

Fluoride in Groundwater, Its Variation with Season and Relationship with Other Water Quality Parameters in Rangareddy District of Telangana, India

ABSTRACT

Fluorine, which occurs naturally as fluoride in the earth's crust in small amounts, is essential to humans and animals and is known to stimulate plant growth when present in small concentrations. However, higher concentrations of fluoride in drinking water cause dental and skeletal fluorosis in animals and humans and when present in high concentrations in groundwater used for irrigation, it accumulates in the plants and the soil and causes undesirable effects. A study was carried out during *kharif* and *rabi* seasons of 2015-16 in Talakondapalle mandal of Rangareddy district, Telangana state, India, to measure and map the distribution of fluoride in groundwater in bore wells used for irrigation, to observe seasonal variation in fluoride content and to examine the relationship of fluoride with other water quality parameters. Fluoride in groundwater ranged between 0.72 to 4.50 ppm with a mean of 2.84 ppm and standard deviation of 1.30 ppm in *kharif* season and from 1.32 to 4.92 ppm with a mean of 3.29 ppm and standard deviation of 0.24 ppm in *rabi* season. Except for two wells in *kharif*, fluoride concentration was higher than the permissible limit of 1 ppm. Groundwater fluoride map of the mandal was generated using kriging technique. Fluoride concentration was higher in all the wells in *rabi* over *kharif* with mean fluoride concentration being 15.8% higher in *rabi* season. Fluoride concentration was significantly positively correlated with pH, HCO_3^- , Na^+ , SAR and RSC of ground water and significantly negatively correlated with Ca^{+2} .

Key words: Fluoride, Groundwater, Water quality and Rangareddy, Telangana

INTRODUCTION

Fluorine is a very reactive element that occurs naturally as fluoride in the earth's crust in small amounts. The primary source of fluoride in soil and groundwater is weathering and dissolution of fluoride containing minerals like fluorspar, cryolite, fluorapatite, fluorite, fluorophlogopite, etc. [1,2]. Anthropogenic activities such as brick production, production of phosphate fertilizers, cement, and other industrial processes discharge fluoride into the environment. Although fluoride in small amounts is essential to humans and animals and is known to stimulate plant growth, its presence in higher concentrations in drinking water causes dental and skeletal fluorosis in animals and humans and when present in high concentrations in groundwater, it leads to decreased plant growth and productivity and accumulation in plant tissue. In many parts of the world, elevated levels of F contaminated groundwater used for irrigation purposes have been reported to cause considerable adverse effects on crops [3,4]. Physiological processes known to be markedly affected by high concentration of fluoride include chlorosis [5], leaf tip burn and necrosis [6] and decreased plant growth [7]. While Lioné *et al.* (1948) suggested 10 mg/litre as the safe limit of fluoride in irrigation water for all types of plants [8], the Food and Agricultural Organisation [9] prescribed limit is 1.0 mg/litre.

Groundwater fluoride concentrations tend to be higher in arid regions, where the groundwater flow is low and the reaction times with rocks are long. The amount of fluoride occurring naturally in groundwater depends **mainly on** climate, composition of the host rock and hydrogeology [4]. In India, the excessive presence of fluorides in groundwater is reported in nearly 177 districts covering 20 states and Telangana is one of them [10]. The present study was undertaken to investigate the fluoride content of groundwater used for irrigation in Talakondapalle **mandal** (revenue division consisting of several villages, also called **block, tehsil, taluk**, etc. elsewhere in India), Rangareddy district, Telangana State, India, to examine seasonal variations in fluoride content and to examine correlations between the concentration of fluoride and other water quality parameters.

MATERIAL AND METHODS

Talakondapalle **mandal** is located in southern part of Rangareddy district with headquarters at Talakondapalle village, located at 16.88.74 North latitude and 78.41.69 East longitude, 72 km from Hyderabad, the capital of Telangana State. The climate of the study area is generally hotsemi-arid with mean annual rainfall is 616.1 mm. The predominant crops grown in the area are paddy, maize, sorghum and vegetables. The crops are irrigated with groundwater from **bore wells**.

Groundwater samples were collected from 25 **borewells** located in 10 villages of Talakondapalle **mandal** (Fig. 1) during both *kharif* (monsoon) and *rabi* (post monsoon) seasons of 2015-16. Samples were collected in 1 litre plastic bottles previously thoroughly cleaned with distilled water and subsequently rinsed with sampled groundwater before filling. Samples were collected after 10 minutes of pumping from the **borewell**. The samples were transferred to the laboratory at Professor Jayashankar Telangana State Agricultural University, Hyderabad. The fluoride concentration in groundwater was determined potentiometrically, using fluoride ion selective electrode. Three ml of total ionic strength adjusting buffer grade III (TISAB III) was added to 30 ml of sample groundwater and fluoride concentration was determined [11]. Other water quality parameters were determined using standard procedures [12]. The pH and EC of water samples were determined using pH meter and EC meter respectively. Chloride (Cl^-) was determined by standard AgNO_3 titration. Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) were determined by titration with 0.1 H_2SO_4 . Sulphate (SO_4^{2-}) was determined using UV-visible spectrophotometer. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined titrimetrically using standard EDTA method. Sodium (Na^+) and potassium (K^+) were measured by flame photometry. Sampling, preservation and analysis of water samples were carried out following the method recommended by American Public Health Association (APHA). Residual sodium carbonate (RSC) and sodium adsorption ratio (SAR) were computed as follows:

$$\text{RSC} = (\text{CO}_3^- + \text{HCO}_3^-) - (\text{Ca}^{++} + \text{Mg}^{++})$$

$$\text{SAR} = \text{Na}^+ / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}$$

RESULTS AND DISCUSSION

Fluoride content of irrigation water samples varied from 0.72 to 4.49 ppm with a mean of 2.84 ppm and standard deviation of 1.30 ppm in the *kharif* season (Table 1). The lowest fluoride content was recorded in well no. 6 located in Talakondapalle village (0.72 ppm) and the highest, in well no. 24 in Venkatrapeta village (4.49 ppm). In the *rabi* season, the average fluoride content of irrigation water samples was 3.29 ppm with a range of 1.32 to 4.91 ppm and a standard deviation of 0.24 ppm (Table 2). Well no. 13 in Rampur village (4.91 ppm) exhibited the highest fluoride content and well no. 6 in Talakondapalle village, the lowest (1.32 ppm). In the study area, groundwater in only 2 wells (wells 6 and 7) had fluoride content lower than the permissible limit of 1 ppm (mg/litre) prescribed by Food and Agriculture Organization (FAO) in *kharif*, while in *rabi* all the samples had fluoride higher than the permissible limit. Sundaraiah *et al.* have earlier reported that 35% of ground water samples in Kalwakurthy area of Mahabubnagar district had high fluoride content [13] and Ranjith *et al.* reported a range of fluoride content from 0.79 to 4.20 ppm in ground water samples in Kalwakurthy mandal of Mahabubnagar district, Telangana [14].

Maps of groundwater fluoride concentration (Fig. 2 and 3) were prepared for both the seasons using kriging, a geostatistical interpolation technique that considers both the distance and degree of variation between known data points to estimate values for unknown areas [15]. Data of other water quality parameters are presented in tables 1 and 2. The groundwater samples were slightly to moderately alkaline. Salinity was within permissible limits for irrigation. Concentrations of anions (chloride, carbonate, bicarbonate and sulphate) and cations (calcium, magnesium, sodium and potassium) were within permissible limits prescribed for irrigation water. RSC and SAR were also within permissible limits. The only major problem with the irrigation water was excess fluoride.

Seasonal variation in fluoride concentration

Seasonal variation in fluoride content was observed in the bore wells in the study area (Tables 1 and 2; Fig. 1 and 2). Fluoride content in irrigation water of all the borewells in all the villages was lower in *kharif* compared to *rabi*. Mean fluoride concentration of the sample wells in *rabi* was 15.8% higher over *kharif*. The widest seasonal variation was observed in well no. 7 in Talakondapalle village, where fluoride concentration in *rabi* was 69.7% higher over *kharif*. The lower fluoride concentration in all the wells in *kharif* may be attributed to dilution of fluoride due to replenishment of the groundwater by rainfall during the *kharif* season. Seasonal distribution of fluoride is dependent on a variety of factors such as amount of soluble and insoluble F in source rocks, the duration of contact of water with rocks and soil temperature, rainfall and oxidation-reduction process [16].

Relationships between fluoride and other water quality parameters

Pearson correlation coefficients (r) were estimated between the F content and other water quality parameters and are presented in Table 3. Significant positive correlations of fluoride content were observed with pH, bicarbonate, sodium, SAR and RSC in both the seasons and calcium in *rabi* season. A significant positive correlation ($r = 0.543$ in *kharif* and 0.482 in *rabi*) was observed between fluoride concentration and pH of groundwater samples. The pH of irrigation water in the study area was neutral to alkaline, which favours the solubility of fluorine bearing

minerals. Reddy *et al.* and Janardhanaraju *et al.* have also indicated that weathering and leaching of fluorine in rock formations under alkaline environment leads to the enrichment of fluoride in the groundwater [17,18]. Alkaline water activates the processes of dissociation and dissolution of F from weathered rocks [19].

Fluoride concentration was significantly positively correlated with sodium, carbonates, RSC and SAR. This suggests that an increase activity of carbonate and bicarbonate ions coupled with the sodium content increased the solubility and release of F from the F bearing parent material. Water rich in sodium and carbonates in weathered rock formations allows precipitation of calcite from Ca^{2+} and CO_3^{2-} ions and accelerates the dissolution of CaF_2 , thereby releasing fluoride into the groundwater [20] and also found good correlation of fluoride content with carbonates, bicarbonates, sodium, RSC and SAR [14].

A significant negative correlation was observed between F and calcium in groundwater of the study area during *rabi* season. Janardhanaraju *et al.* reported that high fluoride concentration was correlated with low calcium values and high sodium content in the groundwater [18]. High-fluoride ground waters are mainly associated with a sodium-bicarbonate water type and relatively low calcium and magnesium concentrations and such water types usually have high pH (>7) values [21].

CONCLUSION

Analysis of groundwater samples from 25 borewells in Talakondalpalke mandal of Rangareddy district, India, showed that all the wells except two had fluoride concentration greater than the prescribed limit of 1 ppm in *kharif*, while in *rabi* all the wells had fluoride concentration greater than the prescribed limit. Fluoride concentrations were higher in *rabi* season compared to *kharif*. Fluoride content in groundwater was significantly positively correlated with pH, bicarbonate, sodium, SAR and RSC in both the seasons and significantly negatively correlated with calcium in *rabi* season. The groundwater in all the wells was unsuitable for irrigation, and appropriate remediation measures are essential for successful crop production.

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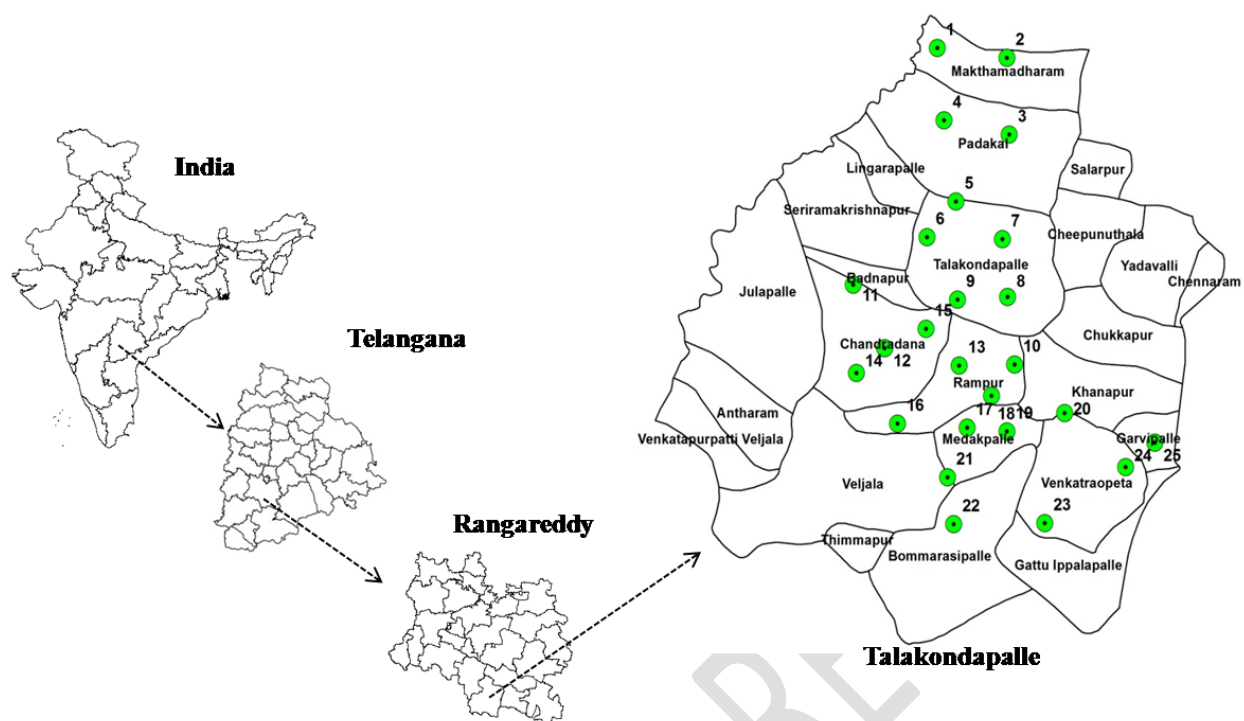


Fig. 1. Location of map and well locations in Talakondapalle mandal

Table 1. Fluoride and other quality parameters of the water samples in Talakondapallemandal (Kharif, 2015-16)

Well No.	F ⁻ ppm	pH	EC (dS m ⁻¹)	Cl ⁻	CO ₃ ⁻²	HCO ₃ ⁻	SO ₄ ⁻²	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	RSC me L ⁻¹	SAR
1	1.70	8.20	0.60	1.10	0.00	7.80	0.22	5.80	2.50	2.00	0.14	-0.50	0.98
2	1.40	7.81	0.65	1.30	0.00	7.50	0.19	5.20	2.80	2.30	0.07	-0.50	1.15
3	1.70	7.90	0.80	0.80	0.20	7.70	0.21	5.90	2.70	1.10	0.10	-0.70	0.53
4	1.30	8.25	1.32	1.10	0.00	6.50	0.18	5.70	2.90	1.50	0.12	-2.10	0.72
5	1.80	8.20	0.50	0.90	0.00	8.90	0.28	5.20	3.00	1.60	0.11	0.70	0.79
6	0.72	7.94	1.05	1.30	0.00	7.20	0.11	6.70	3.50	1.20	0.24	-3.00	0.53
7	0.89	7.92	1.32	0.90	0.00	8.90	0.23	6.50	3.70	1.30	0.31	-1.30	0.58
8	1.10	7.83	1.42	1.30	0.00	8.00	0.34	5.80	3.00	0.90	0.17	-0.80	0.43
9	1.70	8.02	0.95	1.00	0.00	7.30	0.33	6.10	2.40	1.10	0.23	-1.20	0.53
10	1.90	7.69	0.63	1.50	0.00	8.10	0.21	5.50	3.10	0.70	0.15	-0.50	0.34
11	4.10	8.53	0.95	0.90	0.30	7.80	0.43	4.50	2.40	3.20	0.11	1.20	1.72
12	3.85	8.28	0.76	1.70	0.00	8.10	0.33	6.60	2.20	2.40	0.10	-0.70	1.14
13	4.49	8.61	1.10	1.80	0.00	8.60	0.51	5.40	2.50	1.80	0.37	0.70	0.91
14	3.91	8.05	0.72	1.50	0.00	8.40	0.16	5.10	2.80	1.40	0.15	0.50	0.70
15	4.20	8.60	0.56	1.20	0.00	9.60	0.24	6.20	3.80	3.10	0.11	-0.40	1.39
16	3.50	7.96	0.85	1.60	0.00	9.30	0.22	5.40	4.00	1.90	0.10	-0.10	0.88
17	4.30	8.16	0.89	1.20	0.00	9.40	0.19	4.70	3.80	3.20	0.21	0.90	1.55
18	4.10	8.34	0.62	1.10	0.40	8.50	0.22	5.40	3.10	2.70	0.17	0.40	1.31
19	3.20	7.90	0.94	1.00	0.00	9.50	0.31	6.80	3.00	2.10	0.09	-0.30	0.95
20	4.40	8.70	1.23	0.80	0.00	8.10	0.18	4.50	2.50	3.60	0.13	1.10	1.92
21	3.00	7.51	0.59	1.50	0.00	9.40	0.26	6.10	4.00	2.10	0.10	-0.70	0.93
22	3.00	8.13	0.75	1.80	0.00	7.60	0.32	4.30	3.10	1.90	0.14	0.20	0.99
23	2.40	7.96	1.02	0.90	0.20	8.30	0.37	4.90	3.50	1.40	0.12	0.10	0.68
24	4.50	7.90	0.97	1.10	0.00	8.50	0.21	5.40	2.80	2.80	0.15	0.30	1.38
25	3.90	8.40	0.90	1.10	0.00	9.10	0.24	5.70	3.20	2.50	0.11	0.20	1.19
Range	0.72-4.49	7.51-8.70	0.50-1.42	0.80-1.80	0.00-0.40	6.50-9.60	0.11-0.51	4.30-6.80	2.20-4.00	0.70-3.60	0.07-0.37	-3.0-1.20	0.34-1.92
Mean	2.84	8.07	0.88	1.20	0.04	8.32	0.26	5.58	3.05	1.99	0.15	-0.26	0.97
SD	1.30	0.30	0.26	0.32	0.11	0.81	0.09	0.70	0.52	0.79	0.07	0.98	0.41

Table 2. Fluoride and other quality parameters of the water samples in **Thalakondapallymandal** (Rabi, 2015-16)

Well No.	F ⁻ ppm	pH	EC (dS m ⁻¹)	Cl ⁻	CO ₃ ⁻²	HCO ₃ ⁻	SO ₄ ⁻²	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	RSC	SAR
								me L ⁻¹				me L ⁻¹	
1	2.23	8.05	0.45	1.3	0.00	9.3	0.51	6.5	3.0	2.1	0.15	-0.20	1.0
2	1.81	7.65	1.60	1.7	0.00	8.8	0.20	7.2	4.7	1.0	0.07	-3.10	0.4
3	2.25	8.03	0.59	0.9	0.00	9.1	0.38	6.9	2.7	1.8	0.09	-0.50	0.8
4	1.46	8.55	0.88	1.6	0.20	5.8	0.32	6.6	4.1	1.1	0.13	-4.70	0.5
5	2.69	8.46	0.61	1.2	0.00	7.1	0.42	5.8	3.3	2.4	0.11	-2.00	1.1
6	1.32	7.42	1.21	3.1	0.00	7.0	0.18	7.4	4.5	2.0	0.24	-4.90	0.8
7	1.51	7.62	1.53	2.6	0.00	8.7	0.24	7.3	3.8	1.8	0.29	-2.40	0.8
8	1.86	7.93	0.72	2.0	0.00	8.1	0.37	6.4	4.2	1.5	0.07	-2.50	0.7
9	2.30	7.82	0.58	1.5	0.50	8.4	0.32	6.1	3.8	1.9	0.12	-1.00	0.9
10	2.82	7.74	0.77	1.8	0.00	8.8	0.21	6.0	4.0	3.1	0.08	-1.20	1.4
11	4.45	8.35	0.83	1.6	0.00	9.1	0.42	6.3	4.3	1.6	0.12	-1.50	0.7
12	4.10	8.41	0.72	2.1	0.00	9.6	0.36	5.9	3.7	1.9	0.43	0.00	0.9
13	4.91	7.95	1.10	2.4	0.60	9.5	0.66	5.5	4.6	2.1	0.18	0.00	0.9
14	4.15	8.02	0.93	1.8	0.00	9.1	0.25	5.8	3.5	3.3	0.07	-0.20	1.5
15	4.55	8.56	1.16	2.3	0.00	9.4	0.31	5.7	3.8	2.5	0.12	-0.10	1.1
16	4.02	8.02	0.83	3.5	0.00	9.6	0.27	7.1	2.9	2.8	0.10	-0.40	1.3
17	4.72	8.26	0.67	1.4	0.00	10.5	0.20	6.4	4.3	1.7	0.08	-0.20	0.7
18	4.23	8.08	0.71	1.5	0.00	9.7	0.31	5.9	3.9	2.1	0.11	-0.10	0.9
19	3.74	8.01	0.79	1.1	0.00	10.1	0.45	6.5	3.7	2.9	0.09	-0.10	1.3
20	4.61	8.15	0.93	2.3	0.00	9.8	0.29	6.7	3.3	3.8	0.14	-0.20	1.7
21	3.29	8.10	0.85	1.9	0.00	9.5	0.35	5.8	4.3	3.4	0.11	-0.60	1.5
22	3.25	8.19	0.78	1.3	0.00	8.8	0.28	6.0	3.5	2.1	0.07	-0.70	1.0
23	3.14	8.05	0.70	2.4	0.00	8.1	0.32	5.1	3.3	2.3	0.09	-0.30	1.1
24	4.61	8.36	1.02	3.6	0.30	9.4	0.20	5.7	3.8	2.3	0.08	0.20	1.1
25	4.15	8.04	0.90	1.1	0.00	9.1	0.26	5.5	3.7	2.8	0.11	-0.10	1.3
Range	1.32-4.91	7.42-8.56	0.45-1.60	0.90-3.60	0.00-0.60	5.80-10.50	0.18-0.66	5.10-7.40	2.70-4.70	1.00-3.80	0.07-0.43	-4.90-0.20	0.41-1.70
Mean	3.29	8.07	0.87	1.92	0.06	8.90	0.32	6.24	3.78	2.25	0.13	-1.07	1.01
SD	0.24	0.29	0.28	0.72	0.16	1.04	0.11	0.61	0.52	0.70	0.08	1.43	0.33

Table 3. Pearson's coefficients of correlation (r) between fluoride concentration and other water quality parameters

S.No	Parameters	'r' value	
		<i>Kharif</i>	<i>Rabi</i>
1	Fluoride vs pH	0.543 [†]	0.482*
2	Fluoride vs EC	-0.196	-0.134
3	Fluoride vs Chloride	0.157	0.119
4	Fluoride vs Sulphate	0.224	0.160
5	Fluoride vs Carbonate	0.168	0.112
6	Fluoride vs Bicarbonate	0.513 [†]	0.709 [†]
7	Fluoride vs Calcium	-0.372	-0.537 [†]
8	Fluoride vs Magnesium	-0.057	-0.043
9	Fluoride vs Sodium	0.754 [†]	0.462*
10	Fluoride vs Potassium	-0.079	-0.091
11	Fluoride vs SAR	0.745 [†]	0.480*
12	Fluoride vs RSC	0.739 [†]	0.774 [†]

Note: * $P < 0.01$, $^{\dagger}P < 0.05$

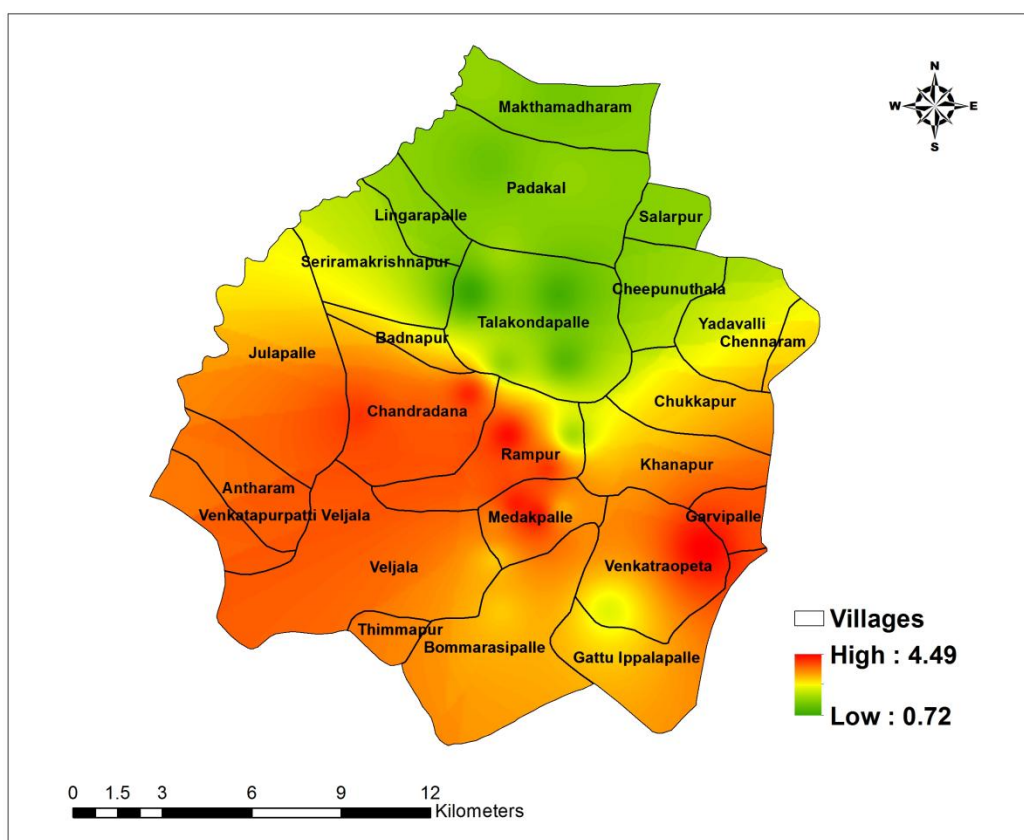


Fig 2. Fluoride distribution in groundwater during *kharif* season

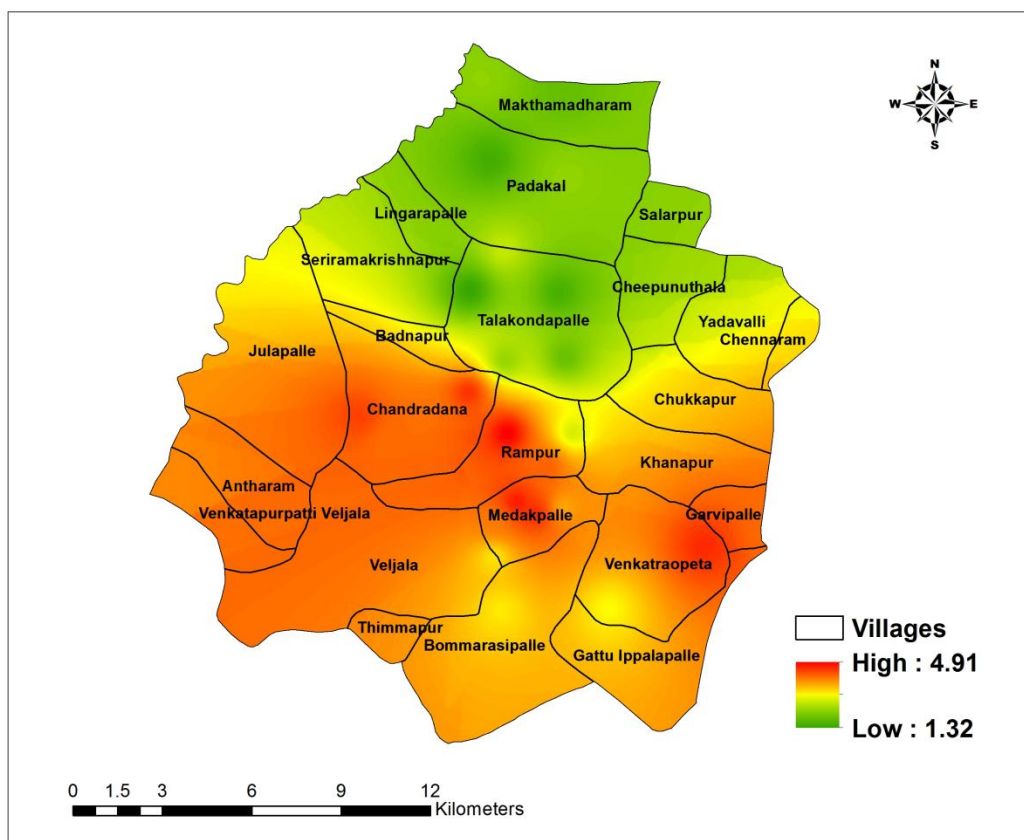


Fig.3. Fluoride distribution in groundwater during *rabi* season