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Two Dimensional Model for Fluoride Ion Transport in Soil for Steady Flow

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ABSTRACT: Whatever may be the source of fluoride in the environment, it passes to and from air, water and soil and living organisms through some biochemical pathways and ultimately reaches the higher trophic levels. The excess accumulation of fluorides in vegetation leads to visible leaf injury, damage to fruits, changes in the yield. Hirakud Smelter, a unit of Hindalco is operating at Hirakud town of western Orissa since 1958 producing primary aluminium by Horizontal stud Soderberg Technology. Starting with a capacity of 10,000 T of aluminium per annum in 1959. It has increased its capacity to 30,000 T in 1996 - 1997, 65,000 T in 2003 and 100000 T in 2007. Fluoride is a major pollutant in Aluminium smelter polluting the air, water and soil. A study conducted in 1996 by the senior author revealed a fluoride levels of 0.12 - 0.34 ppm in ground water, 0.13 - 0.87 ppm in surface water, 76.99 - 359.0 ppm in soil, 25 ppm in leaf tissue with a concentration factor from 260 - 941 in surface soil, 160 - 605 in deeper soil (>10 cm), 5 - 150 in herbaceous vegetation and 5 - 260 in leaf samples of perennial trees from surface water fluoride content it is reported the prevalence of fluorosis among the cattle population of Hirakud. Presently the capacity of the Smelter has increased by 300% with more emission of Fluoride to the environment. The present study is a part of the comprehensive research project to assess the environmental status of Hirakud urban ecosystems with reference to Aluminium Smelter and Thermal Power Plant. Here an attempt has been made to evaluate the extent of fluoride content in Hirakud environment in order to develop appropriate management strategy to contain it.

I. INTRODUCTION

Minerals are the major source of fluoride. Soil receives fluoride-contaminated minerals from the environment. Fluorides can cause many damaging effects not only to human beings but also to animals, aquatic organisms and vegetation. The variations in fluoride content in soil collected from both control and experimental sites are presented in Figure 3. The soil fluoride content in control site ranged from a minimum of 112.35 in crop field to a maximum of 138.70 ppm in fallow land soil. [1] In Hirakud Township, the fallow land soil showed a lower average fluoride content of 127.85 to a maximum of 139.35 ppm in crop field soils. The analysis of variance did not reveal any significant difference in fluoride content in both the type of soil and as well the distances. Factors that influence the mobility of inorganic fluorides in soil are pH and the formation of stable aluminium and calcium complexes. In more acidic soils, concentrations of inorganic fluoride were considerably higher in the deeper horizons. The low affinity of fluorides for organic material results in leaching from the more acidic surface horizon and increased retention by clay minerals and silts in the more alkaline deeper horizons. This distribution profile is not observed in either alkaline or saline soils. The fate of inorganic fluorides released to soil also depends on the chemical form, rate of deposition, soil chemistry and climate it is determined changes in free fluoride ions and total fluoride levels in materials that had different cation-exchange capacities, such as synthetic resins, clay minerals, manganese oxide and a humic acid. Increased amounts of fluoride were released from fluoride salts and fluoride-rich wastes when solids capable of exchanging cations were present. The effect was greatest when there were more exchange sites available and when the fluoride compound cation had greater affinity for the exchange material. In sandy acidic soils, fluoride tends to be present in water-soluble forms. It is determined the activity of the fluoride ion in acid sandy soils that had been limed. Fluorite was shown to be the solid phase controlling fluoride ion activity in soils between pH 5.5 and 7.0. At pH values below 5.0, the fluoride ion activity indicated super-saturation with respect to fluorite. [2,3]

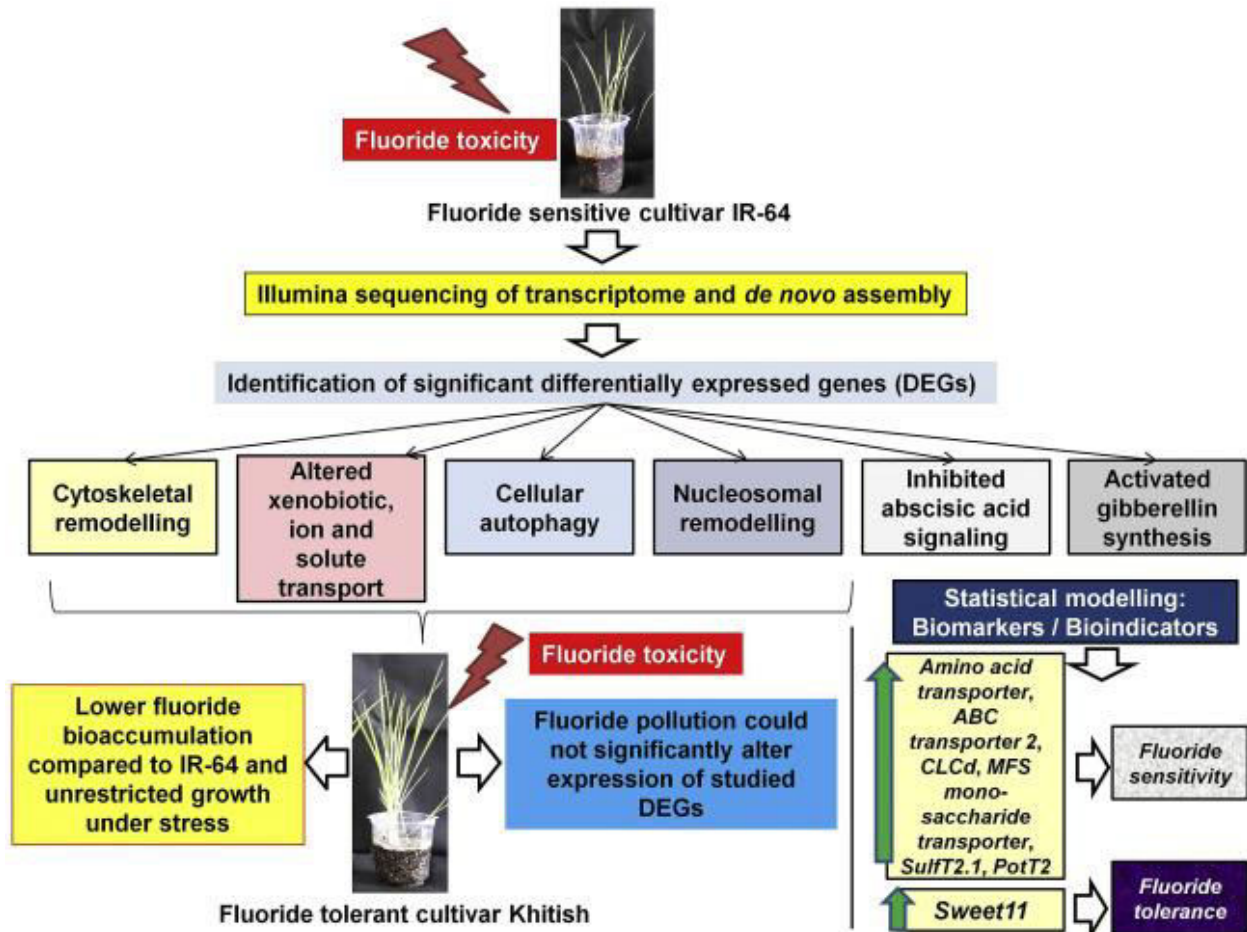


FIG.1: FLORIDE POLLUTION IN SOIL

These data indicate that liming of acid soils may precipitate fluorite, with a subsequent reduction in the concentration of fluoride ion in solution. It is reported that low amounts of fluoride were leached from a highly disturbed sandy podzol soil of no distinct structure. Even at high fluoride application rates (3.2 - 80 g per soil column of diameter 0.1 m with a depth of 2 m), only 2.6 - 4.6% of the fluoride applied was leached in the water-soluble form. The pH of the elute increased with increasing fluoride application, and this was probably due to adsorption of fluoride, releasing hydroxide ions from the soil metal hydroxides. Over time, the concentration of water-soluble fluoride decreased due to increased adsorption on soil particles. Mean soil concentrations in Pennsylvania, USA, were 377, 0.38 and 21.7 ppm for total fluoride, watersoluble fluoride and resin exchangeable fluoride, respectively. Fluoride is relatively immobile in soil, since most of the fluoride was not readily soluble or exchangeable. [4,5]

II. DISCUSSION

EXPERIMENTS SHOWING FLOURIDE UPTAKE BY PLANTS

Experiment 1

Tea seeds were germinated in river sand at room temperature (20–25 °C). At the four-to-five-leaf stage, uniform seedlings were selected for the uptake experiments and the cotyledons removed. A simple uptake solution containing 105 μmol L⁻¹ F⁻ as NH₄F was prepared with de-ionized water. Other nutrients (e.g. Ca and Mg) were not included to avoid any possible masking of effects. The original pH of the solution was 5.9 at a room temperature of 20–25 °C. It was adjusted to 4.0, 4.5, 5.0 and 5.5 by the addition of 0.1 mol L⁻¹ HNO₃. Each pot contained 1.5 L of aerated solution and three plants. After 48 h, plants were sampled, separated into roots, leaves and stems, oven-dried, and ground for F determination. There were three replicates of each pH treatment. [6,7]



Experiment 2

The effect of pH on F uptake by tea plants was also investigated in a soil experiment. The soil, taken from a tea field, had these properties: pH, 4.32; organic matter, 23.1 g kg⁻¹; exchangeable Ca, 410 mg kg⁻¹; water-soluble F, 0.04 mg kg⁻¹. The soil was air-dried, passed through a 5 mm sieve, then mixed thoroughly with CaO at 0, 1.05, 1.65, 2.15 and 2.70 g kg⁻¹ to correspond to soil pH values of 4.32, 4.91, 5.43, 5.89 and 6.55, respectively. The soils were stored for 2 weeks before the experiment was started. Each pot was filled with 2 kg soil and sown with 15 tea seeds in late October. After germination, each pot was thinned to ten relatively uniform seedlings. There were five replicates of each CaO treatment. The plants were grown outdoors and watered when necessary. In late June, plants were sampled, separated into roots, stems and leaves, and oven-dried. Soil samples were air-dried then passed through a 1-mm sieve for further analysis.[8,9]

Experiment 3

This experiment was designed to investigate the effect of Ca in solution on F uptake by tea plants. The tea plants were cultivated and treated as in expt 1. The uptake solutions contained F as NH₄F at 52.6 μmol L⁻¹ and were supplemented by a series of Ca concentrations at 0, 12.5, 25.0, 50.0, and 125.0 μmol L⁻¹. The Ca was supplied as Ca(NO₃)₂. Additional NH₄NO₃ was included to match the total N concentrations (NH₄⁺ and NO₃⁻) of the uptake solutions. There were three replicates of each Ca concentration. After 22 h, plants were sampled and dried for F and other element determinations. The experiment was repeated under similar conditions but with F concentrations of 105.2 μmol L⁻¹ in the solution and the uptake duration extended to 72 h.[10,11]

Experiment 4

This experiment was conducted to investigate the effect of Ca on F uptake by tea plants grown in soil. Each pot was filled with 5.5 kg of air-dried soil taken from a tea field and planted with four 1-year-old rooted cuttings. After 2 years of growth without fertilization, pots containing uniform plants were selected for the experiment. The treatments were control (no additional F) or 30 mg kg⁻¹ F as NH₄F, in combination with three levels of Ca at 0, 100 and 500 mg kg⁻¹ as Ca(NO₃)₂, arranged in a completely randomized design. Additional NH₄NO₃ was applied so that all treatments received an identical amount of N (0.37 g kg⁻¹). Ca, F and NH₄NO₃ were applied twice in July, with a 1-week interval between each application. All treatments were replicated three times. The plants were grown outdoors and watered when necessary. Thirty days after treatment, samples of leaves and young shoots were taken. Leaves were taken from similar positions on branches so that they were of the same developmental age. Samples of young shoots consisted of one bud and three leaves, which represented the crop usually harvested for summer green-tea production. Plant samples were oven-dried at 60 °C and ground for element analysis. Soil samples were air dried and passed through a 1-mm sieve for further analysis.[12,13]

III. ANALYSES

For F determinations, plant samples (0.2–0.5 g) were digested with 5 mL concentrated HNO₃ in a microwave digestion unit equipped with a temperature control system (Model Mars 5, CEM Corporation, Matthews, USA) and measured with a fluoride ion selective electrode (F-ISE) as previously used by Stevens *et al.* (1995), but with modifications. After cold digestion in the sealed vessels for one night, the samples were digested at 120 °C as described by Keerthisinghe *et al.* (1991), for 20 min. The digest solutions were diluted with deionized water and a 5-mL aliquot was added to 20 mL 1.5 mol L⁻¹ trisodium citrate (pH 5.25) for millivolt potential measurements. Concentrations of Ca, potassium (K), Mg and Al in the remaining digest solution were determined using an Induced Couple Plasma–Atomic Emission Spectrometer (ICP–AES). Soil water-soluble F was determined as described by Frankenberger *et al.* (1996). Fifty grams of air-dried soil was shaken with 50 ml deionized water, filtered, and measured with an F-ISE with a total ionic strength adjustment buffer (TISAB) (1 : 1). The detection limit of the F-ISE was approx. 0.02 μg mL⁻¹. Soil pH was measured in 1 : 1 water paste. The exchangeable cations Ca, K and Mg were extracted with 1 mol L⁻¹ ammonium acetate (pH 7) at a soil to solution ratio of 1 : 10. Labile Al was extracted with 0.02 mol L⁻¹ CaCl₂ for 30 min as Dong *et al.* (1999) have shown that this procedure provides a good prediction of Al concentrations in tea leaves. Elements in soil extracts were measured using an ICP–AES. The experimental data were subjected to one- or two-way analysis of variance (ANOVA) to examine the effects of treatments on various dependent variables. Fisher's least

significant difference (l.s.d.) test was used to determine whether or not treatment means differed significantly ($P < 0.05$). Pearson’s product moment correlation was performed to calculate correlation coefficients

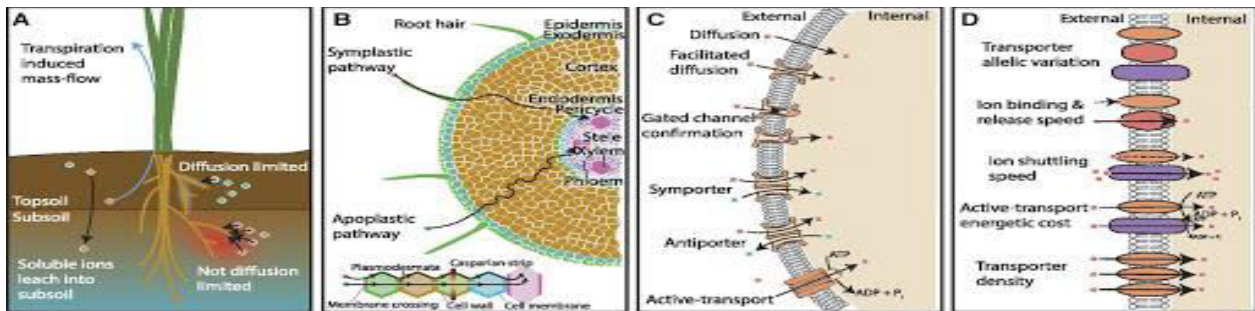


FIG.2: FLOURIDE UPTAKE MODEL

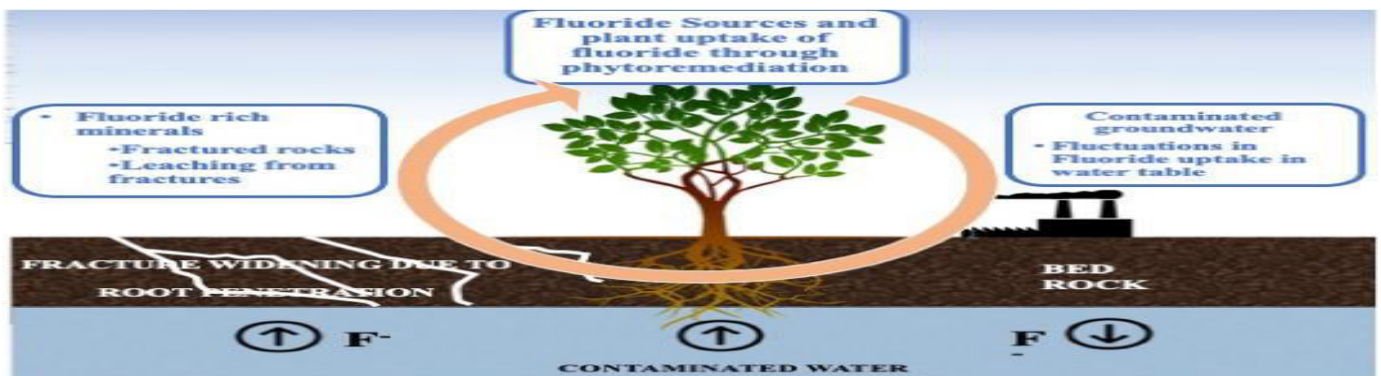


FIG.3: FLOURIDE UPTAKE FROM SOIL THROUGH PHYTOREMEDIATION

IV. RESULT

Effects of uptake solution pH on F concentrations in tea plants (expt 1)

Leaf F concentrations were highest when the solution pH was 5.5, and significantly lower when it was 4.0 (Fig. 1). A similar effect of pH was observed with a lower solution F concentration ($52.6 \mu\text{mol L}^{-1}$) and with a shorter uptake period (22 h) (data not shown). Root F concentrations followed the same trend as leaf F concentrations but the effect of pH was not statistically significant ($P > 0.05$). Solution pH had no effect on stem F.[14]

Effect of liming on F uptake by tea plants (expt 2)

The properties of soil sampled at harvest are shown in Table 1. Soil pH changed a little after planting compared with its initial value. Liming significantly increased exchangeable Ca, K and Mg concentrations, but reduced labile Al concentration. Water-soluble F concentrations were also increased when the applied amount of CaO exceeded 1.65 g kg^{-1} , and remained unchanged thereafter. Dry matter production was unaffected by liming treatment (data not shown). Leaf F concentrations were dramatically reduced by liming (Fig. 2A), being reduced by 37.2 and 88.7 % following CaO application at 1.05 and 2.70 g kg^{-1} , respectively, compared with the unlimed control. Leaf F concentrations linearly and negatively correlated with the amounts of CaO applied [$F_{\text{leaves}} = 837 - 290L, R^2 = 0.95, P < 0.001$; where F is the leaf F concentration (mg kg^{-1}) and L is the amount of CaO applied (g kg^{-1})]. Root F concentrations were also decreased by liming at 1.05 g kg^{-1} and remained unchanged thereafter, whereas stem F concentrations were unaffected (Fig. 2B). Liming reduced Al concentration while increasing Ca and Mg concentrations in the leaves (Table 2). Concentrations of K (Table 2), S, Fe and Zn were unaffected by liming (data not shown).[15]



Effect of Ca in solution on F uptake by tea plants (expt 3)

The addition of Ca to the uptake solution significantly decreased leaf F concentrations, the effect being evident even when $12.5 \mu\text{mol L}^{-1}$ Ca was applied (Fig. 3A). At this level of Ca, leaf F concentration was decreased by 10.5 % ($P < 0.05$) compared with the control without Ca. Leaf F concentrations were further decreased with increasing Ca concentrations in the uptake solution. Root and stem F concentrations (Fig. 3A), and leaf Ca concentrations (data not shown) were unaffected. The distribution pattern of F was unaltered by Ca, with most F being found in leaves. Doubling the F concentration in the uptake solution to $105 \mu\text{mol L}^{-1}$ and extending the uptake period to 72 h increased the plant F concentration, and the effect of Ca on F uptake was more pronounced (Fig. 3B). Leaf F concentrations were decreased by 17.3 and 42.9 % when the solution Ca was 50 and $75 \mu\text{mol L}^{-1}$, respectively. However, F uptake was unaffected when the solution Ca was $12.5 \mu\text{mol L}^{-1}$. Again, root and stem F concentrations were unaffected by solution Ca (data not shown).[16]

Effect of Ca addition to soil on F uptake by tea plants (expt 4)

The addition of F to soil significantly increased the water-soluble F concentration in the soil (Table 3). Soil pH, exchangeable Ca and K were unaffected by F treatment. Exchangeable Mg was significantly increased only by F and Ca at 500 mg kg^{-1} . Soil labile Al was increased by F application when Ca was not added but changed little when Ca was added. The addition of Ca significantly increased water-soluble F in treatments without F application but not in its presence. Exchangeable Ca content and soil pH were both increased by Ca application but exchangeable K was increased only when F was also applied. Labile Al decreased in soil following Ca application at 500 mg kg^{-1} .

Leaf and young shoot F concentrations were significantly decreased by the addition of Ca at 500 mg kg^{-1} (Fig. 4). The application of Ca at 100 mg kg^{-1} did not affect young shoot F in either F treatment or in leaves when no additional F was applied to the soil. Following F application, leaf F was decreased by Ca applied at this level. Leaf and young shoot F concentrations were negatively correlated ($P < 0.01$) with the exchangeable Ca content of the soil (Fig. 5A and B). The addition of F to the soil only increased F concentrations in young shoots but not in leaves 1 month after treatment. However, after a longer period, a higher leaf F concentration was also observed (data not shown). Concentrations of other elements in leaves and young shoots are presented in Tables 4 and 5. In leaves, Ca and Mg concentrations were unaffected by Ca and F treatments. leaf K was higher when Ca was applied at 500 mg kg^{-1} but without the addition of F. Al concentration was lower in the leaves of plants supplied with F than in those without, and was further slightly, but not significantly, decreased following the addition of Ca. In young shoots, Ca was significantly increased following the addition of Ca. Concentrations of Al, K and Mg were unaffected by F and Ca applications. The results of the correlation analysis between F concentrations and other elements in plants and soil properties are presented in Table 6. Leaf F concentrations were positively correlated with labile Al and negatively with soil pH and exchangeable Ca content. Significantly positive and negative correlations were found between young shoot F and soil labile Al and exchangeable Ca, respectively. Water-soluble F content correlated significantly with young shoot F but not with that in leaves. No significant correlations were found between plant F and Al, Mg or soil exchangeable Mg. Correlations between plant F and K or Ca were less consistent, being significant only in leaves for K and in young shoots for Ca.[17]

V. CONCLUSION

The uptake of F by tea plants was highest at solution pH 5.5 and lower at pH 4.0, although the percentage of HF increased to 6.15 % at pH 4.0 from 0.08 % at pH 5.94, as calculated by GEOCHEM-PC (Parker *et al.*, 1995). This seems inconsistent with the previous findings of Stevens *et al.* (1998a) who demonstrated that the HF uptake rate was orders of magnitude higher than F^- at similar ion activities because HF readily diffused across the cell membrane. These authors found that with decreasing solution pH the proportion of HF increased considerably, leading to significantly higher F concentrations in tomato and oat plants. The inconsistency of the present results with these findings might be attributed to the difference in plant species, with tea being an F accumulator, and possibly also to the difference in solution F concentrations used in the experiments. It was apparent from the work of Stevens *et al.* (1998a) that the plant F concentration increased sharply only after the activities of HF exceeded critical values ($73 \mu\text{mol L}^{-1}$ for tomato and $169 \mu\text{mol L}^{-1}$ for oat). In the present study, a much lower F concentration (total $105 \mu\text{mol L}^{-1}$) was used and the activity of HF (approx. $7.2 \mu\text{mol l}^{-1}$ at pH 4.0) was more than one order of magnitude lower. In most tea soils, soil solution F concentrations are below $50 \mu\text{mol L}^{-1}$



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