Int.J.Curr.Microbiol.App.Sci (2017) *6*(5): 1042-1050

International Journal of Current Microbiology and Applied Sciences
ISSN: 2319-7706 **Volume 6 Number 5 (2017) pp. 1042-1050**
Journal homepage: http://www.ijcmas.com

Original Research Article https://doi.org/10.20546/ijcmas.2017.605.113

Geochemistry of Ground Water with Special Emphasis on Fluoride and its Seasonal Variations in Parts of Nalgonda District, Telangana State, India

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Keywords

Ground water, Geochemistry, Fluoride, Seasonal variations, Nalgonda.

Article Info

Accepted:
12 April 2017
Available Online:
10 May 2017

A B S T R A C T

A study was carried out to assess the physico-chemical characteristics of ground water with special emphasis on fluoride in parts of Nalgonda district, Telangana State. The water samples were collected from the tube wells located in 82 selected villages in three mandals during *pre* and *post-monsoon* seasons. The ground water samples in the study area interpreted as neutral to slightly alkaline in reaction, non-saline in nature. The mean values of fluoride present in the ground water samples of Ramannapet, Narkatpalli and Aatmakoor mandals were 2.08, 2.88 and 2.45 mg L^{-1}, respectively in *pre-monsoon* and 1.71, 2.28 and 1.72 mg L^{-1}, respectively in *post monsoon* season. As per drinking water standards, 83% (68 samples) and 58.5% (48 samples) of the groundwater samples in *pre and post monsoon* seasons, respectively and have F content greater than that of permissible limit of 1.50 mg L^{-1}. The chloride (Cl^-), sulphate (SO_4^{-2}) and borate (B) concentrations of all the water samples in both *pre* and *post monsoon* seasons were below the permissible limits for irrigation as well as drinking purposes. No water sample tested in the present investigation had more than desirable limits of sodium (Na), calcium (Ca), magnesium (Mg), carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), sodium adsorption ratio (SAR) and residual sodium carbonate (RSC) hence, all the water from the studied sources can be safely used for drinking and irrigation purposes. As per the threshold limits of Cu, Mn, Fe, Zn Cd, Cr, Ni, Pb and Co for drinking and irrigation water recommendations, all the samples analyzed during both the seasons fell within the permissible limits.

Introduction

The study area forms a part of Nalgonda district, Telangana, which is located at a distance of 90 km away from Hyderabad. This area experiences arid to semiarid climate. The study area goes through hot climate during the summer (March–May) with a temperature range from 30ºC to 46.5ºC, and in winter (November–January), it varies between 14ºC and 29ºC. The average annual rainfall in this area is about 1,000 mm, occurring mostly during south-west monsoon (June–September). The geology of the area is mainly dominated by granite, gneiss complex, sandstone and limestone.

The characterization of ground water quality plays a vital role in deciding its management strategies for profitable farming. Ground water aquifer, a main source of water supply in arid and semiarid regions of India is most

vulnerable to salinity and sodicity problem resulting in considerable reduction in crop productivity (Kamra *et al.,* 2002). Groundwater quality data provides important clues to the geologic history of rocks and indications of groundwater movement, recharge and storage. Major chemical elements including Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, CO^{3-},HCO^{3-} and SO_4^{2-} play a significant role in determining key quality parameters for classifying and assessing groundwater quality. Whereas, for use of groundwater for drinking and irrigation, numerous studies have determined its suitability from the values of sodium adsorption ratio (SAR) and residual sodium carbonate (RSC).

The occurrence of the high fluoride concentrations in ground water is a problem faced by many countries; India is one among the 23 nations in the world. Fluoride epidemic has been reported in as many as 20 Indian states and Union Territories.

At present Telangana state is facing major problem with fluoride pollution because ground water is used as drinking and an irrigation source, a natural occurrence of excessive amounts of fluoride levels in ground water. Nalgonda is the worst effected district with a presence of excess fluoride in ground water in the state of Telangana. In spite of continuous efforts by the government, external support agencies, NGOs and private enterprises the problem still remains unsolved. Therefore, it is necessary to study the geochemistry of groundwater and to investigate temporal changes in fluoride content in ground water to ascertain the role of dilution vis-à-vis leaching due to monsoonal recharge in the district. With this background, the present study was carried out in parts of Nalgonda district with the objectives to assess groundwater quality in different mandals; to find the overall suitability of groundwater for irrigation combining all these parameters.

Materials and Methods

Eighty two (82) water samples from bore wells located in different villages in Ramannapet, Narkatpally and Atmakoor mandals of Nalgonda district, Telangana State, India were collected during the *pre-monsoon* (May) and *post monsoon* (September) seasons of 2013. Stoppered polythene bottles of one liter capacity were used for collecting water samples. Each bottle was washed with dilute HCl and then rinsed thoroughly with distilled water. Prior to sampling, the bottle was rinsed thoroughly with the water drawn from the source. During collection of water samples, water was pumped out from bore wells and open wells for about half an hour. The samples were fortified with 1 ml toluene to arrest any biological activity and stored at 4^0C.

The physical and chemical parameters were analyzed for major ion chemistry employing the standard methods (Richards, 1954) such as hydrogen ion concentration (pH) and electrical conductivity (EC) were measured, using pH and EC meters. Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^{-}) were estimated by titrating with sulphuric acid. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were analyzed titrimetrically, using standard EDTA. Sodium (Na^{+}) and potassium (K^{+}) were measured by flame photometer. Chloride (Cl^{-}) was estimated by standard $AgNO_3$ titration. Sulphate ($SO4^{-2}$) was determined gravimetrically by precipitating $BaSO_4$ from $BaCl_2$ using a spectrophotometer. To determine the suitability for irrigation use, parameters like SAR and RSC were calculated and plotted on USSL Diagram (Richards 1954; Hem 1985). Fluoride (F^{-}) was determined by using an optimum buffer (TISAB) system with Fluoride Ion Selective Electrode.

Results and Discussion

The results obtained on different quality parameters of ground water samples in the study area were presented in tables 1 and 2.

pH: The pH of water samples collected from bore wells was slightly alkaline. The pH values of ground water in Ramannapet, Narkatpalli and Aatmakoor mandals during *pre-monsoon* season varied from 7.04 to 8.72, 7.24 to 8.74 and 7.24 to 8.56 and the mean values of 7.91, 7.95 and 7.91, respectively. In *post monsoon* it varies from 7.02 to 8.66, 7.22 to 8.68 and 7.13 to 8.33 and the mean values of 7.80, 7.76 and 7.70, respectively.

The normal or suitable pH in irrigation water is ranging from 6.5 to 8.7, according to FAO (1994). The water samples had a pH within the recommended level of irrigation water as prescribed by FAO (1994), ISI (1983) and ICMR (1975). Similarly, the pH of waters for irrigation purpose is within the tolerable limits *i.e*. between 6.0 and 9.0 as suggested by Desai *et al.,* (1990). Similar results reported by Brindha *et al.,* (2010a) in groundwater samples of Nalgonda district of Telangana and Gautam *et al.,* (2010) in Nagaur district of Rajasthan.

EC (dS m^{-1}): In Ramannapet, Narkatpalli and Aatmakoor mandals the electrical conductivity varied from 0.24 to 0.92, 0.25 to 0.89 and 0.27 to 0.83 dS m^{-1}, respectively in *pre-monsoon* and 0.20 to 0.79, 0.24 to 0.85 and 0.25 to 0.82 dS m^{-1}, respectively in *post monsoon* season. The results revealed that EC values of most of the waters were interpreted as slightly saline to moderately saline in nature. The normal, moderately and not suitable range of electrical conductivity in irrigation water is from 0.25, 0.25-0.75 and > 0.75 dS m^{-1}, respectively (FAO, 1994). The most desirable limit of EC in drinking water is 1.5 dS m^{-1} as prescribed by WHO, 2004. The results revealed that EC values of most of the waters were interpreted as non-saline in nature. Similar results reported by Ramanaiah *et al.,* (2006) in ground water samples of Prakasham district.

Chlorides: The average content of Cl in irrigation water samples of Ramannapet, Narkatpalli and Aatmakoor mandals was 3.34, 3.60 and 3.33 me L^{-1}, respectively in *pre-monsoon* and 2.4, 3.0 and 2.9 me L^{-1}, respectively in *post monsoon* season. The normal and moderate range of chlorides concentration in irrigation water is from < 4 and 4 to 10 me L^{-1}, respectively. Out of 82 villages of three mandals, water samples of 18 villages in pre monsoon and 4 villages in *post monsoon* come under moderately suitable for irrigation. The chloride concentrations of all the water samples are below the permissible limits (10 me L^{-1}) for irrigation as well as drinking purposes, as prescribed by ISI, 1982. These results are in agreement with the findings of Jinwal and Dixit (2008).

Carbonates and bicarbonates: The carbonates present in Ramannapet, Narkatpalli and Aatmakoor mandals of irrigated water samples varied from 0 to 0.8, 0.9 and 0.6 me L^{-1} with, respectively in *pre-monsoon* and 0 to 0.7, 0.8 and 0.5 me L^{-1}, respectively in *post monsoon* season. While, the bicarbonate content of these mandals ranged from 6.1 to 9.6, 6.4 to 8.6 and 6.2 to 8.6 me L^{-1}, respectively in *pre-monsoon* and 4.6 to 8.5, 4.8 to 8.6 and 4.5 to 8.3 me L^{-1}, respectively in *post monsoon* season. An increased activity of HCO_3^- and CO_3^{2-} ions coupled with a sodium concentration increased solubility and release of fluoride from the fluoride bearing parent materials (Hebbara *et al.,* 2010).

Calcium and magnesium: The calcium content in water samples in *pre-monsoon* season varied from 5.4 to 8.5, 5.2 to 8.2 and

5.1 to 8.4 meq L^{-1} with the mean values of 6.9, 6.8 and 6.8 me L^{-1} in respective mandals of Ramannapet, Narkatpalli and Aatmakoor. In *post monsoon* season, the Ca content in water samples varied from 4.2 to 8.1, 5.2 to 7.7 and 4.8 to 8.1 me L^{-1} with the mean values of 6.1, 6.2 and 6.2 me L^{-1} in respective mandals of Ramannapet, Narkatpalli and Aatmakoor. The desirable concentration of calcium in drinking water as per WHO (1971) and ICMR (1975) standards is 3.75 me L^{-1} and the maximum permissible concentration as per the above standards is 10 me L^{-1}. Because the maximum concentration of calcium in ground waters tested is 8.5 and 8.1 me L^{-1} during pre and *post monsoon* season, respectively, the water can be used for drinking purpose provided other constituents are not in harmful range. Similar observations were made by Naidu (1994).

The magnesium content varied from 2.5 to 5.6, 2.7 to 4.4 and 2.4 to 4.5 me L^{-1} in in *pre-monsoon* and 2.4 to 5.3, 2.6 to 4.3 and 2.2 to 4.4 me L^{-1} in *post monsoon* season in different villages of Ramannapet, Narkatpalli and Aatmakoor mandal, respectively. The desirable and maximum permissible concentrations of magnesium in drinking water as per WHO (1971) standards are 2.5 and 12.5 me L^{-1}, respectively. Similarly as per ICMR (1975) standards, the highest and maximum permissible concentrations of magnesium in drinking water are 4.2 and 8.4 me L^{-1}, respectively. No water sample was tested in the present investigation had more than 8.4 me L^{-1} of Mg per liter, hence, all the waters can be safely used for drinking purpose provided other constituents do not exceed the harmful levels. With respect to irrigation water, prescribed limits were not mentioned by any worker as far calcium and magnesium is considered. Generally if the magnesium content of waters is high, the SAR and RSC will be low. Similar observations were made by Naidu (1994).

Sodium: The mean Na content in water samples of Ramannapet, Narkatpalli and Aatmakoor mandals was 2.7, 2.7 and 2.7 me L^{-1}, respectively in *pre-monsoon* and 4.0, 3.7 and 3.6 me L^{-1}, respectively in *post monsoon*. The maximum permissible limit of Na is 200 mg L^{-1} (8.7 me L^{-1}) in drinking and irrigation water and it reveals that all the samples fall within desirable limit of WHO (1997) and ISI (1982).

Sulphates and Borates: In Ramannapet, Narkatpalli, Aatmakoor mandals, the sulphate contents varied from 0.2 to 0.8, 0.3 to 0.9 and 0.2 to 0.9 ppm, respectively in *pre-monsoon* and 0.12 to 0.98, 0.13 to 0.78 and 0.18 to 0.89 ppm, respectively in *post monsoon* season. In Ramannapet, Narkatpalli, Aatmakoor mandals, the mean borate contents was 0.4, 0.5 and 0.4 ppm, respectively in *pre-monsoon* and 0.4, 0.4 and 0.4 mg L^{-1}, respectively in *post monsoon* season.

RSC: The RSC values in the irrigation water samples of Ramannapet, Narkatpalli and Aatmakoor mandals varied from -6.0 to 0.4, -5.1 to 0.0 and -5.6 to 0.9 me $L^{-1}$with average values of -2.2, -2.8 and -2.4 me L^{-1}, respectively in *pre-monsoon* season. In *post monsoon* season it was ranged from -6.7 to 0.4, -6.4 to -0.6 and -7.4 to 0.4 me $L^{-1}$with average values of -2.5, -3.0 and -3.0 me L^{-1}, respectively. The normal and moderate range of RSC values in irrigation water is classified as < 1.25 and 1.25 to 2.5 me L^{-1}, respectively as prescribed by USSL (1954). The results revealed that all the water samples were in safe (< 1.25 me L^{-1}) and can be used for irrigation. These results are in conformity with the findings of Suresh *et al.,* (2014).

SAR: The SAR values of irrigation water in Ramannapet, Narkatpalli and Aatmakoor mandals varied from 1.3 to 2.2, 1.2 to 2.3 and 1.1 to 2.1, respectively in *pre-monsoon* and 0.8 to 1.8, 0.8 to 2.0 and 0.8 to 2.3,

repectively in *post monsoon* season. The low, moderate, high and very high range of SAR values in irrigation water is classified as < 10, 10 to 18, 18 to 26 and > 26, respectively as prescribed by USSL (1954). The SAR values of irrigation water samples collected from different bore wells from the study area was in normal range which can be safely used for irrigation. Out of the 82 water samples collected 3, 63 and 16 samples were classified under C_1S_1, C_2S_1 and C_3S_1 quality class, respectively. These results are in conformity with the findings of Suresh *et al.*, (2014).

Fluoride: The F present in the irrigation water samples of Ramannapet, Narkatpalli and Aatmakoor mandals showed wide variation but their mean values were 2.08, 2.88 and 2.45 mg L^{-1} F, respectively in *pre-monsoon* season and 1.71, 2.28 and 1.72 mg L^{-1} F, respectively in *post monsoon* season. As per drinking water standards, 83% (68 samples) of the groundwater samples during *pre-monsoon* season and 58.5% (48 samples) of the ground water samples during *post monsoon* and have F content greater than that of maximum permissible limit of 1.50 mg L^{-1} F. Therefore drinking water is sufficient to produce severe form of dental fluorosis and mild form of skeletal fluorosis consumed for a long period.

Safe limit of 10 mg fluoride L^{-1} irrigation water has been proposed for all type of crop plants by Leone *et al.*, (1948). All the samples were to be well within permissible limits. According to FAO (1994), the normal and moderately suitable range of fluorides concentration in irrigation water is from < 19 ppm (1.0 me L^{-1}) and 19 to 171 ppm (1.0-15 me L^{-1}) F, respectively. The present investigation showed that none of the water samples have found to cross this limits and hence suitable for irrigation purpose.

Micronutrients: The micronutrients like Cu, Mn, Fe and Zn content during *pre-monsoon* season varied from traces to 0.35, 0.56**,** 0.56 and 0.89, respectively in water samples Ramannapet mandal, traces to 0.41, 0.35**,** 0.56 and 0.91 mg L^{-1}, respectively in water samples of Narkatpalli mandal and traces to 0.35, 0.55**,** 0.77 and 0.56 mg L^{-1}, respectively in water samples of Aatmakoor mandal. In *post monsoon* season, the available micronutrients like Cu, Mn, Fe and Zn content was in the range of traces to 0.20, 0.09**,** 0.58 and 0.09 mg L^{-1}, respectively in water samples of Ramannapet mandal, traces to 0.50, 0.86**,** 0.56 and 0.13 mg L^{-1}, respectively in water samples of Narkatpalli mandal and traces to 0.24, 0.86**,** 0.91 and 0.89 mg L^{-1}, respectively in water samples of Aatmakoor mandal.

As per drinking water standards of WHO (1996), all the samples analyzed fell within the permissible limits of 0.3, 0.1 and 3.0 mg L^{-1} for Fe, Mn and Zn, respectively in ground water. With respect to irrigation water, recommended maximum concentrations of Fe, Mn, Zn and Cu are 5.0, 0.2, 2.0 and 0.2 mg L^{-1}, respectively given by National Academy of Sciences (1972). No water sample tested in the present investigation had more than permissible limits, hence, all the waters can be safely used for irrigation purposes. Trace metals are widely distributed in the environment with sources mainly from weathering of minerals and soils. Similar observations were also reported by Ackah *et al.*, (2011).

Heavy metals: The heavy metals like Cd, Cr, Ni, Pb and Co content during *pre-monsoon* season varied from traces to 0.24, 0.75**,** 0.45, 0.56 and 0.58 mg L^{-1}, respectively in water samples of Ramannapet mandal, traces to 0.51, 0.51**,** 0.34, 0.36 and 0.41 mg L^{-1}, respectively in water samples of Narkatpalli mandal and traces to 0.31, 0.34, 0.86, 0.56 and 0.56 mg L^{-1}, respectively in water samples of Aatmakoor mandal. In *post*

monsoon season, the heavy metals like Cd, Cr, Ni, Pb and Co content varied from traces to 0.56, 0.23**,** 0.56, 0.41 and 0.56 mg L^{-1}, respectively in water samples of Ramannapet mandal, traces to 0.09, 0.28**,** 0.89, 0.18 and 0.45 mg L^{-1}, respectively in water samples of Narkatpalli mandal and traces to 0.89, 0.25**,** 0.86, 0.58 and 0.56 mg L^{-1}, respectively in water samples of Aatmakoor mandal.

As per the threshold limits for drinking water recommendations by WHO (1996) all the samples analyzed fell within the permissible limits of 0 to 0.01, 0.002 to 0.01 and >0.02 mg L^{-1} for Pb, Cd and Ni respectively in ground water. The recommended maximum concentrations of Cd, Ni, Pb and Co are 0.01, 0.2, 5.0 and 0.05 mg L^{-1}, respectively for irrigation purposes given by National Academy of Sciences (1972). All the samples analyzed fell within the permissible limits for irrigation.

Table.1 Descriptive statistics of irrigation water quality parameters collected from different mandals of Nalgonda district (Pre-monsoon, 2013)

Parameters	Ramannapet		Narkatpalli		Aatmakoor	
	Range	Mean	Range	Mean	Range	Mean
pH	7.04-8.72	7.91	7.24-8.74	7.95	7.24-8.56	7.91
EC (dS m^{-1})	0.24-0.92	0.51	0.25-0.89	0.52	0.27-0.83	0.54
F (mg L^{-1})	0.99-3.94	2.08	1.16-5.34	2.88	1.12-4.67	2.45
Cl (me L^{-1})	1.7-5.3	3.34	1.8-4.9	3.60	1.9-5.1	3.33
CO_3^{-2} (me L^{-1})	0.0-0.8	0.2	0.0-0.9	0.13	0.0-0.6	0.17
HCO_3^- (me L^{-1})	6.1-9.6	8.0	6.4-8.6	7.48	6.2-8.6	7.58
SO_4^{2-} (me L^{-1})	0.20-0.80	0.50	0.30-0.90	0.58	0.20-0.90	0.57
B (mg L^{-1})	0.12-0.98	0.38	0.13-0.78	0.45	0.18-0.89	0.42
Ca (me L^{-1})	5.4-8.5	6.9	5.2-8.2	6.8	5.1-8.4	6.8
Mg (me L^{-1})	2.5-5.6	3.6	2.7-4.4	3.7	2.4-4.5	3.4
Na (me L^{-1})	3.0-5.0	4.0	2.8-5.1	3.7	2.2-5.1	3.6
RSC (me L^{-1})	-6.0-0.4	-2.2	-5.1-0.0	-2.8	-5.6-0.9	-2.4
SAR	1.3-2.2	1.7	1.2-2.3	1.60	1.1-2.1	1.6
Cu (mg L^{-1})	0-0.35	0.09	0-0.41	0.11	0-0.35	0.09
Mn (mg L^{-1})	0-0.56	0.15	0-0.35	0.14	0-0.55	0.17
Fe (mg L^{-1})	0-0.56	0.18	0-0.56	0.17	0-0.77	0.26
Zn (mg L^{-1})	0-0.89	0.15	0-0.91	0.13	0-0.56	0.09
Cd (mg L^{-1})	0-0.24	0.05	0-0.51	0.10	0-0.31	0.07
Cr (mg L^{-1})	0-0.75	0.12	0-0.51	0.10	0-0.34	0.09
Ni (mg L^{-1})	0-0.45	0.08	0-0.34	0.11	0-0.86	0.18
Pb (mg L^{-1})	0-0.56	0.10	0-0.36	0.10	0-0.56	0.14
Co (mg L^{-1})	0-0.58	0.12	0-0.41	0.11	0-0.56	0.15

Table.2 Descriptive statistics of irrigation water quality parameters collected from different mandals of Nalgonda district (Post monsoon, 2013)

Parameters	Ramannapet		Narkatpalli		Aatmakoor	
	Range	Mean	Range	Mean	Range	Mean
pH	7.02-8.66	7.80	7.22-8.68	7.76	7.13-8.33	7.70
EC (dS m^{-1})	0.20-0.79	0.42	0.24-0.85	0.49	0.25-0.82	0.51
F (mg L^{-1})	0.53-3.86	1.71	0.56-5.25	2.28	0.73-3.25	1.72
Cl (me L^{-1})	1.2-4.1	2.4	1.2-4.6	3.0	1.1-4.7	2.9
CO_3^{-2} (me L^{-1})	0-0.7	0.2	0-0.8	0.1	0-0.5	0.1
HCO_3^{-} (me L^{-1})	4.6-8.5	6.9	4.8-8.6	6.6	4.5-8.3	6.3
SO_4^{2-} (me L^{-1})	0.2-0.6	0.3	0.2-0.7	0.4	0.2-0.6	0.4
B (mg L^{-1})	0.07-0.94	0.40	0.02-0.76	0.40	0.08-0.84	0.4
Ca (me L^{-1})	4.2-8.1	6.1	5.2-7.7	6.2	4.8-8.1	6.2
Mg (me L^{-1})	2.4-5.3	3.4	2.6-4.3	3.5	2.2-4.4	3.2
Na (me L^{-1})	1.9-3.6	2.7	1.7-4.1	2.7	1.9-4.8	2.7
RSC (me L^{-1})	-6.7-0.4	-2.5	-6.4 - -0.6	-3.0	-7.4-0.4	-3.0
SAR	0.8-1.8	1.2	0.8-2.0	1.2	0.8-2.3	1.3
Cu (mg L^{-1})	0-0.20	0.04	0-0.50	0.08	0-0.24	0.05
Mn (mg L^{-1})	0-0.09	0.03	0-0.86	0.12	0-0.86	0.16
Fe (mg L^{-1})	0-0.58	0.08	0-0.56	0.13	0-0.91	0.16
Zn (mg L^{-1})	0-0.09	0.02	0-0.13	0.02	0-0.89	0.15
Cd (mg L^{-1})	0-0.56	0.07	0-0.09	0.03	0-0.89	0.09
Cr (mg L^{-1})	0-0.23	0.04	0-0.28	0.05	0-0.25	0.05
Ni (mg L^{-1})	0-0.56	0.11	0-0.89	0.13	0-0.86	0.13
Pb (mg L^{-1})	0-0.41	0.07	0-0.18	0.03	0-0.58	0.16
Co (mg L^{-1})	0-0.56	0.13	0-0.45	0.07	0-0.56	0.09

Table.3 Correlation coefficients (r) between fluoride concentration and other chemical properties of ground water

S. No	Correlation Among	r value in					
		Ramannapet		Narkatpalli		Aatmakoor	
		Pre-monsoon	*Post monsoon*	*Pre-monsoon*	*Post monsoon*	*Pre-monsoon*	*Post monsoon*
1	Fluoride vs pH	0.561**	0.564**	0.704**	0.741**	0.525**	0.791**
2	Fluoride vs EC	-0.120	-0.146	-0.182	-0.199	-0.013	-0.491
3	Fluoride vs Chloride	0.226	0.412	0.245	0.724	0.353	0.392
4	Fluoride vs Sulphate	0.071	0.052	0.288	0.062	0.251	0.019
5	Fluoride vs Carbonate	0.120	0.434	0.037	0.143	0.232	0.243
6	Fluoride vs Bi-carbonate	0.198	0.435	0.532	0.457	0.260	0.621
7	Fluoride vs Calcium	-0.380	-0.360	-0.263	-0.563	-0.413	-0.597
8	Fluoride vs Magnesium	-0.139	-0.268	-0.343	-0.546	-0.017	-0.033
9	Fluoride vs Sodium	0.437	0.790	0.543	0.693	0.541	0.763
10	Fluoride vs SAR	0.535	0.806	0.576	0.756	0.561	0.804
11	Fluoride vs RSC	0.424	0.599	0.519	0.703	0.175	0.745
		*5 % (0.3730)		*5 % (0.3889)			
		**1 % (0.4774)		**1 % (0.4994)			

Correlation of fluoride concentration with other physicochemical parameters

The significantly positive correlation of fluoride with pH indicates that alkaline groundwater is likely to have a higher amount of fluoride, suggesting that the pH of the groundwater is more important in determining the concentration of fluoride. This is because of the similarity between the ionic radius of fluoride and hydroxyl ion thereby replacing each other at higher pH. A positive correlation (r= 0.893) has also been observed between fluoride and pH reported by Teotia *et al.*, (1981), Trivedi (1988) and Gupta and Deshpande (1998). The relationship between fluoride and electrical conductivity was negative but no significant correlation was observed. The relationship between fluoride and chloride, fluoride and sulphate was positive and significant. These results are conformity with the observations of Chakrabarty and Sarma (2011) (Table 3).

A significantly strong negative correlation has been observed between fluoride and calcium in the ground waters (r values of -0.380 in *pre-monsoon* and -0.360 in *post monsoon* season of Ramannapet mandal) is attributed to high solubility of fluoride from these cation bearing rocks. If calcium is present in higher concentration it is most effective in reducing

the fluoride concentration. This is also suggestive towards the possibility of ion-exchange process (Chakrabarty and Sarma, 2011). Overall, high pH, high carbonate plus bicarbonate, and low calcium plus magnesium in groundwater leads to leaching of fluoride which results increase in the concentration of groundwater fluoride. Such an observation was also made by Rao *et al.*, (1993).

Seasonal variation of fluoride in ground water

When compared to two seasons, the concentration of fluoride in groundwater during *post monsoon* was lower than the *pre-monsoon*. Seasonal distribution is found significantly and the variation of fluoride is dependent on many factors. During the *post monsoon* season, dilution may be attributed to replenishment of the groundwater by rainfall indicated a clean recharge without pollution from external sources. During *pre-monsoon* season, high fluoride concentration due to over-exploitation of groundwater resources for agricultural and drinking water purposes, seasonal distribution of fluoride is dependent on a variety of factors such as amount of soluble and insoluble fluoride in source rocks, the duration of contact of water with rocks and soil temperature, rainfall and oxidation-reduction process (Mahapatra *et al.,* 2005 and Paya and Bhatt, 2010).

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How to cite this article:

Vijaya Lakshmi, D., K. Jeevan Rao, T. Ramprakash and Pratap Kumar Reddy, A. 2017. Geochemistry of Ground Water with Special Emphasis on Fluoride and its Seasonal Variations in Parts of Nalgonda District, Telangana State, India. *Int.J.Curr.Microbiol.App.Sci.* 6(5): 1042-1050. doi: https://doi.org/10.20546/ijcmas.2017.605.113