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Impact of Fluoride on Flora in and around Hindalco Industries Ltd., Renukoot (India)

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ABSTRACT: Atmospheric fluoride can occur either as a gas, particulates, or as gaseous fluoride absorbed to other particulate matter. Gaseous hydrogen fluoride is generally considered as probably the most phytotoxic air pollutant and affects plants at extremely low concentration since it accumulates in the leaves of sensitive plants against a concentration gradient. Fluoride is highly soluble in water and can impact indirectly on vegetation through the lowering of the soil pH, thereby decreasing the availability of soil nutrients. This accumulation of fluoride may leads to marginal necrosis that being at leaf tips and progress to leaf bases. The present study carried out fluoride concentration of different plant in and around Hindalco Industries Ltd. Renukoot, India.

Keywords: Fluoride; air pollutant; Nutrient distribution.

INTRODUCTION

Plant leaves and pods from a natural part of the diet of many ruminant species and have been used tradition as source of forage for domesticated livestock in Asia, Africa and the pacific. Although not all forage tree and legumes, more than 200 species of leguminous tree are reported to be used for forage, with most species being tropical or subtropical in origin. The most commonly used species cone from the genera *Acacia, Calliandra, Desmanthus, Desmodium, Gliricidia, Leucaena, Prosopis and Sesbania*. Compared with herbaceous legumes, tree and shrub legumes have received relatively little attention in the search for productive and persistent forage for the tropics.

Leaves of plants that were fumigated with hydrogen fluoride contained markedly decreased concentrations of sucrose and increased concentrations of reducing sugars compared with those in leaves of control plants (Yang & Miller, 1963). To most plants, fluoride (F) is phytotoxic through altering a series of metabolic pathways (Horntvedt, 1997; Miller, 1993; Giannini *et al*., 1985). Fluoride can be deposited into soil from several anthropogenic sources, both directly through phosphate fertilizers or indirectly through atmospheric pollution from industrial activities and burning of fossil fuels (Arnesen, 1998; Stevens *et al*., 1997). From the soil, Fluoride is absorbed by plant roots and then transported via xylematic flow to the transpiratory organs, mainly the leaves, where it can accumulate with adverse effects that have been described in the literature (Klumpp *et al*., 1996; Davison and Weinstein, 1998).The rate at which symptoms appear depends on many environmental factors, such as the type and concentration of pollutants, distance from the emission source, length of exposure, and meteorological conditions.

Effect of Fluoride on Flora

Plants are exposed to fluoride in the soil and in the air. Fluoride is taken up from the soil by passive diffusion and then reaches the shoot by transpiration. A number of species accumulate high concentration, even when grown on low fluoride soil, perhaps as a result of complex formation with aluminium. Gaseous fluorides inter leaves through stomata pores. Fluoride that penetrates the internal tissue of leaves or that is deposited on active surfaces such as stigmata may affect a variety of metabolic process and results in effected on appearance, chlorophyll contents, growth or reproduction. The visible effects of toxic concentrations of Fluoride on plants include chlorosis, peripheral necrosis, leaf distortion and malformation or abnormal fruit development. Uptake of Fluoride in the plants mainly occurs through the root from the soil and through the leaves from the air. Fluoride may induce changes in metabolism, decreased growth and yield, leaf chlorosis or necrosis, and in extreme cases plant death. Considerable differences exits in the plant sensitivity to atmospheric Fluoride, but little or no injury will occur when the most sensitive species are exposed to about 0.2μg/m3 air, and many species tolerate concentrations many times higher than this. Application of 100-PPM fluorine as calcium to field plots increased the yield in some cases. Maze considered that fluorine is a necessary element for corn but Wilson and Woher found that it had a toxic effect upon the plants they observed. The former worker found that tobacco plant responds to sodium fluoride by transforming free water into bound water in such quantities as to indicate that this compound includes a state of physiological drought. Barthdomew found that concentration of fluoride as high as 50 PPM did not significantly decrease the germination of Sudan grass, cowpeas, soybean, or red clover. The addition of soluble

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fluorides to the amount of 10 PPM did not decrease the amount of dry matter produced by cowpeas growing in a nutrient solution. The fluoride was found mostly in the roots of these plants.
A number of species accumulate high concentration, even when grown on low-fluoride soils, perhaps as a result of complex formation with aluminium. The tea family, thecae in best known of these accumulators, but there are several others that warrant further investigations. Gaseous and particular fluorides in the air are deposited on exposed plants surfaces; while gaseous fluoride enters leavers through stomata pores. Fluoride is also constantly lost from plants by a variety of little understood processes. Superficial deposits may be tenaciously held and may account for over 60% of the total fluoride content of the leaf. Though such deposited are of negligible toxicity to the plant, they may present a hazard for grazing animals. Fluoride that penetrates the internal tissue of leaves or that is deposited on active surface such as stigmata may affect a variety of metabolic processes and result in effect on appearance, growth, or reproduction. The visible effects of toxic concentrations of Fluoride on plants are well documented they may include chlorosis, peripheral necrosis, leaf distortion, and malformation or abnormal fruit development. None of these symptoms are specific to fluoride, and the effect of many other stresses may appear very similar. Under the most circumstances, little fluoride is taken up by root from the soil so the concentration in the shoots of plant in non-polluted atmospheres is usually less than 10 mg F per kg dry weight. However, there is exception, such as when plants grow on soil that contents high-fluoride minerals or plants of unusual physiology that accumulated high concentrations from low-fluoride soils. In industrial areas, atmospheric hydrogen fluoride pollution can be a serious case of fluoride toxicity to plants. Several workers in different plants of India have reported chronic endemic Fluorosis, due to fluoride toxicity. *Occidientalis, Prunus persica, Pinus contorta, Sylvestris, Pinus pinus, Pinus mugho, Pinus ponderosa, Prunus domestica, Picea pungens, Tulipa gesneriana, Acer negundo, Vaccinium sp., Pseudotsuga taxifolia, Gladiolus sp., Vitus vinifera, Mahonia repens, Larix etc.* are sensitive from Fluoride.

MATERIALS AND METHODS

Study Area

Hindalco Industries Ltd. Renukoot is one of the major producers of Primary Aluminium metal and Semis in the country, is the biggest industrial enterprise of India. It is the largest integrated aluminium plant in world with all its production facilities viz., Alumina, Aluminium and Fabrication located at Renukoot near Rihand Dam in Sonbhadra (U.P.). Hindalco Power Division is situated at Renusagar about 35 Kms from Renukoot. In September 1959, an industrial license was granted by the Government for setting up an integrated aluminium plant at Renukoot with an initial installed capacity of 20,000 MT.

Hindalco has installed high efficiency ESP's in all of its new Boilers and Calciners. These ESP's are capable of ensuring low emissions well with-in the prescribed parameters. There are various fluoride containing salts are used for making proper electrolyte to reduce alumina on passing current which causes generation of hydrogen fluoride (HF) as well as per fluorocarbon like CF_4, C_2F_6 etc. these HF, CF_4, C_2F_6 emit into the atmosphere and effect to the flora and fauna. In spite of the gaseous fluoride, fugitive particulate fluoride is also generated and affects the flora & fauna. The bath composition is mentioned as under

Alumina (Al_2O_3)	: 2-3%
Cryolite (NA_3AlF_6)	:82%
Aluminium Fluoride (AlF_3)	:9.7%
Spar (CaF)	: 6-7%

The above composition of both indicates fluoride containing compound therefore it is obvious to generate gaseous as well as particulate fluoride.

METHODOLOGY

Reagent Preparation

- Sodium Carbonate-Lithium Carbonate Solution
  Dissolve 40 g of anhydrous sodium carbonate & log of Lithium Carbonate (Li_2CO_3) in water & dilute to 1000 ml. store in a plastic bottle.
- Citrate Buffer
  Weigh 22.63 g of citric acid into 100 ml beaker. Add 50.0 ml. of 20% NaOH solution make up to approx. 90 ml with deionized distill water. Still to dissolve the acid, allow cooling and measuring the pH with a good pH meter. The pH should be between 5.5 and 5.7. If the pH is too low add 20% NaOH solution until a pH of 5.5 is reached. Transfer the solution to a 100 ml. volumetric flask, make up to mark (at 20°C) with deionized distill water & mix well.

Procedure

1. Keep 50 gm of leaves sample in oven at 62°C for 24 hrs.
2. Weight 2-4 gm. of dried sample in platinum dish & add 30 ml of Sodium Carbonate-Lithium Carbonate solution.
3. Evaporate this on hot plate & ignite it for 1 hr. in electric muffle furnace at 700°C.
4. Wash the ash in crucible with 25 ml. distilled water and pour it in the beaker. Then again wash the crucible with 35 ml perchloric acid ($HClO_4$) and pour it in the same beaker.
5. Then performed distillation of the above solution in steam distillation unit.
6. Then collect approximately 250 ml. of distillated solution in a beaker further take 5 ml citrate buffer in flask and mix in above distillated solution and make up 250 ml. by volume.
7. Now, take 10 ml of above in a small plastic beaker mixes 10 ml. of TISAB (total ionic strength anionic buffer) solution in to it.
8. Now, read the value of F (fluoride) by using expandable ion analyzer.

Fluoride concentration = R (mg/lit.) x V (ml) / W (gm.)

Where, R = final reading of expandable ion analyzer
V = final volume i.e. 250 ml
W = wt of leaf sampled (2-4 gm)

RESULTS

According to our experimental estimation, fluoride content was found about 44.1 ppm as maximum near Potline 4 in flora sample and 8.4 ppm as minimum near river side. This result indicates that fluoride content is much below the permissible limit in the flora sample i.e.; 80 ppm as stated in CREP.

Table 1: Fluoride concentration in plants

Sl. No.	Location	Botanical Name	Local Name	Fluoride (ppm)
01.	**Below Vishwakarma Statue**	*Cynadon dactylon*	Grass	35.6
02.	Potline # III	*Ficus religosa*	Pipal	25.0
03.	Potline # III	*Cynadon dactylon*	Grass	43.6
04.	Potline # II	*Mangifera indica*	Aam	33.4
05.	G -6, Hindalco Colony	*Azadiracha indica*	Neem	18.6
06.	Near Guest House (Rihand dam)	*Mangifera indica*	Aam	18.6
07	Potline # IV	*Ficus religiosa*	Pipal	44.1
08.	Plant # 2 Colony	*Cynadon dactylon*	Grass	28.4
09.	Near STP	*Solanum tuberosum*	Brinjal	19.7
10.	Near WTP	*Mangifera indica*	Aam	21.0
11.	Near STP	*Zizyphus mauritiana*	Bher	17.4
12.	Near Potline # IV	*Ficus religiosa*	Pipal	23.6
13.	Near Banvashi ashram	*Azadirachta indica*	Neem	34.1
14.	Near village Katauli	***Azadirachta indica***	Neem	31.7
15.	Near village Murdhawa	*Lantana camra*	Lantana	10.7
16.	Near village Pipri	*Bauhinia variegata*	Kachnar	28.7
17.	Near Hanuman Temple	*Mangifera indica*	Aam	33.4
18.	Near Guest House	*Mangifera indica*	Aam	9.7
19.	Near Guest House	*Cynodon dactylon*	Grass	16.4
20.	River Side	*Cynodon dactylon*	Grass	8.4
21.	Near village Turra	*Ficus religiosa*	Pipal	19.7
22.	Near village Turra	*Madhuca longifolia*	Mahua	31.0
23.	River Side	*Zizyphus mauritiana*	Bher	28.7
24.	Near village Muirpur	*Tamarindus indica*	Imli	18.2
25.	Near village Muirpur	*Zea mays*	Maize	23.4
26.	Near village Katauli	*Triticum aestivum*	Wheat	17.4
27.	Sagaria Nallah	*Ficus religiosa*	Pipal	17.2
28.	Plant II Colony	*Anthocephalus cadamba*	Kadamb	34.0
29.	Railway Colony	***Mangifera indica***	Aam	15.3
30.	Tharpather Village	*Bauhinia variegata*	kachnar	16.0

CONCLUSION

As we know that the industries activity has a significant impact on surrounding abiotic and biotic environment, Literature survey reveals that fluoride is the main pollutant in the industries like Aluminium industries, ceramic industries, smelting units etc. Hindalco industries limited, which has been working in the field of aluminium production for past four decades is the subject of the present study. The most impact phytotoxic pollutants emitted in the aluminium reduction process is fluoride and is found as Hydrogen fluoride and particulate Fluoride i.e. cryolite (Na_3AlF_6) Calcium Fluoride (CaF_2). These are produced mainly by volatilization of fluoride containing electrolyte.

The present report is based on the extensive field and laboratory study carried out within 15 km radius of the Hindalco Industries Ltd. Here an attempt has been made to quantify the polluted condition of the Flora with special reference to fluoride pollution. This is observed that sensitive plant with respect to fluoride accumulation like *Occidientalis, Prumus persica, Pinus contorta* etc. are growing properly within the premises of Hindalco industry.

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