[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

FLUORIDE CONTAMINATION IN THE IRRIGATION WATER, SOIL, AND CROPS OF THE RANGAREDDY DISTRICT OF TELANGANA STATE, INDIA

M Ranjith,[a,*] S Sridevi,[b] K Jeevanrao,[a] T Ramesh[c]

Hyderabad, India

ABSTRACT: The aim of present study was to assess the fluoride (F) content in the irrigation water, soil, and crop plants in the Amangal mandal of Rangareddy district, Telangana state, India. The F content in the irrigation water ranged from 0.27 to 4.40 ppm with a mean value of 1.75 ppm during the *kharif* (monsoon) season, while in the *rabi* (post monsoon) season, it was between 0.68 to 4.61 with an average of 2.22 ppm. The F concentration in the irrigation water was higher in the *rabi* season compared to the *kharif* season and found to be significantly positively correlated with pH, bicarbonate, sodium, sodium adsorption ratio, and residual sodium carbonate, and negatively with calcium. The available F content in the soils during the *kharif* season ranged from 0.04 to 0.29 ppm with an average of 0.13 ppm and during the post rainy season the range was 0.05 to 0.24 ppm with mean value of 0.14 ppm. The available F in the soil was significantly positively correlated with the soil pH and exchangeable sodium. Among the crop plants and their parts, the F concentration was lowest in the *rabi* green gram seed (0.008 mg/kg) and highest in the *kharif* spinach crop root (0.084 mg/kg). Although the F concentrations were higher than the maximum permissible limit (1.0 or 1.5 ppm) in most of the groundwater samples, the available F was low in all the soil samples collected from the farmers' fields irrigated with the groundwater. The F concentrations in the root, shoot, and edible portions of all the fifteen crops studied were well below the toxic limits.

Keywords: Available fluoride; India; Irrigation water; Kriging; Rangareddy; Telangana; Water quality.

INTRODUCTION

Fluoride (F) is a unique and naturally occurring element, but is not an essential nutrient for plants and is often considered to be a contaminant.[1] In water and soil, F is formed naturally through the chemical degradation of F containing minerals. In India, the F contamination in groundwater is widespread, has been reported from 23 out of 37 states and union territories,[2] and has the potential to cause chronic F toxicosis or fluorosis in humans[3] and domestic animals.[4] In soil, F affects the fertility by preventing the decomposition of organic substances.[5]

The F level in soil is primarily influenced by the parent rock and climate. The F content in the sandy soils in the humid regions is less than its content in the heavy clay soils and in the soils derived from weathered rocks.[6] Clays contain higher levels of F compared with silts.[7] The main natural source of inorganic fluorides in soil is the parent rock and it is present in most soil types with a range of approximately 100–1,000 µg/g, with an average of 625 µg/g being a typical value.[8] There are many different sources of F in soil but the main sources are the weathering of rocks, industrial emissions, and atmospheric deposition.[9-11] High concentrations of F are present in granites, quartz monzonites, syenites, biotite, and granodiorites. F

[a]Department of Soil Science, College of Agriculture, Rajendranagar, Professor Jayashankar Telangana State Agricultural University, Hyderabad-500030, India; [b]Agricultural Polytechnic, Tornala, Professor Jayashankar Telangana State Agricultural University, Siddipet-502114, India; [c]Department of Crop Physiology, College of Agriculture, Rajendranagar, Professor Jayashankar Telangana State Agricultural University, Hyderabad-500030, India; *For correspondence: Dr M Ranjith, Research Associate, ICAR-Central Research Institute for Dryland Agriculture, Santoshnagar, Hyderabad-500059, India; E-mail: ranjithagrico34@gmail.com.

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

containing rocks such as muscovite, pegmatites, amphibolites, and biotite micas supply F to groundwater and soil by different processes such as soil forming and weathering.[12]

The F distribution in the environment is controlled by the physical-chemical parameters of emission, rain intensity, and soil properties. F accumulates at the top soil layer because, it is retained by the iron, aluminum hydroxide, oxide, and silicate compounds in the soil.[11,13] F does not easily migrate from the soil to other media. The F from soil and water enters roots by the process of passive diffusion and is then transported through the xylem into the shoots by the apoplastic and symplastic pathways. The flow is unidirectional.[14] The availability of most soil fluorides to vegetation is limited because they are insoluble. The major dietary sources of F for most people are drinking water, food, and beverages.[15] The F exposure of human beings depends mainly on the water quality and the F concentration in water depends on several contributing factors such as pH, total dissolved solids, alkalinity, and hardness.[16] The F levels of specific foods and vegetables depends upon the nature of the soil and the quality of the irrigation water, and vary from place to place.[17,18]

The majority of the studies on F so far have focused on the F in groundwater and the studies on F in the groundwater-soil-plant continuum are limited. Therefore, the present study was undertaken to investigate the F in water, soil, and crop plants in the Amangal mandal of Rangareddy district of Telangana state of India.

MATERIAL AND METHODS

The study area Amangal, is a peri-urban mandal (a subunit of district, comprising of several villages) close to Hyderabad city, the capital of Telangana state, and is located at 16º50’56” North latitude and 78º31’51” East longitude and falls in the Rangareddy district of Telangana state, India. Groundwater, pumped through tube wells, is the main source of irrigation in the area for growing crops, mainly seasonal vegetable crops. Groundwater, soil, and crop samples were collected from 25 farmers’ fields in the mandal (Figure 1) during both the crop growing seasons, viz., the *kharif* (monsoon) and the *rabi* (post monsoon) of the year 2015–2016.

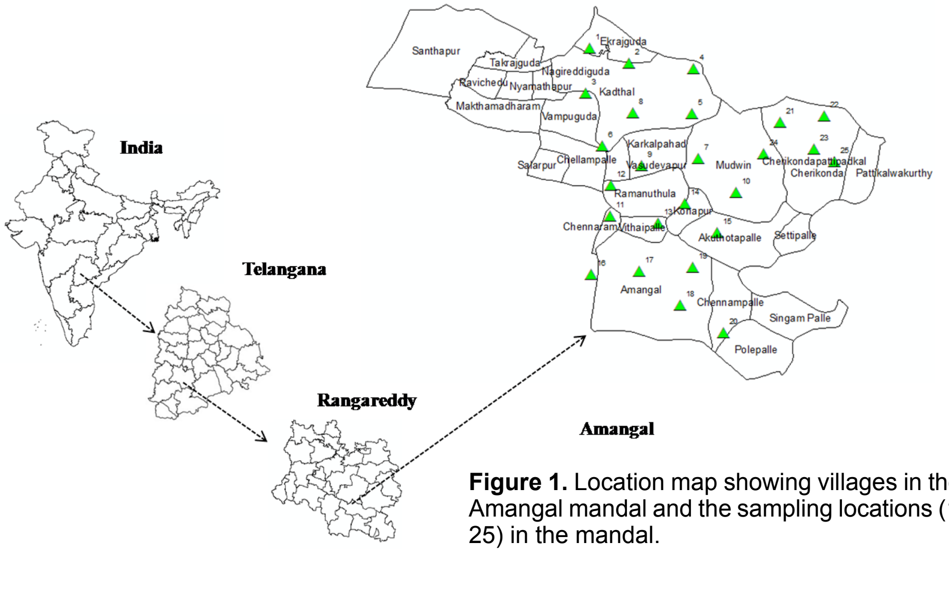

Figure 1. Location map showing villages in the Amangal mandal and the sampling locations (1-25) in the mandal.

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

Collection and analysis of water samples: One liter of the groundwater which was being used to irrigate the crops was collected and transported to the laboratory. The water was collected in pre-cleaned sterilized plastic bottles as per the standard protocol. The water samples were analyzed for F content using a F ion selective electrode.[19] Other water quality parameters, viz., carbonates, bicarbonates, sulphates, chlorides, calcium, magnesium, sodium, and potassium were analyzed using standard procedures.[20]

Collection and analysis of soil samples: Soil samples were collected from 0–15 cm soil depth. Samples were air dried, crushed and then passed through a 2 mm sieve before analysis. The F concentration in the soils was analyzed by a F ion selective electrode with the potentiometric principle.[21] For the available F, the soil was extracted with distilled water and for the total F, the soil was fused with concentrated NaOH. The soil pH, electrical conductivity (EC), organic carbon (OC), cation exchange capacity (CEC), and exchangeable Na, Ca, and Mg, which are likely to affect the F activity in the soil, were determined by adopting standard procedures.[22]

Collection and analysis of crop plant samples: The whole plant samples, including the roots, were collected from crops in the selected farmers' fields, and the root, vegetative, and fruit/grain (edible) parts were separated. The samples were washed with distilled water, dried for 24 to 48 hours at 60ºC, ground to pass through a number 60 sieve, and then stored in clean, dry, and tightly closed plastic bottles. About 1 g of powdered sample was weighed accurately and placed in a 100 mL wide-mouth plastic container. 25 mL of 0.1N perchloric acid was added and the suspension was stirred magnetically for 20 min and then an additional 25 mL of 0.1N perchloric acid was added and the F and reference electrodes were inserted while continuing to stir. Once the reading E_1 stabilized (usually not more than 5 minutes) 0.2 mL of the F standard solution (2,000 mg/L) was added from a micro burette and a stable reading, E_2 was recorded. The F concentration in the sample was determined using following equation. The measurements were carried out at a constant temperature.[23]

$$CF = \frac{Ma}{m\,[\log^{-1}(\Delta E/S) - 1]}$$

Where:

CF	=	Concentration of fluoride
Ma	=	Dry mass of sample in grams
ΔE	=	Potential difference ($E_2 - E_1$)
S	=	Electrode slope or Nernst factor

RESULTS AND DISCUSSION

Fluoride and other water quality parameters in irrigation groundwater: The F content in the irrigation water of the study area ranged from 0.27 to 4.40 ppm with a mean value of 1.75 ppm during the *kharif* season (Table 1).

Table 1. Physico-chemical characteristics of groundwater samples (*Kharif*, 2015)

Sample No.	pH	EC (dS/m)	F mg/L	Cl	CO_3^{-2}	HCO^{-3}	SO_4^{-2}	Ca^{+2}	Mg^{+2}	Na^+	K^+	RSC me/L	SAR
							me/L						
1	7.96	0.58	1.80	1.2	0.0	8.7	0.21	5.6	3.5	0.9	0.05	-0.4	0.4
2	7.81	0.70	1.90	1.5	0.0	9.3	0.30	7.2	3.9	1.2	0.09	-1.8	0.5
3	7.90	0.80	2.00	1.6	0.0	8.3	0.33	6.4	4.0	3.4	0.26	-2.1	1.5
4	7.83	0.81	2.60	2.2	0.0	8.1	0.23	5.7	4.3	3.6	0.22	-1.9	1.6
5	7.80	0.60	2.20	1.6	0.0	8.8	0.18	5.8	3.2	2.0	0.17	-0.2	0.9
6	7.83	0.82	1.50	1.2	0.0	5.8	0.23	4.5	3.4	1.8	0.10	-2.1	0.9
7	7.90	1.10	1.20	0.9	0.0	6.0	0.35	5.8	2.9	0.9	0.18	-2.7	0.4
8	7.72	0.85	1.80	2.2	0.0	5.2	0.44	5.2	2.8	2.0	0.11	-2.8	1.0
9	8.06	0.71	2.40	3.3	0.0	8.8	0.24	5.4	5.3	1.4	0.11	-1.9	0.6
10	7.77	0.90	1.80	1.1	0.0	7.6	0.31	6.1	4.2	3.0	0.06	-2.7	1.3
11	7.41	1.13	0.80	0.8	0.2	6.5	0.08	8.2	3.0	0.9	0.23	-4.5	0.4
12	7.86	0.61	1.20	1.0	0.0	7.1	0.17	4.8	2.5	2.0	0.09	-0.2	1.0
13	7.79	1.01	1.50	2.1	0.0	7.5	0.18	6.4	4.2	1.8	0.18	-3.1	0.8
14	7.87	1.52	1.60	1.8	0.0	9.5	0.27	8.0	3.3	1.6	0.25	-1.8	0.7
15	7.80	0.82	1.70	1.3	0.0	9.1	0.25	8.2	3.6	1.5	0.32	-2.7	0.6
16	7.80	0.90	0.53	2.5	0.0	8.5	0.15	9.2	3.6	1.0	0.21	-4.3	0.4
17	7.71	0.82	0.27	2.1	0.2	6.2	0.19	9.5	4.0	1.7	0.32	-7.1	0.7
18	8.08	1.17	1.90	1.8	0.0	8.2	0.40	5.4	4.5	1.6	0.06	-1.7	0.7
19	7.86	1.24	1.30	1.0	0.0	9.4	0.57	6.7	3.2	1.8	0.12	-0.5	0.8
20	7.81	1.74	1.03	2.5	0.3	9.2	0.18	7.3	5.3	1.9	0.18	-3.1	0.8
21	7.70	0.95	1.28	2.1	0.0	8.8	0.20	6.3	4.5	1.3	0.17	-2.0	0.6
22	8.01	0.90	1.79	2.8	0.0	8.1	0.29	5.8	4.7	1.4	0.16	-2.4	0.6
23	7.65	1.32	1.42	1.4	0.0	5.6	0.38	4.8	3.1	1.1	0.09	-2.3	0.6
24	8.53	1.11	4.39	2.3	0.5	9.5	0.33	6.5	3.0	3.2	0.18	0.5	1.5
25	8.18	1.23	3.80	1.7	0.0	9.1	0.21	6.7	2.6	2.6	0.25	-0.2	1.2
Range	7.41-8.53	0.58-1.74	0.27-4.40	0.8-3.3	0-0.50	5.2-9.5	0.08-0.57	4.5-9.5	2.5-5.3	0.9-3.6	0.05-0.32	-7.10-0.50	0.4-1.6
Mean	7.87	0.97	1.75	1.8	0.05	8.0	0.27	6.5	3.7	1.8	0.17	-2.16	0.8
SD±	0.21	0.29	0.89	0.64	0.12	1.35	0.11	1.33	0.78	0.78	0.08	1.62	0.36

In the *rabi* season, the status ranged from 0.68 to 4.61 ppm with an average of 2.22 ppm (Table 2).

The recommended/permissible concentration of F in irrigation water is 1.0 ppm.[24] In the study area, 88.8% of the irrigation water samples had a F content greater than the permissible limit. A high F content has been reported in 92% of the irrigation water samples in the adjoining area, Kalwakurthy of the Mahaboobnagar district,[25] and F concentrations ranging from 0.99 to 3.94 ppm have been reported in the groundwater samples of the Nalgonda district of Telangana state.[26] Variations were observed in the *kharif* and the *rabi* seasons with respect to the F content (Tables 2 and 3; Figures 2 and 3).

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

Table 2. Physico-chemical characteristics of groundwater samples (*Rabi*, 2015–2016)

Sample No.	pH	EC (dS/m)	F mg/L	Cl	CO_3^{-2}	HCO_3^-	SO_4^{-2} me/L	Ca^{+2}	Mg^{+2}	Na^+	K^+	RSC me/L	SAR
1	8.11	0.78	2.22	1.4	0.00	6.7	0.23	6.2	3.2	2.8	0.12	-2.70	1.3
2	7.90	0.76	2.41	1.8	0.00	7.2	0.32	6.8	3.3	2.1	0.10	-2.90	0.9
3	8.05	0.84	2.98	2.0	0.00	7.5	0.30	6.1	2.5	3.7	0.09	-1.10	1.8
4	7.89	0.88	3.24	3.3	0.00	8.3	0.26	5.3	3.5	2.1	0.06	-0.50	1.0
5	8.00	0.72	3.05	2.1	0.28	9.1	0.18	6.0	3.2	3.9	0.19	0.18	1.8
6	7.85	0.59	1.61	1.5	0.00	7.5	0.25	7.3	4.1	2.3	0.06	-3.90	1.0
7	7.90	0.51	1.56	1.1	0.00	7.1	0.37	7.5	4.0	1.2	0.15	-4.40	0.5
8	7.85	0.86	2.55	2.8	0.00	9.6	0.51	6.5	3.2	2.5	0.10	-0.10	1.1
9	8.02	0.95	2.92	5.1	0.00	9.1	0.55	5.9	3.5	2.6	0.11	-0.30	1.2
10	7.83	0.54	1.96	4.1	0.00	7.1	0.34	7.1	3.8	3.4	0.15	-3.80	1.5
11	7.80	0.75	1.50	2.7	0.00	8.3	0.10	6.8	3.1	1.5	0.09	-1.60	0.7
12	7.88	0.60	2.30	1.4	0.00	9.4	0.18	6.5	3.3	2.6	0.10	-0.40	1.2
13	8.18	1.10	1.75	3.1	0.00	8.7	0.21	7.3	3.8	2.2	0.06	-2.40	0.9
14	7.90	0.85	1.98	2.8	0.00	7.5	0.25	8.1	3.7	2.7	0.24	-4.30	1.1
15	7.98	1.86	2.10	2.5	0.00	9.5	0.21	6.8	2.8	2.3	0.41	-0.10	1.0
16	7.76	0.75	0.91	4.6	0.00	7.1	0.25	6.5	4.5	1.8	0.15	-3.90	0.8
17	7.50	1.25	0.68	4.2	0.34	5.6	0.18	6.1	3.9	1.4	0.19	-4.06	0.6
18	7.80	1.20	2.60	5.8	0.00	9.2	0.45	6.6	4.4	1.9	0.14	-1.80	0.8
19	7.93	1.02	2.20	1.3	0.28	8.8	0.59	6.2	2.9	1.6	0.16	-0.02	0.8
20	8.54	1.79	2.10	7.2	0.00	9.3	0.19	6.3	4.3	2.7	0.22	-1.25	1.2
21	7.30	0.62	1.32	2.9	0.00	6.8	0.21	7.3	4.5	1.1	0.21	-5.00	0.5
22	7.70	1.15	1.52	3.8	0.00	9.5	0.35	6.2	4.4	2.2	0.18	-1.10	1.0
23	7.79	1.61	1.52	1.8	0.00	6.9	0.36	6.8	3.8	1.9	0.09	-3.70	0.8
24	8.56	1.02	4.61	5.4	0.42	9.8	0.30	5.6	4.5	2.7	0.15	0.12	1.2
25	8.23	0.65	3.85	6.2	0.00	10.1	0.20	5.9	4.5	3.8	0.19	-0.30	1.7
Range	7.30-8.56	0.51-1.86	0.68-4.61	1.1-7.2	0-0.42	5.6-10.1	0.10-0.59	5.3-8.1	2.5-4.5	1.1-3.9	0.06 0.41	-5.0-0.018	0.5-1.8
Mean	7.93	0.95	2.22	3.2	0.05	8.2	0.29	6.5	3.7	2.4	0.15	-1.97	1.1
SD±	0.27	0.37	0.89	1.70	0.13	1.23	0.12	0.65	0.60	0.77	0.08	1.74	0.36

The F content was lower in the *kharif* season due to the replenishment of the groundwater by rainfall. The higher F content during the *rabi* season could be due to the over-exploitation of the groundwater resources for agricultural and drinking water purposes and the lowering of the groundwater table. The seasonal distribution of F is dependent on a variety of factors such as the amount of soluble and insoluble F in source rocks, the duration of the contact of water with rocks and the soil temperature, rainfall, and oxidation reduction processes.[2]

Pearson correlation coefficients (r) values between the F content and other chemical constituents of irrigation water: A significant positive correlation between the F and the pH in the irrigation water samples of the study area (0.783, p=0.01, and 0.660, p=0.01, respectively) was observed during the *kharif* and the *rabi* seasons respectively (Table 3). The pH of the irrigation water in the study area was neutral to alkaline, which favours the solubility of fluorine bearing minerals. Weathering and leaching of fluorine in the rock formation under an alkaline environment lead to the enrichment of F in the groundwater.[28,29] Alkaline water activates the processes of dissociation and the dissolution of F from the soils and weathered rocks.[30]

Table 3. Correlation coefficients between fluoride concentration and other chemical properties of irrigation water (EC=electrical conductivity, SAR=sodium adsorption ratio [the ratio of the sodium concentration divided by the square root of half of the sum of the calcium and magnesium concentration], RSC=residual sodium carbonate)

Sample No	Correlation among	*Kharif*	*Rabi*
1	Fluoride vs pH	0.783**	0.660**
2	Fluoride vs EC	– 0.033	– 0.085
3	Fluoride vs chloride	0.202	0.275
4	Fluoride vs sulphate	0.183	0.165
5	Fluoride vs carbonate	0.237	0.264
6	Fluoride vs bicarbonate	0.406*	0.622**
7	Fluoride vs calcium	– 0.329	– 0.563**
8	Fluoride vs magnesium	– 0.131	– 0.088
9	Fluoride vs sodium	0.587**	0.617**
10	Fluoride vs potassium	– 0.050	– 0.073
11	Fluoride vs SAR	0.617**	0.640**
12	Fluoride vs RSC	0.693	0.698

* Significant at p = 0.05; ** Significant at p = 0.01

The correlation between F and the residual sodium carbonate, and between F and the sodium adsorption ratio, was positive and significant. This means that an increase in the activity of carbonate and bicarbonate ions coupled with the sodium content increased the solubility and release of F from the F bearing parent material. Sodium carbonate rich water in weathered rock formations allows the precipitation of calcite from Ca^{2+} and CO_3^{2-} ions and accelerates the dissolution of CaF_2, thereby releasing F into the groundwater.[31] The sodium bicarbonate mineral surfaces associated with the highest F concentration are effective in releasing F from the fluorite-bearing minerals present in the rock.[32] Positive correlations between F and CO_3^{2-}, HCO_3^{-}, Na^{+}, residual sodium carbonate (RSC), and the sodium adsorption ratio (SAR) have also been reported earlier.[33,34] A significant negative correlation was observed with the F and calcium in the irrigation water of the study area during both the *kharif* and the *rabi* seasons. A significant positive relationship of F with pH, sodium, and carbonate, and a negative relation with magnesium and calcium have been reported in the Birbhum district in West Bengal.[35] The highest F concentration was associated with low calcium values and a high sodium content in the groundwater.[29] The F content showed a positive correlation with the bicarbonate and a negative correlation with the calcium concentration.[36] High-fluoride ground waters are mainly associated with a sodium-bicarbonate water type and relatively low calcium and magnesium concentrations. Such water types usually have high pH values (>7).[37,38]

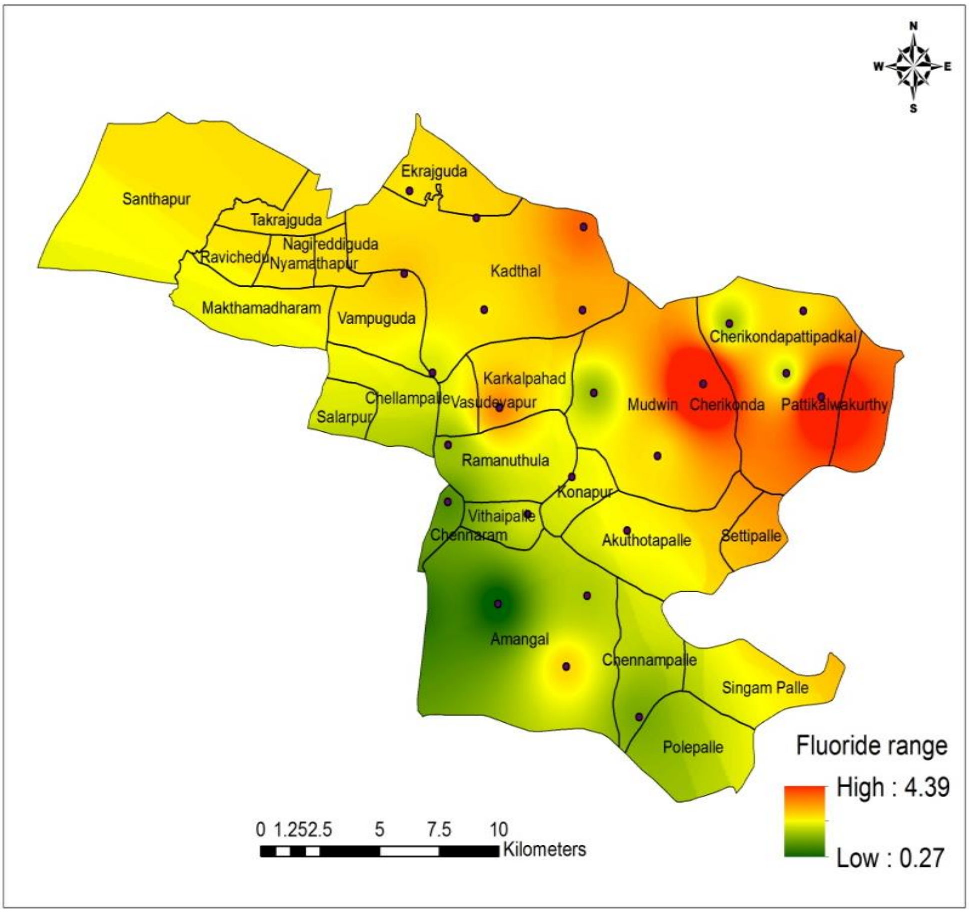

Figure 2. Fluoride distribution in groundwater during the *kharif* season in the Amangal mandal.

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

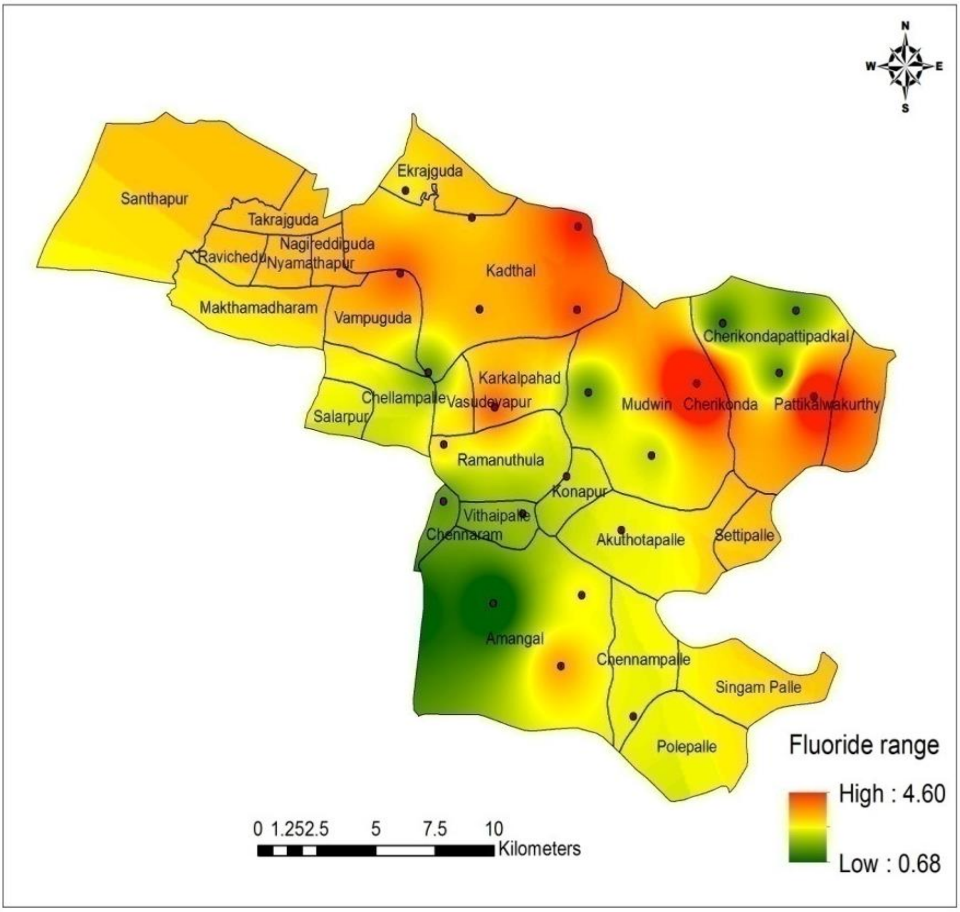

Figure 3. Fluoride distribution in groundwater during the *rabi* season in the Amangal mandal.

Available F and other chemical parameters in soils: The available fluorine status in soils ranged from 0.04 to 0.29 ppm with mean value of 0.13 ppm during the *kharif* season (Table 4). During the *rabi*, the average of the available fluorine in soil was 0.14 ppm and varied from 0.05 to 0.24 ppm (Table 5). The F content in the groundwater water samples was high in the study area but the levels of available F in the soils were low. Mean values of available F in the soil of 0.11 ppm in the *kharif* season and 0.16 ppm in the *rabi* season have been reported in soils of the Mahabubnagar district, Telanagana state.[39] Geological reports of the study area indicate that the parent material is fluoride-rich pink granite with the principal fluorine-bearing minerals fluorite (CaF_2), apatite (Ca_5 $(PO_4)_3$(F, OH, Cl), muscovite {K_2Al_4 [$Si_6Al_2O_{20}$] (OH, F)$_4$}, and biotite {K_2 (Mg,Fe^{2+})$_{6\text{-}4}$ (Fe^{3+}Al, Ti)$_{0\text{-}2}$ ($Si_{6\text{-}5}$ $Al_{2\text{-}3}$ O_{20}) OH, F)$_4$} as accessories and these minerals are a major source for the F in the groundwater and as well as in the soils of the areas concerned, making the problem more serious in terms of endemicity. [40] Most of the fluorine found in soils occurs within minerals or is adsorbed to clays and oxyhydroxides, with only a small percent dissolved in the soil solution.[41]

Table 4. Physico-chemical and chemical characteristics of soil samples (*Kharif*, 2015)

Sample No.	pH	EC (dS/m)	OC (%)	CEC (c mol (p+)/kg)	Exchangeable Na (meq/100g)	Exchangeable Ca (meq/100g)	Exchangeable Mg (meq/100g)	Available F	Total F
								mg/kg	
1	7.37	0.21	0.51	16.2	2.86	5.85	1.84	0.08	226
2	7.52	0.37	0.48	11.2	3.37	4.10	0.75	0.14	289
3	7.19	0.19	0.36	8.6	3.45	3.50	0.61	0.15	201
4	7.64	0.24	0.60	18.5	3.48	6.11	2.36	0.18	226
5	7.56	0.27	0.41	12.0	3.54	4.23	1.12	0.19	205
6	7.31	0.21	0.46	14.1	3.15	4.71	1.62	0.13	314
7	7.53	0.17	0.40	10.6	3.65	3.72	0.94	0.10	295
8	7.35	0.18	0.58	21.9	4.05	6.23	2.56	0.11	310
9	7.80	0.19	0.42	13.7	5.10	4.10	1.36	0.20	306
10	7.42	0.18	0.48	14.0	3.74	4.32	1.65	0.13	384
11	7.36	0.22	0.51	15.2	3.33	5.04	1.50	0.07	276
12	7.51	0.31	0.38	10.8	3.53	4.15	0.74	0.09	253
13	7.82	0.29	0.45	14.1	4.10	4.85	1.89	0.11	295
14	7.30	0.33	0.48	14.9	3.84	5.10	1.70	0.12	328
15	7.42	0.25	0.40	12.6	3.68	4.32	0.69	0.15	295
16	7.21	0.17	0.53	17.2	3.05	3.87	1.43	0.04	261
17	7.45	0.22	0.38	12.6	3.26	3.74	1.11	0.04	214
18	7.33	0.27	0.42	13.4	3.12	4.15	1.64	0.11	300
19	7.69	0.35	0.36	9.70	4.85	4.04	0.63	0.09	274
20	7.54	0.40	0.41	11.8	4.10	3.75	0.92	0.09	245
21	7.42	0.25	0.54	17.6	3.45	5.89	0.95	0.08	254
22	7.46	0.35	0.39	11.3	3.72	4.16	0.84	0.13	326
23	7.07	0.21	0.41	13.7	4.05	5.10	1.07	0.11	312
24	8.05	0.32	0.48	14.1	4.85	5.26	1.54	0.29	326
25	7.84	0.24	0.35	10.8	3.79	4.24	1.02	0.21	281
Range	7.07-8.05	0.17-0.40	0.35-0.60	8.6-21.9	2.86-5.10	3.50-6.23	0.61-2.56	0.04-0.29	201-384
Mean	7.49	0.25	0.45	13.6	3.72	4.58	1.30	0.13	279.8
SD±	0.23	0.07	0.07	3.01	0.56	0.80	0.53	0.06	44.42

Total F: In the *kharif* season, the total F content in the soils varied from 201 to 384 ppm with mean of 279.8 ppm. The total F content ranged from 221 to 415 ppm with average of 281 ppm in the *rabi* season. Studies indicate that the total F concentrations in soils range from 20 to 1,000 µg/g in areas without natural phosphate or F deposits; whereas in organic soils they are usually lower.[42]

Correlation between available F and other properties of soils in study area: The available F in soils was significantly positively correlated with pH (0.634, p=0.01) and exchangeable Na (0.462, p=0.05) (Table 6).These results suggest that the available F content in soil increases with an increase in the soil pH. Similar findings have also been reported earlier.[43] Researchers[44] reported that the exchangeable sodium showed a strong positive correlation with F. The positive correlation between the alkalinity and the F levels might be due to the accumulation of cryolite (Na_3AlF_6) mineral in soil.[45]

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

In the study area, the soil available F content was very low, being less than 1% of the total F, indicating that a major part of the deposited F had transformed itself into insoluble compounds like CaF_2.[46] F is relatively immobile and is not easily leached in soil because most of the F is not readily soluble or exchangeable.[47,48] The total F in soil is considered a poor indicator of soil pollution status due to the great natural variation and variation in sorption strength and sorption capacity in different soils.[49] Calcium fluoride can be formed in soils irrigated with fluorine solutions or when the fluorine adsorption capacity is exceeded and the fluorine and calcium ion activities exceed the ion activity product of calcium fluoride.[50]

Table 5. Physico-chemical and chemical characteristics of soil samples (*Rabi*, 2015–2016)

Sample No.	pH	EC (dS/m)	OC (%)	CEC (c mol (p+)/kg)	Exchangeable Na (meq/100g)	Exchangeable Ca (meq/100g)	Exchangeable Mg (meq/100 g)	Available F	Total F
								mg/kg	
1	7.45	0.32	0.52	18.9	3.39	4.93	1.85	0.16	233
2	7.85	0.24	0.38	10.9	3.85	3.90	0.85	0.19	251
3	7.15	0.13	0.41	9.4	3.12	3.60	0.51	0.15	226
4	7.94	0.25	0.61	19.3	3.75	5.13	1.92	0.19	234
5	7.88	0.27	0.44	12.6	4.04	3.85	0.94	0.21	228
6	7.38	0.28	0.50	15.2	3.72	4.42	1.10	0.14	322
7	7.80	0.22	0.45	12.9	3.95	4.18	0.74	0.10	313
8	8.12	0.31	0.50	18.3	4.16	5.27	1.46	0.15	291
9	7.81	0.44	0.43	14.2	3.69	4.56	1.06	0.22	279
10	8.15	0.33	0.49	15.3	4.28	4.35	1.10	0.13	365
11	7.38	0.27	0.46	13.2	3.15	3.82	0.78	0.09	251
12	7.45	0.28	0.38	9.5	3.53	3.78	0.83	0.16	255
13	7.29	0.47	0.43	15.3	3.87	4.10	0.81	0.12	282
14	7.35	0.39	0.49	17.2	4.48	5.09	1.14	0.13	318
15	7.52	0.41	0.45	10.1	3.91	4.12	0.67	0.16	281
16	7.02	0.28	0.55	15.7	2.78	4.56	0.86	0.05	221
17	7.22	0.33	0.42	13.9	3.19	3.80	0.55	0.08	235
18	7.68	0.36	0.49	15.5	3.64	4.58	1.16	0.16	306
19	7.21	0.41	0.45	10.6	3.35	3.77	0.48	0.12	284
20	7.25	0.49	0.41	12.5	3.72	4.05	0.83	0.14	276
21	7.42	0.31	0.56	18.4	4.12	5.15	2.10	0.09	244
22	7.35	0.47	0.40	13.6	3.87	4.14	1.12	0.10	302
23	7.40	0.24	0.47	14.8	3.50	4.36	1.02	0.11	296
24	8.17	0.51	0.50	15.3	4.29	4.84	1.28	0.24	415
25	8.03	0.48	0.41	12.5	4.08	4.25	0.88	0.21	316
Range	7.02-8.17	0.13-0.51	0.38-0.61	9.40-19.3	2.78-4.48	3.60-5.27	0.48-2.10	0.05-0.24	221-415
Mean	7.57	0.34	0.46	14.2	3.74	4.34	1.04	0.14	281
SD±	0.35	0.10	0.06	2.88	0.41	0.50	0.42	0.05	46.39

Fluoride (mg/kg) in different parts of crop plants: The amount of F in plants depends on their ability to absorb F from the soil, which in turn depends on whether the F is in a form available for uptake or not.[51] The capacity for a plant to absorb inorganic F from the soil will also depend on the species of plant and, to some extent, the ionic species of F present in solution.[52] The fifteen types of crop samples collected during the study across the two seasons, viz., paddy (*Oryza sativa*), sorghum (*Sorghum bicolor*), maize (*Zea mays*), chilli (*Capsicum frutescens*), tomato (*Solanum lycopersicum*), onion (*Allium cepa*), dolichos (*Lablab pupureus*), cucumber (*Cucumis sativus*), brinjal (*Solanum melongena*), palak (*Spinacia oleracea*), capsicum (*Capsicum annuum*), amaranthus (*Amaranthusviridis*), bhendi (*Abelmoschus esculentus*), green gram (*Vigna radiata*), and blackgram (*Vigna mungo*), were found to have a concentration of F ranging from 0.008 (green gram seed, *rabi*) to 0.084 mg/kg (palak root, *kharif*) (Tables 7 and 8). Workers have reported that cereals, pulses, and vegetables grown in fluoride-endemic areas showed a higher content of F when compared with those grown in the areas where the F level was 0.1–0.5 mg/L.[18] Most of the inorganic F in the soil was insoluble and less available to plants. Therefore, the F levels in all the samples were within the normal range.

Table 6. Correlation coefficient (r) between the available fluoride content and the other properties of soils in the study area (EC=electrical conductivity, OC=organic carbon, CEC=cation exchange capacity)

Sample No	Correlation among	r value
1	F *vs* pH	0.634**
2	F *vs* EC	0.242
3	F *vs* OC	– 0.063
4	F *vs* CEC	– 0.095
5	F *vs* Exchangeable Na	0.462*
6	F *vs* Exchangeable Ca	0.072
7	F *vs* Exchangeable Mg	0.048

* Significant at p = 0.05; ** Significant at p = 0.01

Among the plant parts, the accumulation of F was maximum in the roots compared to the stover/straw and the economic part of the crop due to relatively low mobility of F in the root system (Tables 7 and 8). However, none of the crops were found to have a concentration of F higher than the daily toxic dose level of 0.30 mg/kg and the allowed level of 4.00 mg/kg recommended by the WHO, EPA and FAO.[51] (Tables 7 and 8).

It has also been reported that the concentration of F in vegetables ranged between 0.013 and 0.065 mg/kg, with the mean vegetable F content of 0.033, 0.030, 0.041, and 0.046 mg/kg for cabbage, garden egg, onion, and tomato, respectively.[53] According to a previous study, the F content of paddy-I (Ambai-16) was 0.74–2.40 mg kg^{-1} during the southwest monsoon and for paddy-II (TPS-3) it was 0.65–2.40 mg/kg during the northeast monsoon while in black gram it was 0.228–0.780 mg/kg during summer.[54]

Mapping of the *F content with special reference to the groundwater and soil F for both seasons:* Maps (Figures 2 to 5) of the F content of the groundwater and soil during both the seasons were prepared for the study area, using the kriging technique,

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

a geostatistical interpolation technique that considers both the distance and degree of variation between the known data points when estimating values in unknown areas.[55]

Table 7. Fluoride content of crop plant part samples (*Kharif*, 2015)

Sample No.	Crop	(F mg/kg)		
		Edible portion	Shoot	Root
1	Sorghum	0.013	0.022	0.035
2	Sorghum	0.013	0.020	0.029
3	Sorghum	0.018	0.026	0.038
4	Sorghum	0.015	0.021	0.039
5	Tomato	0.026	0.034	0.048
6	Tomato	0.028	0.035	0.055
7	Tomato	0.019	0.024	0.030
8	Tomato	0.017	0.025	0.031
9	Tomato	0.022	0.032	0.041
10	Tomato	0.025	0.045	0.048
11	Chilli	0.025	0.032	0.043
12	Chilli	0.028	0.036	0.047
13	Onion	0.021	0.034	0.049
14	Dolichos bean	0.013	0.018	0.025
15	Cucumber	0.026	0.035	0.046
16	Brinjal	0.022	0.041	0.051
17	Brinjal	0.022	0.029	0.046
18	Brinjal	0.025	0.040	0.051
19	Palak	0.044	0.000	0.071
20	Palak	0.047	0.000	0.084
21	Capsicum	0.021	0.035	0.045
22	Amaranthus	0.038	0.044	0.054
23	No crop	–	–	–
24	No crop	–	–	–
25	No crop	––	–	–

Table 8. Fluoride content of the crop plant parts samples (*Rabi* 2015-16).

Sample No.	Crop	(F mg/kg)		
		Edible	Shoot	Root
1	Sorghum	0.021	0.031	0.043
2	Sorghum	0.019	0.025	0.041
3	Sorghum	0.016	0.027	0.039
4	Sorghum	0.013	0.024	0.038
5	Sorghum	0.015	0.023	0.035
6	Sorghum	0.018	0.027	0.040
7	Paddy	0.017	0.028	0.037
8	Paddy	0.016	0.027	0.039
9	Maize	0.012	0.026	0.037
10	Greengarm	0.012	0.021	0.03
11	Greengarm	0.008	0.017	0.026
12	Greeengram	0.011	0.015	0.023
13	Blackgram	0.010	0.017	0.010
14	Tomato	0.024	0.037	0.058
15	Tomato	0.023	0.041	0.053
16	Tomato	0.024	0.036	0.055
17	Tomato	0.019	0.027	0.044
18	Tomato	0.024	0.032	0.045
19	Bhendi	0.030	0.041	0.055
20	Bhendi	0.018	0.029	0.040
21	Bhendi	0.024	0.035	0.043
22	Brinjal	0.025	0.036	0.051
23	Brinjal	0.021	0.028	0.04
24	Brinjal	0.022	0.031	0.047
25	Palak	0.043	–	0.080

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

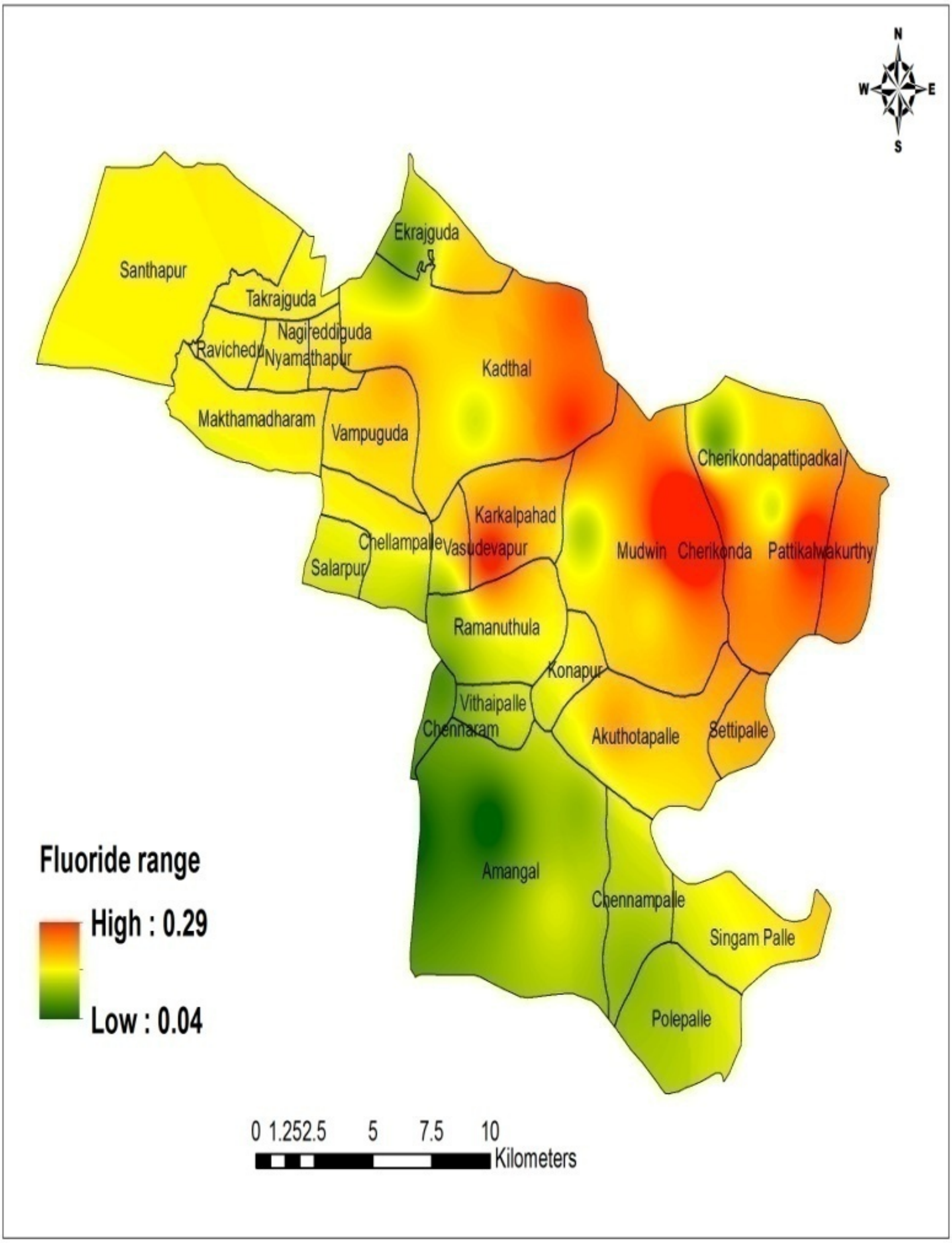

Figure 4. Available fluoride distribution in the soil during the *kharif* season in the Amangal mandal.

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

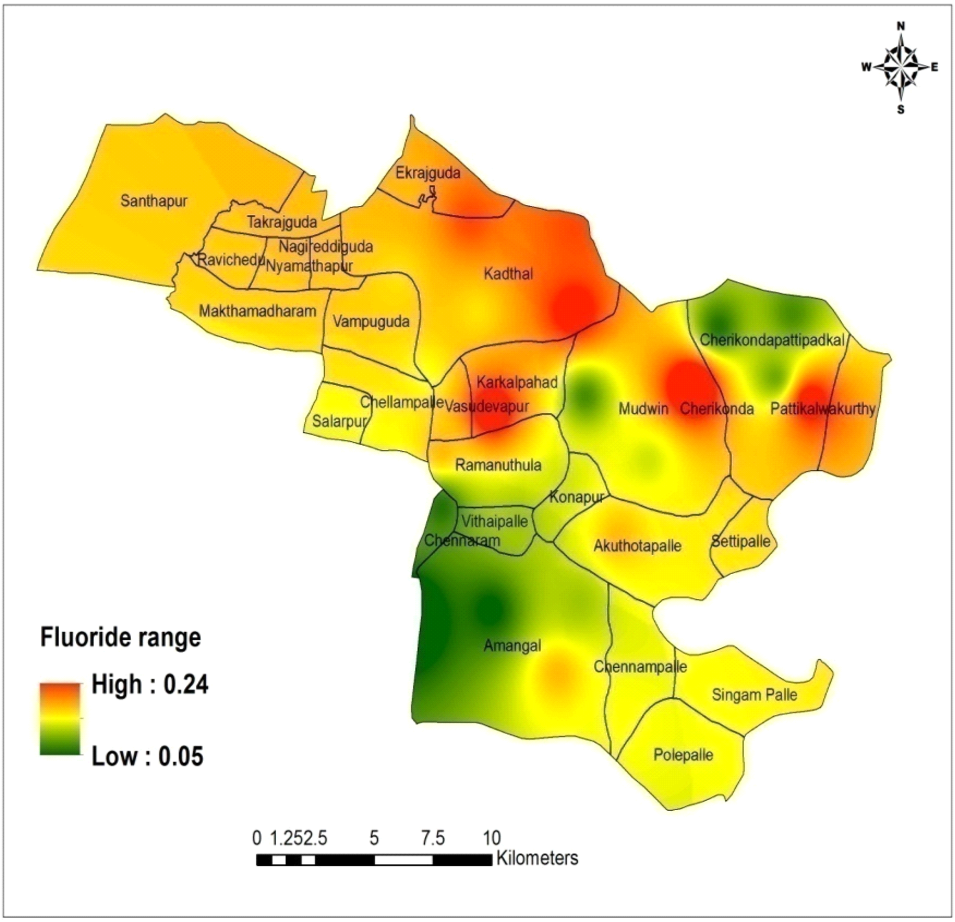

Figure 5. Available fluoride distribution in the soil during the *rabi* season in the Amangal mandal.

CONCLUSIONS

Investigation of the F in irrigation groundwater, soil, and plant samples from farmers' fields in Amangal mandal of Rangareddy district of Telangana state, India, showed that groundwater samples from most of the wells had F concentrations higher than the recommended limit of 1.0 or 1.5 ppm. F concentrations were higher in the post monsoon season compared to the monsoon season. Irrigation with groundwater rich in F did not lead to a build up of the plant available F in soil or the accumulation in the plant parts of crops grown on the soils and irrigated with the F rich groundwater. The threat of high F related illness[56] in the area arises from the direct drinking of groundwater and not from consuming the crops irrigated with the groundwater.

REFERENCES

[1] Mackowiak CL, Grossl PR, Bugbee BG. Plant and environment interactions: Biogeochemistry of fluoride in a plant-solution system. J Environ Qual 2003;32:2230-37.

[2] Choubisa SL. A brief and critical review on hydrofluorosis in diverse species of domestic animals in India. Environ Geochem Health 2018;40(1):99-114. doi 10/1007/s 10653-017-9913-x.

[3] Choubisa SL. Endemic fluorosis in southern Rajasthan (India). Fluoride 2001;34(1):61-70.

[4] Choubisa SL. Fluorotoxicosis in diverse species of domestic animals inhabiting areas with high fluoride in drinking waters of Rajasthan, India. Proc Natl Acad Sci India Sect B Biol Sci 2013;83(3):317-21.

[5] Zhu L, Zhang HH, Xia B, Xu DR. Total fluoride in Guangdong soil profiles, China: Spatial distribution and vertical variation. Environ Int 2007;33:302-8.

[6] Fuge R, Andrews, MJ. Fluorine in the UK Environment. Environ Geochem Health 1988;10;96-104.

[7] Madhavan N, Subramanian V. Fluoride in fractionated soil samples of Ajmer district, Rajasthan. J Environ Monit 2002;4:821-2.

[8] Shahab S, Mustafa G, Khan I, Zahid M, Yasinzai M, Ameer N, et al. Effects of fluoride ion toxicity on animals, plants and soil health: review. Fluoride 2017;50(4):393-408.

[9] Xiaojing L, Binbin W, Baoshan Z. Geochemical process of fluorine in soil. Chin J Geochem 2014; 33:277-9.

[10] Choubisa SL, Choubisa D. Status of industrial fluoride pollution and its diverse adverse health effects in man and domestic animals in India. Environ Sci Pollut Res 2016; 23(8):7244-54. DOI: 10.1007/s11356-016-6319-8.

[11] Choubisa SL. Fluoride distribution in drinking groundwater in Rajasthan, India. Curr Sci, 2018;114(9):1851-7. doi: 10.18520/cs/v114/i09/1851-1857.

[12] Bhat N, Jain S, Asawa K, Tak M, Shinde K, Singh A, et al. Assessment of fluoride concentration of soil and vegetables in vicinity of zinc smelter, Debari, Udaipur, Rajasthan. J Clin Diagn Res 2015;9(10):63-6.

[13] Luther SM, Poulsen MJ, Dudas MJ, Rutherford PM. Fluoride sorption and mineral stability in Alberta soil interacting with phosphogypsum leachate. Can J Soil Sci 1996;76:83-91.

[14] Brahmbhatt NH, Patel RV. Effect of sodium fluoride and magnesium chloride and its interaction on seedling growth of *Medicago sativa*, Anand, Gujarat. Asian J Agric Res 2013; 3(3):80-4.

[15] Liu H, Gao Y, Sun L, Li M, Li B, Sun D. Assessment of relationship on excess fluoride intake from drinking water and carotid atherosclerosis development in adults in fluoride endemic areas. Int J Hyg Environ Health 2014;217:413-20.

[16] Viswanathan G, Jaswanth A, Gopalakrishnan S, Siva Ilango S, Aditya G. Determining the optimal fluoride concentration in drinking water for fluoride endemic regions in South India. Sci Total Environ 2009;407(20):5298-307.

[17] Arora G, Sumit Bhateja S. Estimating the fluoride concentration in soil and crops grown over it in and around Mathura, Uttar Pradesh, India. A J Ethno 2014;1:36-41.

[18] Saxena KL, Sewak R. Fluoride consumption in endemic villages of India and its remedial measures. Int J Eng Sci Invent 2015;4(1):58-73.

[19] Wedepohl KH. Handbook of geochemistry (Geochemistry Vol 1). Berlin: Springer;1969.

[20] APHA (American Public Health Association). Standard methods for the examination of water and waste water, Washington DC, United States of America;1985.

[21] Brewer RF. Fluorine. Black CA, Evans DD, White JL, Ensminger LE, Clark FE. Methods of soil analysis. American Society of Agronomy 1965;2:1135-48.

[22] Jackson ML. Soil chemical analysis. New Delhi: Prentice Hall of India Private Limited,; 1973.

[23] Villa AE. Rapid method for determining fluoride in vegetation using an ion-selective electrode. Analyst 1979;104:545-6.

[24] National Academy of Sciences. Effects of fluoride in plants and humans. A report prepared by the committee on plant and human nutrition. Washington, DC; National Academy of Sciences; 1972.

[25] Ranjith M, Jeevanrao K, Sridevi S, Ramesh T, Bhave MHV. Groundwater quality and fluoride contamination in Kalwakurthy mandal of Mahabubnagar district, Telangana State, India. Int J Pure App Biosci 2017;5(4);1397-05.

[26] Vijayalakshmi D, Jeevanrao K, Ramprakash T, Reddy APK. Assessment of fluoride in ground water for drinking and agricultural purposes in Ramannapet mandal of Nalgonda district, Telangana State, India. J Pharm Chem Biol Sci 2016;4(2):169-75.

[27] Mahapatra MK, Mishra A, Das BP. Fluorosis first reported in Naupada district of Orissa, India. Ecol Environ. Conserv 2005;11(2):277-80.

[28] Reddy BM, Khan JA, Sunitha V, Reddy MR. Fluoride contamination in groundwater from parts of Anantapur district, Andhra Pradesh. Gond Geol Mag 2011;26(2):1-9.

[29] Janardhanaraju N, Dey S, Das K. Fluoride contamination in ground waters of Sonbhadra district, Uttar Pradesh, India. Curr Sci 2009;96(7):979-85.

[30] Gupta SK, Deshpande RD, Agarwal M, Raval BR. Origin of high fluoride in groundwater in the North Gujarat-Cambay region, India. Hydrogeol J 2005; 13:596-605.

[31] Saxena VK, Ahmed S. Inferring the chemical parameters for the dissolution of fluoride in groundwater. Environ Geol 2003; 43:731-6.

[32] Janardhana Raju N. Prevalence of fluorosis in the fluoride enriched groundwater in semi-arid parts of eastern India: Geochemistry and health implications. Quat Int 2016;443(B):265-78.

[33] Vijayalakshmi D, Jeevanrao K, Ramprakash T, Reddy APK. Geochemistry of groundwater with special emphasis on fluoride and its seasonal variations in parts of Nalgonda district, Telangana state, India. Int J Curr Microbiol Appl Sci 2017;6(5):1042-50.

[34] Varadarajan N, Purandara BK. Fluoride contamination in ground water of Malaprabha sub basin. J Environ Sci Eng Technol 2008;50(2):121-6.

[35] Patra PK, Mandal B, Chakraborty S. Hydrogeochemistry of fluoride rich groundwater in Birbhum district of West Bengal, India. The Ecoscan 2010;4(2&3):209-11.

[36] Sreedevi PD, Ahmed S, Made B, Ledoux E, Gandolfi JM. Association of hydrogeological factors in temporal variations of fluoride concentration in a crystalline aquifer in India. Environ Geol 2006;50(1):1-11.

[37] Brunt R, Vasak L, Griffioen J.Fluoride in groundwater: probability of occurrence of excessive concentration on global scale. Report nr SP 2004-2. Utrecht: International Groundwater Resources Assessment Centre (igrac); 2004. Available from: https://www.un-igrac.org/sites/default/files/resources/files/Rapport%202%20-%20Fluoride%20online.pdf

[38] Ramachandra Moorthy T, Paulraj A, Sivaraj C, Kavitha B, Bhuraneswari P. Fluoride ion concentration in the ground water of Tiruchirappalli district, Tamil Nadu. J Ecotoxicol Environ Monit 2004;14(2):147-50.

[Now published in full after the initial publication as an Epub ahead of print on Mar 14, 2021 at www.fluorideresearch.online/epub/files/144.pdf]

[39] Ranjith M, Sridevi S, Jeevanrao K, Tamesh T, Bhave MHV. Fluoride content of agricultural soils and it's relation with physicochemical properties in Kalwakurthy mandal, Mahabubnagar district, Telangana State. Int J Pure Biosci 2017;1588-98.

[40] Venkatayogi S. Geochemistry of fluoride bearing groundwater in parts of Telangana state, India. J Water Res Hyd Eng 2015;4(4):380-7.

[41] Anshumali BK. Fluoride in agricultural soil: A review on its sources and toxicity to plants. Global sustainability transitions: Impacts and innovations 2014;3:29-37.

[42] Hong BD, Joo RN, Lee KS, Lee DS, Rhie J, Min SW, et al. Fluoride in soil and plant. Korean J. Agric. Sci 2016;43:522-36.

[43] Abugri DA, Pelig Ba KB. Assessment of fluoride content in tropical surface soils used for crop cultivation. Afr J Environ Sci Technol 2011;5(9):653-60.

[44] Anbuvel D, Kumaresan S, Jothibai Margret R. Fluoride analysis of soil in cultivated areas of Thovalai channel in Kanyakumari district, Tamilnadu, India: Correlation with physico-chemical parameters. Int J Basic Appl Chem Sci 2014;4(4):20-9.

[45] Shekhar S, Mohiddin SK, Singh PN. Variation in concentration of fluoride in the groundwater of south-west district, NCT Delhi - A case study. In: Ramanathan AL, Bhattacharya P, Keshari A, Bundschuh K, Chandrashekharan D, Singh SK, editors. Assessment of groundwater resources and management. New Delhi, IK International; 2006, pp. 370-6.

[46] Blagojevic S, Jakovljevic M, Radulovic M. Content of fluorine in soils in the vicinity of aluminium in Podgorica. J Agric Sci 2002;47(1):1-8.

[47] Gilpin L, Johnson AH. Fluorine in agriculture in soils of Southeastern Pennsylvania. Soil Sci Soc Am J 1980;44:255-8.

[48] Greenfacts. Fluoride. 2002. Available from: http://www.greenfacts.org/en/fluoride/.

[49] Arnesen AKM, Abrahamsen G, Sandvik G, Krogstad T. Aluminium smelters and fluoride pollution of soil and soil solution in Norway. Sci Total Environ 1995;163:39-53.

[50] Tracy PW, Robbins CW, Lewis GC. Fluoride precipitation in a calcareous soil irrigated with high fluoride water. Soil Sci Soc Am J 1984;48: 1013-6.

[51] Okibe FG, Ekanem EJ, Paul ED, Shallangwa GA, Ekwumemgbo, PA, Sallau MS, et al. Fluoride content of soil and vegetables from irrigation farms on the bank of river Galma, Zaria, Nigeria. Aust J Basic Appl Sci 2010;4 (5):779-84.

[52] Stevens DP, McLaughlin MJ, Alston AM. Phytotoxicity of the aluminium-fluoride complexes and their uptake from solution culture by *Avena sativa* and *Lycopersicon esculentum*. Plant Soil 1997;192: 81-3.

[53] Paul ED, Gimba CE, Kagbu JA, Ndukwe GI, Okibe FG. Spectrometric deterimination of fluoride in water, soil and vegetables from the precinct of river Basawa, Zaria, Nigeria. J Basic Appl Chem 2011;1 (6): 33-8.

[54] Anbuvel D, Kumaresan S, Margret RJ. Fluoride accumulation on paddy (*Oryza sativa*) and black gram (*Phaseolus mungo linn*.) in cultivated areas of Kanyakumari district, Tamilnadu, India. Indian J Fundam Appl Life Sci 2015;5(1):280-5.

[55] Krige DG. A statistical approach to some basic mine valuation problems on the Witwatersrand. J South Afr Inst Min Metall 1951; 52:119-39.

[56] Choubisa SL. A brief and critical review of endemic hydrofluorosis in Rajasthan, India. Fluoride 2018;51(1):13-33.