represented by R2 values (N= north; E= east; S= south; W= west)

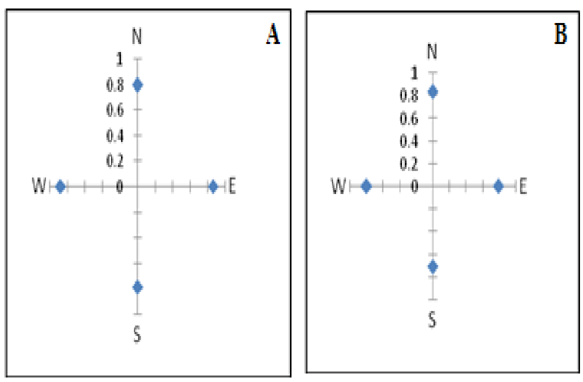


Table 1: Arsenic (As) and fluoride (F) accumulation in lichen *P. cocoes* (Nyl.) Sw., and its substratum at different direction of FGUNTPC (values in each column followed by the same alphabetic letter indicate it is not significant between at $p<0.05\%$ level by least significant difference (LSD) analysis thallus and substratum separately. Mean± S.D., n=3; in $\mu g g^{-1}$ dry weight; N.D.= not detectable.

METALS		DIRECTIONS													
		NORTH				SOUTH			EAST				WEST		
		15Km	10 Km	5Km	0 Km	5Km	10 Km	15Km	15Km	10 Km	5Km	0 Km	5Km	10 Km	15Km
F	THALLUS	55.5 ± 1.2^{a}	23.6 ± 1.0^{a}	12.2 ± 0.9^{b}	Lichen Desert	09.3 ± 0.5^{b}	12.4 ± 0.8^{b}	67.3 ± 1.1^{a}	105.8 ± 2.3^{a}	36.4 ± 1.8^{b}	18.8 ± 1.7^{b}	Lichen Desert	12.3 ± 0.4^{b}	30.2 ± 1.1^{a}	96.0 ± 2.0^{a}
	SUBSTRATUM	N.D.	N.D.	N.D.		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		N.D.	N.D.	N.D.
As	THALLUS	11.2 ± 0.6^{ab}	20.8 ± 1.2^{a}	53.2 ± 2.0^{a}		44.4 ± 1.9^{a}	38.8 ± 2.2^{a}	16.1 ± 1.7^{b}	10.1 ± 1.9^{b}	56.2 ± 1.5^{a}	77.3 ± 2.0^{a}		59.8 ± 2.5^{a}	29.8 ± 1.4^{a}	8.9 ± 0.5^{b}
	SUBSTRATUM	N.D.	N.D.	2.3 ± 0.6^{b}		N.D.	9.7 ± 0.0^{ab}	N.D.	N.D.	2.6 ± 0.9^{c}	5.4 ± 0.7^{c}		3.9 ± 0.7^{b}	1.0 ± 0.0^{b}	N.D.

Mean± S.D., n=3; in $\mu g\ g^{-1}$ dry weight; N.D.= not detectable

Conclusion

This comparison indicates that As and F emitted by coal fired power plant and brick industries may have greater effect than demonstrated, reaching up to the food chain. Lichens once again proved that they are not only effective as monitors of the dispersal of metelloids, but can also be used to identify a potential environmental hazard. Further, the current study has shown that apart from many other metals lichens may be used to detect fluoride in the atmosphere also. In Indian context more studies are required to determine the concentration of As and F in lichen thallus around pollution sources. It is also important to understand the mechanisms of As and F metelloids uptake, translocation and transformation in lichens. Along with the immediate risk to the population living in the vicinity of the power plant, long term hazard due to metal accumulation should be seriously considered. Appropriate abatment strategies should be adopted to avoid environmental contamination and risks for human health. The present level of As and F pollutnats will be a useful baseline data for carrying future studies related to ambient air quality in the area.

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