RESEARCH ARTICLE

Assessment of Fluoride Contamination and its Relationship with Chemical Properties of Soil

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ABSTRACT

The present study deals with surveying and analyzing the Fluoride concentration in the Reddiyarchatram block of Dindigul district of Tamil Nadu and establishing a correlation coefficient with the other soil chemical properties. The result indicated that water soluble fluoride content forms a negative correlation with soil pH, signifying that soil pH plays a prominent role in the solubility of fluoride. Water-soluble fluoride content has a positive relationship with soil available nitrogen, potassium and sodium indicating that presence of F in the soil increase their availability and vice versa. Soil phosphorus forms a significant positive correlation with fluoride. It says that increase in P content increases soil F. Also, a soil organic carbon and calcium presence affects the water soluble fluoride content as they form a significant negative correlation. Water-soluble fluoride forms a negative relationship with soil electrical conductivity, total dissolved solids, available potassium and sodium, suggesting these factors play a major role in F availability in soils. Results concluded from the present study show soils with low pH, low organic matter content, high phosphorus, and low calcium plays a prominent role in F solubility from the fluoride-bearing minerals which directly increase the concentration of the water soluble fluoride in the upper layers of the soil.

Keywords: *Fluoride; Soil; Contamination; Correlation; chemical properties*

INTRODUCTION

Soil contamination due to fluoride has been growing at an alarming rate both by nature and anthropic influence. Currently, Elevated fluoride in groundwater is the first problem in 25 countries and about 200 billion people in the world have to reckon with water containing excessive fluoride (Guth *et al*., 2021). Moreover, soils also contain approximately 300 ppm of fluoride to 1000 ppm wherein the contaminated site-level exceeds 3500 ppm (Zhang *et al.,* 2013). The major cause of the contaminated groundwater is mainly due to the movement of fluoride from surface-contaminated soils (Suzuki *et al.,* 2013). It occurs in soil as a single negatively charged fluoride ion or occasionally as a component of such complex anions as (BF^{-6}), $(AlF_6)^{3-}$ and $(SiF_6)^2$ The harmful effect of soil fluoride is associated only with an available form where total fluoride content is not of great importance (Kumar, 2015). The amount of fluoride content in soil depends on soil type, soil sorption capacity, characteristics of sorption ion and its concentration, soil salinity, type of plant species, and physical and chemical properties. Fluoride presence influences more physico-chemical, thermal, and microbial properties of soil (Ropelewska *et al.,* 2016). Soil fluoride is insoluble and tightly bound to particles by having the same radius as hydroxide ion. Soil pH has a profound effect on the biogeochemistry of fluoride. High organic matter content increases the fluoride adsorption capacity of soils and controls immobilisation (Anshumali, 2014). In India, the Dindigul district of Tamilnadu contains the highest fluoride bearing minerals which in turn reflects soil with high fluoride concentrations. Fluoride in small quantity (1.5 mg L^{-1}) is a required compound for

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dental enamel formation and bone mineralization (Kanagaraj and Elango, 2019) above that it causes lethal effects to humans such as reduced development of intelligence, disturbed hormone production, and fluorosis (Mikkonen *et al.*, 2018). In plants, fluoride produces lethal effects starting from the early stage of germination and continues up to harvest stage. The present study mainly focused on the analysis of water- soluble fluoride in soil and working out the correlation with other soil chemical properties. The sample site is the Reddiyarchatram block of the Dindigul district, Tamilnadu where fluoride contamination in groundwater is a major problem which is well documented by many researchers (Amutha *et al.*, 2012; Vishwanath *et al.*, 2020) restricted only to drinking water. So, the soils of Reddiyarchatram were collected and analyzed to work out the correlation between the other chemical properties.

MATERIAL AND METHODS

The entire block covering all 23 villages of Reddiyarchatram, Dindigul district, was surveyed for collecting soil samples with the help of a handheld geographical positioning system covering 48 benchmark sites. Samples were collected at 0-15 cm depth according to standard procedures, dried, sieved, and processed carefully. Air-dried samples were analyzed for pH (potentiometry), Electrical conductivity (Conductometry) and Total dissolved solids (Jackson, 1973). Other parameters such as available nitrogen (alkaline potassium permanganate method) (Subbaiah,1956), phosphorus (Olsen, 1954), potassium, sodium (Jackson, 1973) calcium and magnesium (Versanate titration) were analyzed as per standard protocol. Organic carbon is analysed by using wet digestion method suggested by (Walkley and Black, 1934). Fluoride content in soil is measured by the potentiometric method by using an ion analyser coupled with an ion-selective electrode using TISAB III (Total ionic strength adjustment buffer)(Frant and Ross, 1968). Statistical analysis was carried out using XLSTAT (2009) and Pearson correlation coefficient (Gomez and Gomez, 1984) was established among the different soil chemical parameters.

RESULTS AND DISCUSSION

Soil chemical properties

Results show that the entire block of Reddiyarchatram having has neutral to alkaline soil reaction except for the areas of Neelamalai hills and Thovar, which is a reserved forest area. The exact alkaline nature of other blocks of Dindigul districts was observed by the other researchers due to calcium carbonate, containing parent materials which was more influenced by the arid climate and low rainfall (Shu *et al.*, 2003). In addition, soil pH reveals a significantly negative correlation with fluoride, ing that F solubility in soil is mostly influenced by the soil pH. Acidic soils have more F content compared to alkali soils because of amorphous aluminum oxide concentration (Singh *et al.,* 2018). In addition, fluoride s a strong tendency to replace hydroxide from the clay colloids and binds instead of them, making it readily soluble and available in soil solution. The presence of alkaline salts and Al oxides determine the blending and leaching ability of fluoride ions. Regarding EC content, soils of Reddiyarchatram falls in the non-saline to medium saline nature in the soil samples collected in post-monsoon season where previous researchers observed saline to alkaline nature. Organic carbon status is medium to high in all parts of the block except in a few villages. The organic carbon strongly influences fluoride retention in soils (Dey *et al*., 2012). Total dissolved salts in the entire block fall with the mean of 78.4 ppm. In addition, available nitrogen, phosphorus and potassium gives the nutrient status of the block showing that the overall block is low in available nitrogen, and phosphorus which may be due to the influenced by other mechanisms by other mechanisms such as organic matter content and soil microbial population. Soil potassium stands in the medium range throughout the block. This gives an idea about the soil fertility status of the block. Exchangeable sodium concentration is low to medium, and sodicity is not a problem. Exchangeable calcium and magnesium status are medium throughout the block but few villages have calcareous soil (Bhat *et al*., 2015). Fluoride has a strong affinity towards the soil calcium content (Anshumali, 2014). Fluoride forms a complex with the calcium forms CaF_2 which is insoluble, thus reducing the bioavailability (Szostek and Ciećko, 2017). Fluoride concentration (water-soluble) varies from 0.98 ppm to 3.32 ppm where permissible is up to 2.64 ppm. High fluoride content is majorly present in the soils of Ammapatti and hilly villages such as Thovar and Nilamalai. Fluoride is highly mobile in soil with acidic pH and F adsorption is ten times higher in acidic soil, forming the complex of $[AlF]^{2+}$ and $[AlF_2]^+$ in soil solution, which is readily available to the plant roots (Maitra *et al*., 2016).

Correlation between fluoride and other chemical properties of soil

Pearson correlation coefficient was worked out between the water-soluble fluoride content and the other chemical properties. A significant negative correlation of fluoride(r=-0.39) shows between pH and fluoride content, indicating that a decrease in pH increases the fluoride content. The presence of Al_2O_3, Fe_2O_3 in the soil solution determines the binding and leaching ability of the fluoride in the soil (Gao *et al.*, 2012). There is a positive correlation between fluoride, nitrogen, potassium, and sodium thus implicates the presence of these ions may increase the solubility of organic matter which shows a significant negative correlation with fluoride thus the presence of highly reactive functional groups such as –COOH, $-NH_2$, -OH readily reacts, forming instable fluoride complex which are further replaced only by heavy metals if the soil is contaminated (Baldock and Nelson, 2000).

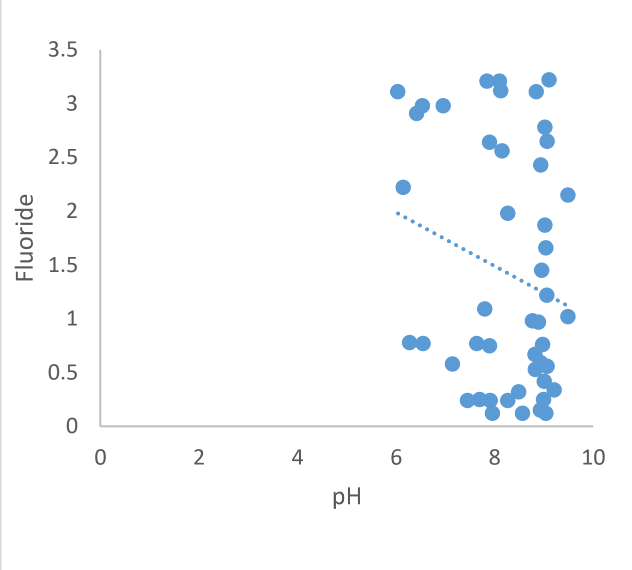

Fig.1 Correlation between soil pH and Fluoride content in soil

Table 1. Range, mean value and Correlation coefficient (r) for soil chemical characteristics with water soluble fluoride

S.No	Soil properties	Range	Mean	Correlation	r value
1	pH	6.18-9.49	8.27	Water soluble fluoride vs pH	-0.39*
2	EC (dSm^{-1})	0.04-1.17	0.12	Water soluble fluoride vs EC	-0.14
3	TDS (ppm)	25.6-1120	74.8	Water soluble fluoride vs TDS	-0.14
4	OC (%)	0.14-1.86	0.71	Water soluble fluoride vs organic carbon	-0.61*
5	Nitrogen (kg ha^{-1})	156.8-436.8	311	Water soluble fluoride vs available nitrogen	0.09
6	P_2O_5 (kg ha^{-1})	11.6-38.3	22.5	Water soluble fluoride vs available P_2O_5	0.41*
7	K_2O (kg ha^{-1})	137-341	270	Water soluble fluoride vs available K_2O	0.28
8	Na ($meq100g^{-1}$)	1.52-7.56	2.19	Water soluble fluoride vs available Na	0.18
9	Ca ($meq100g^{-1}$)	2.24-5.71	4.21	Water soluble fluoride vs available Ca	-0.84**
10	Mg ($meq100g^{-1}$)	0.32-2.34	1.32	Water soluble fluoride vs available Mg	-0.25
12	Fluoride ($meq100g^{-1}$)	0.38-3.32	2.64		

** significant at 0.0l level (2 tailed) * significant at 0.05 level (2 tailed)

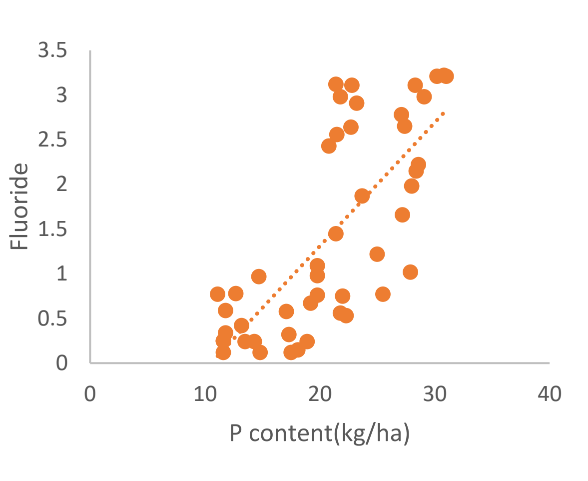

Fig.2 Correlation between available P_2O_5 and F content in soil

The significant positive correlation between fluoride and phosphorus proved the presence of phosphorus favored the solubility of fluoride. Anshumali (2014) explains that fluoride in the soil system follows Langmuir theory of adsorption mobility,which strongly depends on pH and total fluoride concentration. Total fluoride is majorly from the fluoride-bearing minerals such as apatite and fluroapatite, which are also phosphorus-bearing minerals (Okibe *et al*., 2010). Also, phosphorus fertilizer inputs have high amount of fluoride impurities, which can increase the amount of F in soil. Calcium and fluoride show significant negative correlation for the reason that native calcium carbonate present in the soil forms complex with free F^- ion as CaF_2, apatite or similar compounds which is sparingly soluble (Saxena and Ahmed, 2003). These CaF_2^- binds to the clay particles by displacing –OH ions this in turn reducing the bioavailability to the plants (Bhat *et al*., 2015)

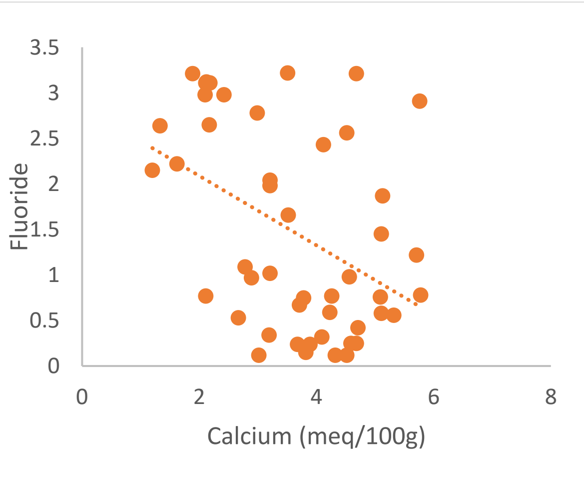

Fig.3. Correlation between exchangeable calcium and Fluoride content.

Conclusion

Mostly obtained results from the tested soil samples of Reddiyarchatram were within the recommended fluoride limits where four villages showed higher concentration of F^-. As for the correlation, soil pH and organic matter played a profound effect on the chemistry of fluoride in the surface soils. The occurrence of fluoride is mainly due to the geogenic process as these areas are high in fluoride-bearing minerals. Also, soil chemical properties majorly influence the dissolution of fluoride from the total to the available fraction. These fluoride concentrations will be readily taken up by plants, thus paving a way into the food chain, so it is necessary to study the plant chemistry and ameliorant potential to reduce fluoride toxicity in these areas

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Competing interest

There is no conflict of interest in publishing the content in this article

Consent for publication

All the authors were agreed to publish the contents in this article

Ethical statement

As no human or animal involved in this study no ethical permits were required

Author Contribution

A.P.: Methodology, formal analysis, investigation, writing-original draft. M.E.: Conceptualization, validation, project administration. N.B.: Resource supervision, writing-review and editing.

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