Fluoride contamination in wetlands of Kuttanad, India: Predisposing edaphic factors

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Abstract
Fluoride contamination has now become an emerging concern in agroecosystems. A diagnostic survey was conducted across the fluoride (F) contaminated wetlands of Kuttanad, India with an aim to examine the influence of edaphic factors on F concentration in soils. The soils (Inceptisols) predominantly sandy had a substantial percentage of clay and the soil characteristics such as bulk density (BD), moisture, temperature, pH, electrical conductivity (EC), cation exchange capacity (CEC) and organic carbon (OC) varied with soils. Similarly, the soil nutrients (NPK) and the oxides of Fe and Al as well as total sesquioxide differed with soils. Principal component analysis (PCA) revealed that the first two components (PC1 and PC2) significantly explained the variability existed in the data while the third component (PC3) did not explain any variation compared to the first two components. PC1, PC2 and PC3 accounted for 52.2%, 12.7% and 11.3% of the variation in the profiles respectively. Out of soil samples, 53% had a similar distribution of soil characteristics and F concentration and are grouped together in PC1 while, the remaining 47% of the samples had a similar distribution of characteristics and are grouped together in PC2. Among the soil characteristics examined, silt content, pH, EC, CEC, OC, N and P had a significant (P<0.001) positive association along PC1 indicating that these factors are contributing to the augmentation of F concentration in the wetlands of Kuttanad.

Keywords: Fluoride contamination, wetland soil, edaphic factors.

Introduction
Fluorine is the most reactive electronegative anion in the halide series (Greenwood and Earnshaw, 1997). Like other halides, it is a monovalent ion which has a strong affinity to combine chemically with other elements to form compounds called fluorides (F). Fluorides are ubiquitous in nature, including water, soil and plants (Singh et al., 2018). Fluoride accounts for about 0.06-0.09% of the Earth's crust (Koritnig, 1951). Major natural sources of F are F-containing mineral rocks like fluorspar, rock phosphate, cryolite, apatite, mica etc. (Kinnunen et al., 2003). Application of F-containing phosphate fertilizers (Loganathan et al., 2001; Borah and Saikia, 2011), fumigants and pesticides (Tsai, 2010; Li et al., 2015), irrigation water (Pettenati et al., 2013; Bustingorri and Lavado, 2014) or by deposition of gaseous and particulate emission from industry (Ozsvath, 2009; Jayaratne et al., 2014; Fuge, 2019) are some of the anthropogenic sources contributing to the elevated concentration of F in soil.

It is well-known that F is beneficial for humans and other animals in small quantities (Underwood, 1977; Adriano, 1986) as it is an essential element required for the integrity of teeth and bones (Jha et al., 2011). However, ingestion of elevated level of F, has a harmful effect, causing dental and skeletal fluorosis in...
humans (Annadurai et al., 2014; Choubisa, 2018a; Kabir et al., 2019; Dharmaratne, 2019) and animals (Choubisa, 2018b; Panchal and Sheikh, 2017; Yuan et al., 2019). In plants, elevated levels of F exposure reduces germination, growth, and productivity (Chakrabarti et al., 2013; Tyagi et al., 2017; Ahmed et al., 2019). Fortunately, the uptake of F by plants from the substrate is typically low because soil-borne F most often occurs in a form unavailable to plants; hence plants will absorb amounts of this element under natural conditions. However, in soils polluted in F, uptake may take up its excessive quantities (Smolek et al., 2011) which affect crop production. Excessive F in the soil is reported to have adverse effect on microbial communities (Ropelewskia et al., 2016; Qiao et al., 2018; Lu et al., 2019) and can inhibit the activity of a variety of microbial enzymes (Telesiński et al., 2008; Mondal et al., 2015).

Kuttanad, the well-known granary is situated in Alappuzha District of Kerala State in south India. It is a unique tropical wetland agroecosystem where below sea level farming practice is being continued for more than a century (Kumar and Devadas, 2016) in 55,000 hectares of rice fields. High F content in the sediments of Kuttanad waters has already been reported (Geetha et al., 2007) which is considered to be originated from dissolution of fluorapatite which is a common mineral in the Tertiary sediments of the area (Varma, 2017). Long residence time, sediment-groundwater interaction and facies changes (Ca-HCO₃ to Na-HCO₃) during groundwater flow regime are pointed out as the major factors responsible for the high F content in the groundwater of this area (Raj and Shaji, 2017). Besides this, Kuttanad being a major producer of rice for the state, to achieve high crop productivity targets, the farmers of this region are compelled to apply F-bearing synthetic fertilizers and plant protection chemicals in large quantities which overburden the ecosystem with F. We presume that the edaphic factors could also have an influence on the F concentration in soil. To test this hypothesis we have conducted a diagnostic survey across the F-contaminated areas of the Kuttanad wetlands with an aim to figure out the influencing edaphic factors which augment/alleviate the F concentration in soils.

Material and Methods

Location and study area

Kuttanad (289.39 km²) located within Alappuzha District in the west coast of Kerala State in India lies between latitude 9⁰ 35’N and longitude 76⁰ 40’E (Figure 1). It has a summit elevation of 2. 2 m bsl. Kuttanad has a tropical humid climate with intermittent dry and wet period. From the middle of May to the middle of November, the wet season prevails with both north-east and south-west monsoons. The rainfall pattern varies with season. The average rainy days are about 120 per year with a mean annual precipitation of 153.28 mm. The mean annual temperature is 29°C and means relative humidity is 79%. January and February are dry and cool months followed by summer from March to May. Kuttanad Below Sea-level Farming System (KBSFS) is unique as it is the only system in India where rice cultivation is practiced below sea level. The major land use structure within the area is flat stretches of rice fields in about 50,000 ha of mostly reclaimed delta swamps.

Sampling scheme

Soil samples were collected from 15 locations of Kuttanad rice fields during the fallow period (January) of 2016. Samples were withdrawn from a depth of 20 cm below the surface layer using a soil auger. Five replicate samples (ca 500 g) taken from each location were collected in polythene bags, labeled and taken to the laboratory and stored at 4°C till analysis. All the soil samples taken were analyzed for soil characteristics and F concentration.

Evaluation of soil characteristics

Texture analysis was done by determining the percentage of sand, silt and clay in the soil sample following the micro-pipette method (Miller and Miller, 1987). The bulk density (BD) was calculated as the ratio between the air-dried soil mass and the soil volume from the fresh soil. Temperature expressed in °C was gauged using a thermometer. Moisture content was determined within 2-3 h of sample collection by drying 10 g soil sample in a hot air oven (105±1°C, 48 h). Gravimetric soil moisture was the difference in soil weights before and after drying (Gardner, 1986). The pH and electrical conductivity (EC) were measured in solution after placing 1 g of soil in 5 ml of deionized water. The pH was determined with a digital pH meter.
(Systronics MK IV, Ahmedabad, India). EC of the soil expressed as dSm⁻¹ was determined using Systronics 304 conductivity meter. Cation exchange capacity (CEC) was measured after saturating the soil with 1N ammonium acetate (NH₄OAc) and displacing it with 1N NaOAc (Chapman, 1965). For the measurement of organic carbon (OC), the method described by Islam and Weil (1998) was followed. Available nitrogen (N) in air-dried soil was determined by alkaline permanganate method (Subbaiah and Asija, 1956), phosphorus (P) by ascorbic acid method (Wantanabe and Olsen, 1965) and exchangeable potassium (K) was extracted in a 1N neutral (pH 7.0) ammonium acetate solution and measured using Elico-CL345 (Elico, India) digital flame photometer (Stanford and English, 1949). Free oxides of iron (Fe) and aluminium (Al) in soil were detected by dithionate extraction method (Mehra and Jackson, 1960). One gram air-dried soil was mixed with 2 g sodium dithionate, 20 g sodium citrate and 50 ml distilled water. After shaking the mixture overnight in a reciprocating shaker at 2000 rpm, the concentration of Fe and Al in the supernatant was measured at 248.3 nm and 309.3 nm respectively using Perkin Elmer-2380 Atomic absorption spectrophotometer. The elemental values were multiplied with the appropriate conversion factor Fe₂O₃ (1.43) and Al₂O₃ (1.89) to obtain their oxide values. The oxide values of Fe and Al were added to determine the total sesquioxides in soil. The sodium 2-(parasulphophenylazo)-1, 8- dihydroxy-3,6- naphthalene disulphonate (SPADNS) method was used to determine the F⁻ content in soil (Baird et al., 2017). Briefly, 0.5 g of air-dried finely ground soil sample was digested with 5 ml aqua regia for 45 min in a microwave digester. The digested sample was allowed to cool and then filtered through Whatman No 4 filter paper. The filtrate was analyzed for F⁻ using UV-Vis spectrophotometer (Systronics, India) at 570 nm.

Statistical analyses
Descriptive statistical methods were used to explain soil characteristics. Principal component analysis (PCA) was applied to summarize correlation among treatment (location/soil characteristics) and variable (soil F⁻) using R software (R Core Team, 2019).

Results and Discussion
Soil characteristics
Wetland soils (Inceptisols) of Kuttanad were predominantly sandy with silt and clay fractions (Table 1). Sand, silt and clay content in the soils ranged from 11.10-65.0, 12.0-53.85 and 6.0-48.50% respectively and the mean percentage were 39.17, 30.37 and 30.44% respectively. In an earlier study Thampatti and Jose (2000) reported that the incidence of same soil fractions in Kuttanad wetlands, nevertheless, they could not find any definite pattern of distribution of sand, silt or clay in these soils.

Table 1. Descriptive statistical measurements of soil characteristics and F⁻ concentration in wetlands of Kuttanad

| Variable                  | Min   | Max   | Mean  | SD   |
|---------------------------|-------|-------|-------|------|
| Sand (%)                  | 11.10 | 65.00 | 39.17 | 15.18|
| Silt (%)                  | 12.00 | 53.85 | 30.37 | 13.22|
| Clay (%)                  | 6.00  | 48.50 | 30.44 | 12.54|
| BD (mg m⁻³)               | 0.50  | 1.80  | 1.14  | 0.19 |
| Moisture (%)              | 4.20  | 13.90 | 8.87  | 2.93 |
| Temperature (°C)          | 22.50 | 25.50 | 24.26 | 0.81 |
| pH (1:5 H₂O)              | 3.40  | 4.80  | 4.23  | 0.32 |
| EC (dS m⁻¹)               | 0.35  | 1.52  | 1.03  | 0.29 |
| CEC (cmol kg⁻¹)           | 30.80 | 60.00 | 44.56 | 8.71 |
| OC (g kg⁻¹)               | 12.00 | 36.80 | 23.40 | 7.63 |
| Available N (kg h⁻¹)      | 275.70| 502.95| 397.68| 80.57|
| Available P (kg h⁻¹)      | 10.10 | 95.00 | 43.60 | 26.58|
| Available K (kg h⁻¹)      | 46.50 | 383.20| 169.66| 112.72|
| Fe₂O₃ (mg kg⁻¹)           | 1378.00| 1431.00| 1405.13| 17.68|
| Al₂O₃ (mg kg⁻¹)           | 222.50| 356.10| 282.43| 35.65|
| Total sesquioxide (mg kg⁻¹)| 1610.50| 1787.00| 1687.56| 50.21|
| Total Fluoride (mg kg⁻¹)  | 5.88  | 37.77 | 25.88 | 7.29 |

Soil compaction is a problem that affects agricultural productivity particularly in clayey soils (Nunes et al., 2015) as it affects root growth and distribution (Taylor and Brar, 1991). The values of BD in the present study varied from 0.50-1.80 mg m⁻³. None of the soils recorded a value beyond the critical limit suggesting that soil compaction is not an alarming issue in Kuttanad agroecosystem. Management of soils through tillage and related practices could be suggested as a reason for low soil compaction in these soils (Unger and Kaspar, 1994).
The soils of Kuttanad encounter frequent changes associated with flooding and associated drying (Suganya and Sivapullaiah, 2015). The soils showed lower moisture content ranging from 4.20-13.90% possibly due to the fast drainage through the spore space (Easton and Bock, 2016).

The results showed that the mean temperature of the soil (0-20 cm depth) ranged from 22.50-25.50°C with an average of 24.26°C which was matching with the atmospheric temperature. This is in agreement with the finding of Beena (2005) that the soil temperature of Kuttanad region is isohyperthermic as the annual soil temperature at a depth of 50 cm is 22°C. It is rather difficult to corroborate with a single reason for the existence of a soil temperature as observed in the present study because of the high heterogeneity and complexity of the relationships (Lehnert, 2014).

All the soils analyzed had an acidic range of pH (3.4-4.8) which is in congruence with the early reports from this region (Beena and Thampatti, 2013). Soil acidity is determined by a number of factors of which the nature of the parent material from which the soil is derived is the principal one (Owolabi et al., 2003). Oxidation of pyrite in soil to sulphuric acid by rainwater during wet season in Kuttanad soils is another reason for the pH to decrease (Mathew et al., 2001).

Saline water intrusion during summer months is an ecological phenomenon contributing to the increase of salinity in Kuttanad soils. The present study reports a value of EC ranging from 0.35-1.52 dSm⁻¹ which remained below the tolerable limit. This could be due to the flushing off/dilution of salts by rain water during monsoon season (Sarkar et al., 2019) or due to the movement of salts to the deeper soil profiles (Thampatti and Jose, 2000).

The CEC ranged from 30.80-60.00 cmol kg⁻¹ in the soil samples. CEC is an important indicator of soil quality in agroecosystems (Khledian et al., 2017) as it represents soil’s ability to hold positively charged ions (Saidi, 2012). The increase of clay fraction in the soil is reported to influence the CEC of soil (Khledian et al., 2017). Soils in general had a high OC (>7.5 g kg⁻¹) ranging from 12-36.80 g kg⁻¹ with a mean value of 23.40 g kg⁻¹ which was reported in other studies (Thafna et al., 2017). The presence of sand layers, differential accumulation of organic matter and sedimentary nature of the parent materials are attributed to be the reason for heterogeneity in OC distribution (Thampatti and Jose, 2000). Incorporation of crop residues into soil after rice cropping in Kuttanad fields could be another possible reason for the increase in OC.

**Soil nutrient status**

Nitrogen is a nutrient being applied in greater quantities in crop production (Pyngrope et al., 2019) which is a common practice in Kuttanad also. Despite this, the soils showed an available N content ranging from 275.70-502.95 kg h⁻¹ which remained below the higher N availability class (>560 kg h⁻¹). This contrasts the finding of Thafna et al. (2017) who observed a high N content (771.91 kg h⁻¹) in Kuttanad soils. This is possibly due to an increased utilization of N by the previous crop (Guo et al., 2017). Losses through the mechanism such as high volatilization, denitrification, chemical and microbial fixation and runoff are suggested as other reasons for the reduction of N in soils (Kumar et al., 2014).

The soils of Kuttanad belonged to the higher (>25 kg h⁻¹) P availability class as it ranged from 10.10-95.0 kg h⁻¹ with a mean P content of 43.60 kg h⁻¹. It is an established fact that the rice crop utilizes only 25-30% of applied P. and the remaining part which is not readily available remain in soil (Gudadhe et al., 2015) which gradually increase as available P over a period of time.

The available K content of the soils ranged from 46.50-383.20 kg h⁻¹ which is in agreement with the earlier finding of Thafna et al. (2017) that the soils in this region had a high content of K. The increase in soil organic matter (Thafna et al., 2017), soil texture and irrigation regime are some of the reasons reported for the increase in K content in soil.

**Elemental oxides in soil**

Oxides of Fe and Al in the soils were in a range between 1378-1430 and 224.10-355 mg kg⁻¹ respectively and its total value (total sesquioxide) ranged between 1612-1785 mg kg⁻¹. In the tropics, the oxides and hydroxides of Fe and Al otherwise known as sesquioxides form soil components of which a small proportion is present in the form of organic complexes (Lekwa and Whiteside, 1986). They are important parameters that influence some soil chemical reaction and properties (Ibía, 2005). Soils of Kuttanad differed in the quantity of sesquioxides they contain indicating that the parent material for the genesis of soils have undergone varied degree of weathering (Shaw and West, 2017). The maintenance of an acidic soil reaction might have triggered the distribution of more Fe and Al (Ebimol et al., 2017) to the soil which in turn reflected on sesquioxides.

**Fluoride concentration in soil**

Soil samples recorded a total F⁻ concentration ranging between 5.88-37.77 mg kg⁻¹ with an average value of 25.88 mg kg⁻¹ which was far above the normal value of 2.5 mg kg⁻¹ reported from Indian soil (Naik et al., 2012). Fluoride concentration in soil samples was in a range of 0.004-0.132 mg kg⁻¹ which was far above the normal value of 0.001 mg kg⁻¹. The presence of sand layers, differential accumulation of organic matter and sedimentary nature of the parent materials are attributed to be the reason for the pH to decrease (Mathew et al., 2001).

Saline water intrusion during summer months is an ecological phenomenon contributing to the increase of salinity in Kuttanad soils. The present study reports a value of EC ranging from 0.35-1.52 dSm⁻¹ which remained below the tolerable limit. This could be due to the flushing off/dilution of salts by rain water during monsoon season (Sarkar et al., 2019) or due to the movement of salts to the deeper soil profiles (Thampatti and Jose, 2000). Incorporation of crop residues into soil after rice cropping in Kuttanad fields could be another possible reason for the increase in OC.
The possible route of F⁻ contamination in Kuttanad soils is mostly through the dissolution of fluorapatite which is a common mineral in the tertiary sediments of this area (Raj and Shaji, 2017). Long-term use of F⁻ containing ground water to irrigate crop (Mondal, 2017), use of synthetic fertilizers, pesticides and other agricultural chemicals (Annadurai et al., 2014) are other possible routes of contamination in Kuttanad soils.

Principal component analysis

Influence of soil characteristics on F⁻ concentration was evaluated by PCA. PC1 accounted for 52.2%, the second component PC2 for 12.7% and the third component PC3 for 11.3% of the variation in the profiles (Table 2). The first two components could explain significant variability existed in the data (~65%) and the third component PC3 did not significantly explain the variance compared to the first two components. It was evident from the biplot (Figure 2) that the soils 1, 3, 5, 6, 10, 12, 13 and 14 had a similar distribution of soil characteristics and F⁻ concentration and are grouped together in PC1 while, the soils 2, 4, 7, 8, 9, 11 and 15 had a similar distribution of soil characteristics and are grouped together in PC2. Among the soil characteristics, soil silt content, pH, EC, CEC, OC, available N and P had a significant (P<0.001) positive association along PC1 whereas, BD, extractable K, Al₂O₃, Fe₂O₃ and total sesquioxide had negative association with PC1. The variables clay content and temperature had a significant positive association along PC2. The soil sand content however exhibited negative association along PC2. Previous studies also corroborate our finding on the factors influencing F⁻ concentration in soil (Skjelkvåle, 1994; Xie et al., 2008). The study therefore warrants the need of a concern of these factors in the mitigation strategies of F⁻ in wetland soils.

Table 2. Loadings on the principal components

| Measurements          | PC1        | PC2        | PC3        |
|-----------------------|------------|------------|------------|
| Eigen value           | 8.88       | 2.16       | 1.93       |
| Percentage variance   | 52.20      | 12.70      | 11.30      |
| Proportion            | 0.52       | 0.13       | 0.11       |
| Sand                  | -0.187     | -0.834a    | -0.375     |
| Silt                  | 0.516a     | 0.291      | 0.495      |
| Clay                  | -0.317     | 0.701a     | -0.067     |
| Moisture              | -0.342a    | 0.057      | -0.591a    |
| Soil Temp             | 0.008      | 0.667a     | -0.135     |
| BD                    | -0.531a    | -0.118     | 0.717a     |
| pH                    | 0.572a     | -0.343     | 0.568      |
| EC                    | 0.904a     | -0.020     | -0.094     |
| CEC                   | 0.894a     | 0.067      | -0.120     |
| OC                    | 0.674a     | 0.482      | -0.017     |
| Av.N                  | 0.850a     | 0.032      | 0.278      |
| Av.P                  | 0.930a     | -0.207     | 0.043      |
| Av.K                  | -0.800a    | -0.040     | 0.367      |
| Fe₂O₃                 | -0.871a    | -0.043     | -0.116     |
| Al₂O₃                 | -0.940a    | 0.129      | 0.099      |
| Total Sesquioxide     | -0.973a    | 0.077      | 0.030      |
| Total Fluoride        | 0.927a     | -0.014     | -0.267     |

*Parameters with significant loadings on the within column principal component

Figure 2. PCA biplot of individuals and variables. BD represent bulk density; OC, organic carbon; CEC, cation exchange capacity; Av. N, available nitrogen; Av. P, available phosphorus; Av. K, available potassium
Conclusion
The study conducted across the wetlands of Kuttanad brought out interesting information on the heterogeneity of soil characteristics and F concentration in soil. Similar was the case with soil nutrients (NPK), oxides of Fe and Al and total sesquioxides in soil. Among the soil characteristics, silt content, pH, EC, CEC, OC, N and P were identified as factors significantly contributing to the augmentation of F concentration in the wetlands of Kuttanad.

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