Assessment of Groundwater quality with special reference to Fluoride in groundwater surrounding abandoned mine sites at Vemula, Y.S.R district, A.P

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Abstract:

Groundwater is the main source of drinking water living in this region. The public water distribution system uses tube wells. The region falls under semi-arid or even arid belt with associated high temperatures. Keeping in view of public health importance around abandoned mines around vemula, hydrochemistry of fluoride has determined the proposed work aims at chemical characterization of groundwater bodies with spatial attention to fluoride concentration. A total of 26 drinking water samples collected in and around Vemula mandal, Y.S.R district, Kadapa, India were analysed for fluoride contamination, besides water quality parameters such as pH, electrical conductivity, total dissolved solids, total alkalinity, total hardness, bicarbonates, calcium, magnesium and fluoride. The concentration of fluoride in the water samples ranged between 0.24 mg/L to 3.0 mg/L. Five locations Gondlapalli (1.6 mg/L) , Chagaleru(1.6 mg/L), Gollalaguduru (2.06 mg/L), Rangoripalli(2.55 mg/L), Pernapadu (3 mg/L) have a mean fluoride concentration beyond 1.5 mg/l. Similarly, the concentrations of electrical conductivity, total dissolved solids, total hardness, chloride were also more than the permissible level. The arid climate of the region alkaline, pH the lithology and low fresh water exchange the main factors responsible for high fluoride concentration in ground water. Igneous and volcanic rocks have a fluorine concentration and in general fluorine accumulates during magmatic crystallization and differentiation processes of the magma. The people in the Villages Chagaleru, Gondlapalli, Gollalaguduru, Rangoripalli, Pernapadu of Vempalli mandal are prone to dental flourosis. It concluded that the water sources can be potable only after prior treatment.

Key words: Groundwater quality, Abandoned mine sites, Vemula, Y.S.R District, Andhra Pradesh.

Introduction:

Groundwater is the vital natural resources required for human consumption for various purposes such as domestic, irrigation, industrial water supply [1]. Groundwater sources are depleting through out of the world [2]. Contaminated water resources deteriorate the public health. Groundwater resources are effected by several factors such as urbanization, industrialization , rainfall pattern , irrigation activities , leaching of pollutants from land fill ,nature of host rock ,mining and geological processes [3,4,5]. Fluorides in drinking water may be beneficial or harmful depending on it concentration and total amount ingested. Fluoride is essential for calcification of dental enamel for young children below eight years of age , when present with in permissible limits of 10-15 mg/L.Health problems related to high fluoride concentration in the range of 1.5 mg/L to 300 mg/L are dental carries, teeth mottling. According to Indian standard specification drinking water 1.5mg/L of Fluoride is the maximum permissible limit [6].When fluoride concentration in drinking water exceed 4-8 mg/L skeletal fluorosis is occurs. Crippling skeletal fluorosis can occur when drinking water has high concentration of fluoride more than 10mg/L [7]. Fluoride in groundwater in parts of Vemula, Y.S.R District ranges from 0.266 to 3.52 mg/L [8]. Due to higher fluoride concentration cases of dental fluorosis have been observed in various regions of Kadapa, Y.S.R District [9, 10, 11]. Several cases of dental and skeletal fluorosis appeared in Vemula Mandal [12]. Keeping in view of public health importance around abandoned mines around vemula, hydrochemistry of fluoride has determined the proposed work aims at chemical characterization of groundwater bodies with spatial attention to fluoride concentration.

Study Area:

The study area (240 Sq. Km) located 64 Km towards west of Kadapa Y.S.R District. It lies between latitude 14^{o} 21' 00'' N; longitude 78^{o} 22' 30'' E falls in Toposheet No.57J/7(Fig: 1). The major important villages are Vemula,Velpula, Gollalaguduru, V.Kothapalli, Gondhipalli etc. Denudation hills, Pediments, Pediplain, Structural hill are the important geomorphic units. The study area consists of the lower Cuddapah super group comprising Papaghni & Chitravati groups [13]. Conglomerate, Shale, Basalt, Dolomite, Limestone and Dolomitic limestones, flat topped basalts are important litho units observed in the study area (Fig:2). The average rainfall is 600-650 mm and the average temperature various from 20.4^{0}C to 43.2^{0}C [14].

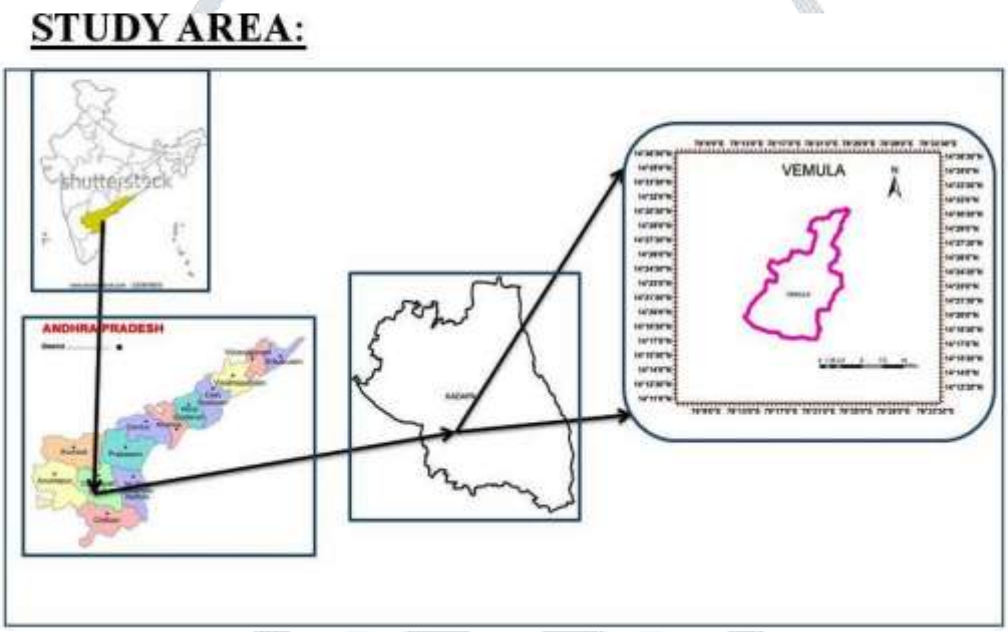

Fig:1 Map of the Study area

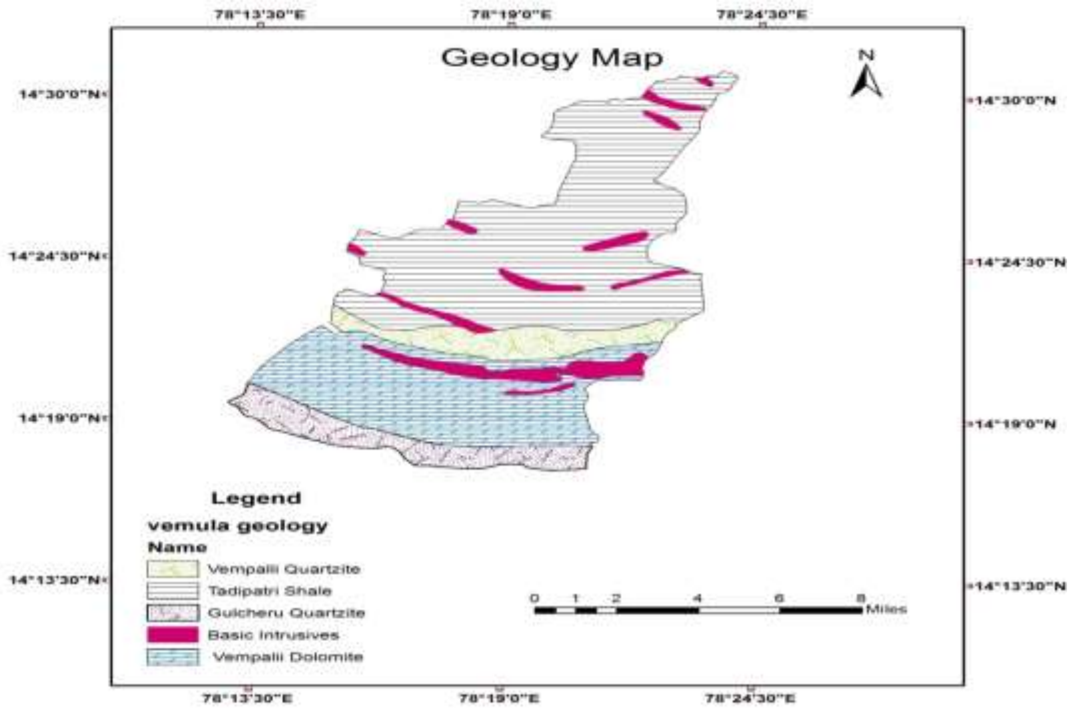

Fig: 2 Geology map of the Study area.

Materials And Methods

Twenty six Groundwater samples were collected in and around Vemula, Y.S.R District, Andhra Pradesh; sampling was carried out in the month of September 2017. Sampling locations were recorded using a potable GPS device. Samples were collected in pre cleaned and well-dried polyethylene bottles. The samples were collected from bore wells which were extensively used for drinking and other domestic purposes. The water samples collected in the field were analysed for electrical conductivity (EC), pH, total dissolved solids (TDS), major cations such as calcium, magnesium, and anions such as bicarbonate, carbonate, chloride and fluoride, adopting the standard methods[15,16,3] and suggested precautions were taken to avoid contamination pH and EC were determined by pH, conductivity meter, TDS by TDS meter, TH, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^- and Cl^- were determined by titrimetry, F^- Was determined by using ion selective electrode (Orion 4 star ion meter, Model: pH/ISE). All the experimental were carried out in triplicate and the results were found reproducible with in a ± 3% error limit.

Results and Discussion:

The limit of pH value for drinking water is specified as 6.5 to 8.5 [17]. Most ground waters have a pH range of 6 to 8.5 [18]. pH of groundwater in the study area is ranging from 7.05 to 8.97 with a mean of 8.28. pH values for all the samples are within the desirable limits. The pH values of groundwater samples varied between 7.0-8.97(Table1&2). Maximum pH 8.97 was recorded at station in Rangoripalli village and minimum pH 7.05 was recorded at station in village Gondipalli. It is observed that most of the groundwater is alkaline in nature. Electrical conductivity of the groundwater is ranging from 869 to 2590µS/cm at 25^0C with a mean of 1211µS/cm (Table: 1). In the present investigation minimum concentration of EC 869 µS/cm was observed at northern part of Gollalaguduru village and maximum EC 2590µS/cm was observed at southern part of Gollalaguduru village. 3% of samples are exceeding the permissible limit of EC (Table: 1). High electrical conductivity in these samples may be due to extensive agricultural practices. In the study area the TDS value varies between a minimum of 188 mg/L/l and a maximum of 1340 mg/L (Table: 1&2) indicating that most of the groundwater samples lies within the maximum permissible limit of TDS. It is clear from Table 4 that 88.46% of groundwater samples fall into freshwater category, whereas 11.5% of groundwater samples fall into slightly saline category (Table 4).In the present study minimum concentration of TDS 188 mg/L was observed at northern part of Gollalaguduru village and maximum concentration of 1340 mg/L was observed at southern part of Gollalaguduru village. High concentration of TDS in the groundwater sample is due to leaching of salts from soil and also percolation of ochre mine wastage may percolate into the groundwater which may lead to increase in TDS values. The total hardness is varying from 100 to 520 mg/l (Tables1&2). In the present study minimum concentration of TDS 100 mg/L was observed at southern Part of Gollalaguduru village and maximum concentration of 520 mg/L was observed at Gondhiaplli village, vempalli mandal. The acceptable limit of total hardness (TH) (as $CaCO_3$) is 300 mg/L, which can be extended up to 600 mg/L in case of non-availability of any alternate water source (WHO 1990). According to Sawyer et al. (2003) groundwater is considered as safe:<75,

Table 1: Analytical data for the groundwater samples from the study area (EC in µS/cm, remaining mg/L, except pH)

S.No	Sample ID	pH	EC µS/cm	TDS mg/L	TH mg/L	Ca^{2+} mg/L	Mg2+ mg/L	$CO3^-$ mg/L	HCO_3^- mg/L	Cl^- mg/L	F^- mg/L
1	S1	8.42	823	382	160	24	34.2	12	292.8	28.4	0.39
2	S2	8.85	390	203	160	8	9.72	24	73.2	35.5	0.24
3	S3	8.1	1450	750	300	48	58.32	24	146	312.4	0.27
4	S4	8.5	2590	1340	280	16	43.74	24	317.2	454.4	1.27
5	S5	8.25	369	188	100	40	14.58	12	122	42.6	0.626
6	S6	8.8	1500	800	200	16	38.88	36	317.2	35.5	2.06
7	S7	8.04	2150	1100	280	16	58.32	24	292.8	78.1	0.73
8	S8	8.4	1040	540	200	16	38.88	12	219.6	142	0.66
9	S9	8.07	634	327	180	16	19.44	24	195.2	134.9	0.46
10	S10	7.05	1070	555	220	40	38.88	12	268.4	21.3	0.79
11	S11	8.39	1430	740	340	24	77.76	36	244	220	0.71
12	S12	8.21	1760	910	140	24	0	24	219.6	134.9	1.6
13	S13	8.67	2170	1120	520	56	116.64	36	244	369.2	1.22
14	S14	8.97	1450	750	180	16	9.72	48	366	85.2	2.55
15	S15	8.61	1180	610	140	56	24.3	24	317.2	56.8	3
16	S16	7.87	1710	880	280	16	43.74	60	24.4	234.3	0.877
17	S17	8.51	826	423	200	40	24.3	24	122	71	1.6
18	S18	8.8	1220	630	160	40	14.58	36	268.4	120.7	0.88
19	S19	8.05	1000	516	260	88	38.88	24	170.8	106.5	0.8
20	S20	7.95	1150	590	360	40	53.46	12	195.2	85.2	0.66
21	S21	8.1	811	421	200	40	29.16	24	195.2	49.7	0.87
22	S22	8.13	1070	550	240	24	43.74	24	47.9	99.4	0.92
23	S23	7.75	967	500	260	24	38.88	36	38.3	78.1	0.74
24	S24	8.31	792	409	200	40	24.3	12	38.8	42.6	0.66
25	S25	8.43	774	400	200	40	29.16	36	40	35.5	1.19
26	S26	8.2	1170	600	300	32	53.46	12	41	85.2	1.55

Table: 2 Statistical summary of physico-chemical parameters in the study area

Parameters	Unit	Minimum	Maximum	Mean	SD	CV	Median
pH		7.05	8.97	8.28	0.40	4.88	8.28
EC	µS/cm	369	2590	1211.3	537.3	44.3	1110
TDS	mg/L	188	1340	624.3	279.08	44.6	572.5
TH	mg/L	100	520	233	87.25	37.4	200
Ca^{2+}	mg/L	8	88	32.3	17.5	54.46	28
Mg^{2+}	mg/L	0	116.4	37.57	23.98	63.8	38.8
Salinity	mg/L	209	2060	958.8	439.3	45.8	880
CO_3^-	mg/L	12	60	25.8	12.09	46.7	24
HCO_3^-	mg/L	24.4	366	185.2	106.4	57.4	195.2
Cl^-	mg/L	21.3	454.4	121.5	110.5	90.9	85.2
F^-	mg/L	0.24	3	1.05	0.67	63.8	0.83

moderate to hard: 75-150; Hard 150-300; Very hard:>300 and most of the groundwater(76.92%) of the present study area is rated as hard and requires processing before use. Chloride concentration in the study area varies from 21 mg/L to 454 mg/L with a mean of 121 mg/l. The desirable limit of chloride in potable water is 250 mg/L and the permissible limit is 1000 mg/L [19]. Higher concentration of 454 mg/l at station in gollalaguduru village can be groundwater contamination from ochre mine. This can also be due to leaching of upper soil layers due to industrial & domestic activities and dry climate [20]. The desirable limit of chloride in potable water is 250 mg/L and the permissible limit is 1000 mg/L [19]. Most of the samples are within the permissible limit of calcium suggested by [19] (Table: 3). Magnesium in the groundwater of the study area is varying from 0 to 116 mg/L and the average value is 37.57 mg/L (Tables 2, 3). Maximum value of the magnesium was recorded as 116 mg/L at sampling location Gondhipalli. The required permissible limit of magnesium in groundwater for drinking purpose is 30 mg/L [19] and the concentrations are found to be within the permissible limits (Tables 2, 3).

Table: 3 Comparison of quality parameters of Groundwater with W.H.O and BIS for drinking purpose

Water Quality Parameter	W.H.O Max accept limit	W.H.O Max allow limit	BIS Max accept limit	BIS Max allow limit	Concentration in study area	% of samples exceeding the permissible limit
pH	7.0	8.5	6.5	8.5	7.05-8.97	19%
EC (µS/cm)	400	1500	500	1500	369-2590	15%
TDS (mg/L)	500	1500	500	1500	188-1340	Nil
TH (mg/L)	100	500	300	600	100-520	3%
Ca^{2+} (mg/L)	75	200	75	200	8-88	Nil
Mg^{2+} (mg/L)	50	150	30	100	0-116.6	Nil
HCO_3^- (mg/L)	150	300	-	-	24.4-366	15%
Cl^- (mg/L)	200	600	250	1000	21.3-454.4	11%
F^- (mg/L)	0.6	1.5	0.6	1.5	0.24-3	19%

Fluoride:

Fluoride concentration varies from 0.24mg/L (Votlapalli) to 3.0 mg/L (Pernapadu) with a mean of 1.05 mg/L. The desirable limit of fluoride in drinking water is between 0.5 to 1.5 mg/L. The permissible limit in drinking water 1.5mg/L[19]. Out of the total sample analysis 20% of the samples are above the permissible limit of 1.5 mg/L. Five locations Gondlapalli (1.6 mg/L), Chagaleru(1.6 mg/L), Gollalaguduru (2.06 mg/L), Rangoripalli(2.55 mg/L), Pernapadu (3 mg/L) (Fig:4) have a mean fluoride concentration beyond 1.5 mg/l.

Volcanic intrusions observed at these villages might have contributed fluoride contamination in groundwater. The residents in the village that rely purely on ground water for drinking purposes and the people in study area are exposed to higher levels of Fluoride contamination in groundwater. The groundwater of these study area is alkaline and observed that increase in the alkalinity made a similar increase in the fluoride concentration [21, 22]. In the alkaline environment F^- ions can be easily liberated and OH^- and F^- ions have similar radiant easily exchange with each other. Presence of fluoride bearing minerals and their interaction with water in dry climate is considered to the major cause of fluoride concentration. It can be concluded that fluoride bearing water are usually high in the alkalinity and low in hardness and chloride, sulphate [23]. The sources of geogenic (apatite, biotite, and clays) with a combination of higher rate of evaporation and longer interaction of water with the aquifer materials under alkaline environment are the key factors for the concentration of F- in the study area [24]. Prolonged water rock interactions facilitate fluoride enrichment in groundwater [25, 26, 27, 28]. Geological settings and type of rocks play a crucial role in fluoride contamination in groundwater. Fluorides occur in three forms, namely fluorspar or calcium fluoride (CaF_2), apatite or rock phosphate [$Ca_3F\ (PO_4)3$] and cryolite (Na_3AlF_6) [29]. Out of 416 fluoride-bearing rock minerals, only topaz, fluorite, villiaunite, and cryolite contain fluorine as an essential constituent in the formula. The remaining fluoride-bearing minerals possess fluoride as an isomorphous replacement in the OH position [30] due to the fact that the ionic radius of fluoride is similar to that of the hydroxyl ion (F 133 pm, OH 140 pm) [31]. Therefore fluoride problems tend to occur in places where these minerals are most abundant in the host rocks. Igneous and volcanic rocks have a fluorine concentration from 100 ppm (ultramafic) up to >1000 ppm (alkalic) [32]. In general fluorine accumulates during magmatic crystallization and differentiation processes of the magma. Consequently, the residual magma is often enriched in fluorine. Groundwaters from crystalline rocks, especially (alkaline) granites (deficient in calcium) are particularly sensitive to relative high fluoride concentrations. Such rocks are found especially in Precambrian basement areas. The various actors that govern the release of fluoride into groundwater are temperature, pH, and solubility of fluoride-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-), the nature of geological formations drained by water, and the contact time of water with the source minerals [33].

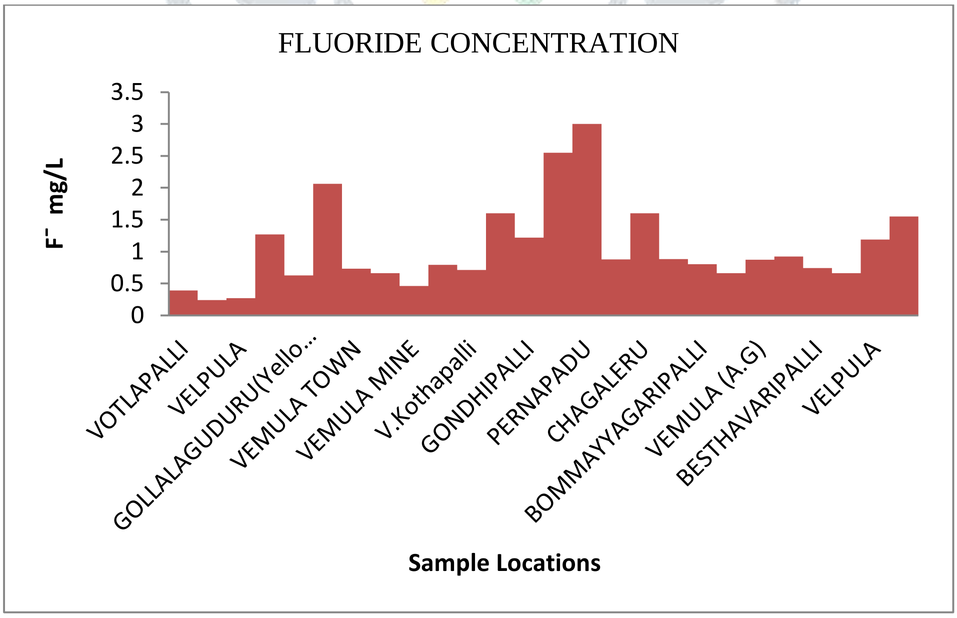

Fig: 4 Fluoride concentration in vemula mandal, Y.S.R District, A.P

Conclusion:

Fluoride concentration in the water samples ranged between 0.24 mg/L to 3.0 mg/L. Five locations Gondlapalli (1.6 mg/L), Chagaleru(1.6 mg/L), Gollalaguduru (2.06 mg/L), Rangoripalli (2.55 mg/L), Pernapadu (3 mg/L) have a mean fluoride concentration beyond 1.5 mg/l. Similarly, the concentrations of electrical conductivity, total dissolved solids, total hardness, chloride were also more than the permissible level. Geological formation is found to be a basic cause for the higher concentration of fluoride in most of the sampling points. Water–rock interaction, evapotranspiration, low rainfall is responsible for the major ion chemistry of the groundwater. Therefore, it is concluded that the occurrence of high fluoride groundwater is controlled by various factors including rock chemistry, residence time, well depth, preferential pathways for the upward movement of deep groundwater, and hydrologic condition of the pathways. Dental manifestations of fluorosis are also reported in the study area, which shows that the population of the study area is at higher risk due to excessive fluoride intake especially when they are unaware of the amount of fluoride being ingested due to lack of awareness. The problem is further aggravated by the fact that the residents of the study area neither have access to fluoride treated water nor are economically sound to have household water treatment plant exclusively for fluoride. If the same trend continuous without any treatment technique for the water samples containing fluoride content greater than 1.5 mg/l, the percentage of dental fluorosis victims will increase in the near future. The most effective and a simple approach to the fluoride trouble would be low-cost defluoridation techniques, which should be planned for smaller rural communities. In addition, such information should be made available to health professionals in order to avoid feasible overmedication and treat through use of children's vitamins and other dental caries prevention programs. An environmental awareness programme is recommended, in which the health implications of fluoride are emphasized through education of the public and community participation in this Vemula region of Y.S.R district, Kadapa, Andhra Pradesh.

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