Fluoride: Diffusive mobility in soil and some remedial measures to control its plant uptake

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Dietary (human) intake of fluoride (F) largely through consumption of agricultural produce grown in F contaminated environment, has recently been viewed as an important cause for several F related health problems in many parts of the world. Being a non-essential element, F is usually taken up by plants through passive uptake – a process which is dominantly diffusion controlled. Still very little is known regarding F diffusion in soil. In present study, diffusion of F in the alluvial soil (Entisol) of Dayalbagh (Agra) has been investigated as a function of soil water content (θ) and F concentration gradient. The data on F diffusion coefficients were recorded by determining the F concentration profile in horizontally incubated and homogenized soil columns, under varied experimental conditions (θ = 0.12–0.25 cm⁻¹, pH = 7.3 ± 0.2, incubation time (t) = 96–384 h, temperature = 303 ± 1.2 K). The effects of aluminium and calcium, which are known to be strong binders for F in soil, on the F diffusion have also been investigated. The study, particularly, throws light on the possible dual role of aluminium in affecting the diffusion of F in soil which might prove critical in the ultimate uptake of F by plants in specific environmental conditions.

The beneficial and harmful effects of fluoride (F) in the human body have been debated about a lot in recent times. The widespread prevalence of fluorosis, a disease caused by excess intake of F, in parts of Rajasthan, Tamil Nadu, Uttar Pradesh, Delhi, Andhra Pradesh and Madhya Pradesh suggests that the aspects of excess F intake and their associated harmful effects are more relevant in the context of India compared to most Western countries where fluoridation of water is rather recommended to help prevent dental caries. F is a naturally occurring pollutant, which is often released into the soil-environment through the use of phosphatic fertilizers and other pesticidal sprays, as well as through the disposal of industrial sludges. The migration of F from such localized F-rich sources to adjoining top soil layers followed by its uptake by the plants, is a complicated but crucial process of high biological significance as it may decide the ultimate levels of dietary intake of F by animal and human populations in an area.

Studies on ion mobility in soil have so far recognized its importance in controlling the flow of nutrient ions/molecules and the toxic metals from the bulk of soil to roots. However, the observations are quite at variance. While mass flow reportedly plays an important role in the plant uptake of nitrates, diffusion supplies almost all the plant’s phosphate and most of its potassium. In a recent study, it has been shown that the uptake of Fe by rice is also largely diffusion controlled and the contribution of mass flow is limited to only 5–9%. Regarding F also, its diffusion in soil may be crucial in regulating its movement from the bulk of soil to root zone, particularly in plants grown in arid and semi-arid conditions. This contention is partly supported by F uptake values reported for certain plants grown in solution, sand and soil culture, where good correlation (r = 0.99) between the total F concentration in solution and F taken up by plants was found. However, the phenomenon of F mobility in soil, particularly its diffusion aspect, is still not well studied and data in this regard are lacking. In this paper we are reporting the results of a study on diffusive mobility of F in an alluvial soil (Entisol) as a function of soil water content, F concentration gradient and soil amendment with aluminium and calcium.

Samples of soil (Entisol) were collected from open uncultivated fields spread all around Agra city (27°10′N, 78°05′E, 168 m above sea level). The physico-chemical characteristics of the dried and sieved soil (S₁, particle size < 2 mm) were determined using standard methods. S₁ soil taken in closed containers (700 g in each) was treated separately with 42, 35, 28, 21, 14 and 10.5 mg Al and Ca by adding 100 cm³ of AlCl₃ and CaCl₂ solutions, respectively, of appropriate molarities, in small aliquots with thorough gentle mixing. Resulting soil-water slurries were incubated at 303 K for 25 days after which the dried soils were mildly crushed, sieved and used for diffusion studies.

Soil columns were prepared by packing soil in PVC pipes made of segmented cylindrical rings (inner diameter and length were 2.13 and 1 cm, respectively), at the bulk

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density 1.56 g cm\(^{-3}\) and the desired water content. Insignificant F sorption by used PVC pipes was earlier confirmed by soaking their 2 cm long pieces (5 in number) in 0.1 M F solution for ~ 24 h, which resulted in < 0.02% fall in F concentration in the solution. The diffusion experiments were performed by joining, through pushing with a piston, both the ends of a 5 cm long soil column (containing NaF) with another column of soil 6 cm long (without NaF). F diffusions were determined by incubating the above assembly horizontally for 96–384 h at 303 K, after sealing all the joints and ends of the column to avoid moisture loss, and then measuring F profile in the entire column length. Variations in water content with column distance were found insignificant (at \(\alpha = 0.05\)) mainly due to 5–6 weeks equilibration period before incubation. For F determination 2–3 g wet soil from each 1 cm segment of the column was shaken with 25 cm\(^3\) of water for 1 h and centrifuged at 4000 rpm for 10 min. The supernates mixed with suitable TISAB solution (1 : 1 v/v) were subjected to F measurements employing an Orion F selective electrode (Model 9409 BN) coupled to Orion Microprocessor Ion Analyser (Model EA 940). Only AR grade reagents and double-distilled deionized water were used throughout the study. The determinations on linear (x-dimensional) transient diffusion and the computations of diffusion coefficient \((D_p)\) of F in soil were based upon the method described elsewhere\(^{11}\).

Physico-chemical characteristics of the soil used in the study are presented in Table 1. It has been shown by numerous workers that the physical condition of the soil affects the diffusion process markedly. Besides, if the water content is maintained too low, it would require much larger equilibration period for soil columns before the diffusion study can be performed. If the soil is too wet it would be difficult to get a smooth soil surface when cutting with a blade. Hence, in our study the water content was kept at the experimentally determined optimum range of 8–20% on weight basis. Duration of diffusion not only determines the diffusing distance, but can also affect the diffusion coefficient significantly in some cases. Therefore, in this study most diffusion coefficient data have been recorded at an arbitrarily chosen (by trial) proper duration of 384 h. However, in some experiments 384 h diffusion observations were compared with 96 h results.

The measured weights of the soil columns before and after the diffusion run being nearly the same (differences in weights < 0.29%), insignificant moisture loss during incubation was confirmed. Besides, the measured water content profiles after incubation clearly indicated that the water content had remained constant throughout the column length. There must be some amount of water (liquid and vapour) movement induced by the osmotic potential gradient in the soil columns. However, this water flow seems so small that it has little effect on the water content profiles and determinations of \(D_p\).

Besides cation and anion exchange capacities, soluble and replaceable phosphorus contents of the soil are known to affect the reactions of F in the soil, which will also have a marked effect on F mobility in the soil. The soil used in the present investigation is also containing significant amount of phosphorus (measured by the method of Olsen et al.\(^{12}\)), which is likely to interfere in the reactions of soil-Ca and soil-Al with F. This contention is amply clear from the observed slight increase in pH value of the soil in a suspension of KCl and CaCl\(_2\).

The observed F diffusion coefficients in soil as a function of \(\theta\) have been shown in Figure 1. The observed \(D_p\) values in soil are less by a factor of \(10^{-2}–10^3\) compared to values in bulk solution, i.e. \(D_0\). The value of \(D_p\) for F diffusion, calculated from limiting equivalent conductivities data is \(1.48 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}\) at 25°C (ref. 11). The observed restricted diffusion of F at low water contents is seem-
ingly due to the existence of most of the soil solution in the electric double layer on the surface of solid particles, where ion molecular diffusion is restricted compared with bulk solution. Besides at low θ, when the thickness of water films in the soil becomes non uniform, F will get preferentially concentrated in portions of thicker water films separated by thinner water films, where it would be repelled.

When source sections were loaded with NaF solution of different concentrations, the F diffusion coefficients were found to vary with the quantity of the diffusing source (Figure 2). The observed rise in F diffusion in soil section \( (x = 0-6 \text{ cm}, \ t = 384 \text{ h}) \) with the increase in the initially added quantity of F in source section can be explained by the distribution of F ions between the adsorbed/bound state and the dissociated state. Because adsorbed ions migrate more slowly than do ions in solution, the diffusion coefficient values will be larger when the fraction of F ions in solution is more. This fraction will be even larger if the diffusing F species/ions are repelled by soil surfaces also, mainly due to electrostatic forces.

Measured values of F diffusion coefficients, in soil amended with aluminium and calcium are presented in Table 2. It has been found that the significant effects of soil amendments on \( D_p \) occur when amending concentrations of added metals are ≥ 40 (for Al) and ≥ 15 μg g\(^{-1}\) (for Ca). In Ca amended soils, \( D_p \) values are significantly low and decrease linearly as the amending concentration or the incubation time increases. In Al amended soils, the observed \( D_q \) values at 96 h incubation are significantly high and rise with the increase in Al concentration. However, at 384 h incubation, the \( D_q \) values are drastically reduced and the observed variation with respect to Al concentration is also reverse. F is known to have a strong affinity for Al and forms complexes even when more than 90% of total soil F is adsorbed. Significantly high \( D_q \) at 96 h incubation in Al-amended soils may, therefore, be attributed to the presence of such fluoro-aluminium complexes, which are highly mobile in soil. This contention is in agreement with similar views expressed earlier by some researchers, albeit without any evidence. Reporting accumulation of high concentration of F in many species of plants, especially of the tea family, Theaceae, even when grown on low F soils, it was suggested by some workers that probably this phenomenon was largely mediated through prior complexation of F with Al\(^{15}\). The drastic drop in F diffusion in Al-amended soil at 384 h incubation is probably suggestive of slow conversion of initially formed complexes to insoluble species of the type AlCl\(_3\) (s) and Al(OH)\(_3\) (gibbsite). Besides, the competitive interferences of reactions leading to the formation of insoluble species like Al(OH)\(_{2+}\) and Al(OH)\(_{3+}\) cannot be ruled out. The decrease in F diffusion with the rise in Ca content in soil may be due to the precipitation of F as fluoro-calcite (CaF\(_2\)) or fluoroapatite (Ca\(_{5}\) (PO\(_4\))\(_3\) F\(_{16}\)). In either case it will result in restricted F diffusion. The possibility of CaF\(_2\) formation by reaction of F with soluble or exchangeable Ca of the soil at near neutral pH has been mentioned by several workers\(^{17,18}\). On the other hand, looking at the calcareous nature of the studied soil, the formation of later species seems more likely.

It is surprising to note that the addition of Ca or Al in soil in amounts, which are insignificant compared to their expected natural total content in soil, so significantly affected the F mobility in the soil. Probably this suggests that the externally added Ca or Al, before their fixation in soil, remain for a considerably long period of time in a form which freely interacts with diffusing F. In contrast in unamended soil most of the naturally present Ca or Al, as a result of many physico-chemical fixation processes occurring in the soil, is more likely to be already converted to a form which is strongly binded with soil matrix.

<table>
<thead>
<tr>
<th>Amending amount of aluminium/calcium per g of soil (μg)</th>
<th>(D_q \times 10^9) (cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>* 16.4 ± 1.41, 1.6 ± 0.13</td>
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<tr>
<td></td>
<td>** 2.2 ± 0.18, 0.9 ± 0.10</td>
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<tr>
<td>50</td>
<td>* 13.2 ± 1.22, 2.4 ± 0.18</td>
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<tr>
<td></td>
<td>** 3.1 ± 0.28, 1.3 ± 0.10</td>
</tr>
<tr>
<td>40</td>
<td>* 8.9 ± 0.77, 3.4 ± 0.28</td>
</tr>
<tr>
<td></td>
<td>** 3.8 ± 0.35, 1.8 ± 0.14</td>
</tr>
<tr>
<td>30</td>
<td>* 7.8 ± 0.72, 4.1 ± 0.38</td>
</tr>
<tr>
<td></td>
<td>** 4.4 ± 0.41, 2.2 ± 0.16</td>
</tr>
<tr>
<td>20</td>
<td>* 8.0 ± 0.74, 5.3 ± 0.46</td>
</tr>
<tr>
<td></td>
<td>** 4.1 ± 0.34, 2.7 ± 0.21</td>
</tr>
<tr>
<td>15</td>
<td>* 7.8 ± 0.71, 5.6 ± 0.52</td>
</tr>
<tr>
<td></td>
<td>** 4.4 ± 0.40, 3.0 ± 0.28</td>
</tr>
<tr>
<td>nil</td>
<td>* 7.7 ± 1.81, 7.7 ± 1.81</td>
</tr>
<tr>
<td></td>
<td>** 4.1 ± 0.73, 4.1 ± 0.73</td>
</tr>
</tbody>
</table>

Incubation time (t) = 96 h (⋆), 384 h (★★).

![](image.png) Figure 2. Plot of \(D_q\) vs initial source concentration for F diffusion at: pH (soil : water = 1 : 2 w/v) = 7.3 ± 0.2, \(t = 384\) h, \(\theta = 0.25\) cm\(^{-1}\) cm\(^{-2}\), temperature = 303 ± 1.2 K.
The present study, thus, leads to following conclusions: (i) The diffusive mobility of F in soil increases significantly with the rise in soil water content and F concentration gradient. With the rise in incubation period the observed $D_p$ decreases, indicating the simultaneous occurrence of F fixation processes in soil along with diffusion; (ii) Presence of Al in soil helps in F diffusion in early phases, possibly due to the formation of the mobile fluoro-aluminium complexes. This may lead to greater uptake of F by plants which have faster growth, e.g. leafy vegetable plants, especially during the time span immediately after irrigation with fluoride-rich water or else manuring soil with phosphatic fertilizers or some industrial sludges, which are known high F materials. However, the study also indicates that at incubation time ≥ 384 h, the process of F fixation in the soil gets facilitated in the presence of added Al. Nevertheless these conclusions would require correlation with the field situation also before anything can be concluded with certainty; (iii) Amending soil with Ca drastically reduces F diffusion in the soil. Therefore adding a calculated minimum quantity of some F-free calcium salt (dissolved in irrigation water) in the soil might help in restricting the F entry from soil solution to inside the plant body, considerably. This might help to provide a solution for controlling the dietary intake of F, particularly in areas severely affected with endemic fluorosis. This conclusion seems to be unjustified because most of the areas affected by fluorosis are in dry regions with already high calcium content in soils. However, since there is a clear distinction between the naturally occurring total content of Ca in the soil and a small part of it which is freely available to interact with added F, even in areas where soils are rich in Ca, it is quite likely that most of the Ca might be present in the soil in an insolubilized/precipitated form, which is strongly binded with soil matrix and is, therefore, not freely accessible to the added F. This justifies the conclusions of this study. Further studies on the role of externally added Ca and Al in regulating F mobility in soil particularly under field conditions are being pursued.


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Increasing the efficacy of difluoromethylornithine to inhibit the growth of three phytopathogenic fungi by membrane modifying agents

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The selective inhibition of fungal polyamine biosynthesis using difluoromethylornithine (DFMO) has been a promising approach for plant chemotherapy. However, some plant pathogenic fungi have been found to be resistant to high concentrations of DFMO. Therefore, some attempt was made to increase the efficacy of DFMO to inhibit the growth of three phytopathogenic fungi (Pythium aphanidermatum, Helminthosporium oryzae and Rhizoctonia solani) by using CaCl$_2$ and polyethylene glycol (PEG). The growth inhibition was increased by 12–30% for all the fungi tested with adjuvant concentrations in a selected range (5 mM CaCl$_2$ and 5% PEG), which were otherwise not inhibitory for normal growth of fungi. These results suggest that the effective control of plant pathogenic fungi may be achieved by the use of DFMO in conjunction with CaCl$_2$ or PEG.

POLYAMINES (PAs) are essential for normal growth and development and also in the regulation of several cellular and molecular functions1–3. Putrescine (Put), which is

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