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Research Paper

Groundwater Quality Evaluation with Special reference to Fluoride and Nitrate Pollution in Uravakonda, Anantapur District, Andhra Pradesh– a case Study

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Abstract *- Water is essential natural resource for sustaining life and environment which we have always thought to be available in abundance and free gift of nature. Though ground water is the major drinking water source, deterioration in its quality is going unchecked. In such agro-economy based rural areas, the nitrate contamination is rampant and much attention has not been drawn towards this anthropogenic pollution. In the study area ground water samples from different hydro geological set-up have been collected during the pre and post monsoon seasons and analyzed for the major ions such as* Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-} *and* F^{-}*.The study revealed that 95% of the samples were found to be unsuitable for drinking purposes in the pre-monsoon season and 90% in the post monsoon due to excess nitrate (>45 mg/l) content in the ground water. Intense agriculture practices, improper sewerage and organic waste disposal methods were observed to contribute nitrate to the shallow and moderately deep aquifers. Fluoride concentrations in groundwater samples were determined in the study area. Fluoride concentrations in groundwater samples of these villages varied between 0.5 mg/l and 7.2 mg/l. Majority of the samples are exceeding the permissible limit of fluoride 1.5 mg/l [1]. Probable sources of fluoride are weathering and leaching of fluoride bearing minerals under the alkaline environment. Further the concentration of fluoride is aided by high rate of evaporation, longer residence time of waters in the aquifer zone, intensive and long term irrigation. Dental and skeletal fluorosis and deformation of bones in children as well as adults were observed in the study area indicating the health impact of fluoride in groundwater.*

Keywords: Quality, fluoride, nitrate, uravakonda, Anantapur.

Introduction

Water is essential natural resource for sustaining life and environment which we have always thought to be available in abundance and free gift of nature. Groundwater forms a major source of drinking water in urban as well as in rural areas. Groundwater has the properties of dissolving and carrying in solution, a variety of chemical and other materials. More than 90% of the rural population uses groundwater for domestic purposes. Major problems are being faced by the country due to the presence of excess fluoride, arsenic and nitrate in groundwater in certain parts of country. At present twenty nine countries are reported to be affected with fluorosis, the fluoride related disease. Fluoride problems are wide spread in nine states covering almost the entire country. In India about 62 million people in 17 states including Andhra Pradesh are affected with dental, skeletal and or non-skeletal fluorosis [2]. Free fluorine plays no part in toxicology because it reacts immediately to form fluoride compounds. The presence of dissolved fluorides in natural waters is possible only when conditions facilitate long residence times of the F^{-} species in solution. Occurrence of fluorine in groundwater has drawn worldwide attention due to its considerable impact on human physiology. The permissible limit of F^{-} in drinking water is 1.5 mg/.l [3]. The fate of fluoride in the soil environment and groundwater is of concern for several reasons. It is generally accepted that fluoride stimulates bone formation [4] and optimum concentration of fluorides have beneficial effects on the teeth by hardening the enamel and reducing the incidence of caries [5]. At lower levels (<2 ppm) soluble fluoride in the drinking water may cause mottled enamel during the formation of teeth, but at higher levels other toxic effects may be observed. Excessive intake of fluoride results in skeletal and dental fluorosis [6]. Severe symptoms lead to death when fluoride doses reach 250-450 ppm [7]. It is found that the IQ of the children in the high fluoride areas was significantly low [8].

Nitrate (NO_3^-) contamination of the groundwater, due to the intensive use of fertilizers has become a serious ecological problem in many rural areas of India and in many developing nations worldwide. The level of nitrate in groundwater has been increasing over the past three decades [9,10].Producing an adequate quantity of healthy food without polluting the environment is a formidable challenge for future agriculture in the world. The global mean nitrogen use efficiency is estimated to be about 50% [11].The remaining quantity of nitrogen is lost into the environment. A large population of this nitrogen gets converted into nitrate which, being soluble in water and not retained by soils, gets leached into water bodies. Leaching of nitrate from agricultural land and from other sources to groundwater is a global phenomenon. A number of workers from India and abroad have reported the presence of high concentration (3800 ppm) of nitrate in groundwater [12,18] and identified their probable sources. However, the mechanism of nitrate in different hydrogeological conditions and its seasonal response in the study area have not been well documented. In this context, part of Anantapur district in Andhra Pradesh, India, representing a typical rural location, has been selected for a systematic study to establish the baseline characteristics of the ground water and the sources of contamination.

Study Area

The study area lies between longitudes 77^0 15' – 77^0 20' east and latitudes 15^0 0' -14^0 50' north and falls in the Survey of India Toposheet No: 57 F/5 sample locations are shown in figure -1. The study area comprises pink Granites, schists, composite gneisses of Dharwar intruded by a few pegmatite dykes and numerous dolerite dykes and the possible diamondiferous volcanic pipes [19,20]. The major geomorphic units of the study area are Denudational Hills, Dissected pedimonts, Pediplain, and Alluvium. The study area lying off the coast does not enjoy the full benefit of the north. See Figure 1.

Material and Methods

Twenty Five groundwater samples were collected from 20 different locations of Uravakonda area, Anantapur District, Andhra Pradesh during April and November 2004. The location map of the study area is shown in Figure1. The samples were collected from bore wells which are extensively used for drinking and other domestic purposes. The collected groundwater samples were analyzed for pH, electrical conductivity (EC), using pH and EC meters, Total dissolved solids (TDS), which were computed by multiplying the EC with a factor (0.55 to 0.75) that depend on the relative concentrations of ions; Total alkalinity (TA) as $CaCO_3$ and bicarbonate HCO_3 were estimated by titrating with HCl, Total hardness (TH) as $CaCO_3$ and Calcium (Ca^{2+}) were analyzed titrimetrically, using standard EDTA, Magnesium (Mg^{2+}) was calculated on the basis of the difference in the concentration between TH and Ca^{2+}, Sodium(Na^+) and Potassium (K^+) were measured by flame photometry, chloride (Cl^-) was estimated by standard $AgNO_3$ titration, sulphate (SO_4^{2-}), nitrate (NO_3^-) was analysed by spectrophotometer, fluoride (F^-) concentrations in mg/l except pH (units) and EC in microseimens/cm. The method of collection and analysis of water samples followed are essentially the same as given by APHA 1992.

Results and Discussion

Quality of Groundwater

The results of chemical analysis of groundwater samples from the study area is represented in tables 1and 2.The quality of groundwater in villages of uravakonda mandal, was studied with a view to evaluate the suitability of this groundwater for domestic and irrigation purposes. The analytical data revealed that the groundwater in the study area with pH values ranging from 7.0 to 8.6 with an average of 7.0 during pre-monsoon period and from 7.2 to 8.6 with an average of 7.5 during post-monsoon season indicating alkaline nature representing the buffering capacity of water and its ability to resist a change in pH. Some well water having higher concentration of pH due to weathering of plagioclase feldspars by dissolved atmospheric carbon dioxide that will release sodium and calcium which progressively increase the pH and alkalinity this kind of result observed by Njitchoua et al. 1997. The electrical conductivity of the groundwater ranges from 230 to 2580 µSiemens/cm at 25°C with an average of 944 µSiemens/cm during post-monsoon period. Nearly 85% of the samples during pre-monsoon and post monsoon lie within the highest desirable limit for drinking purpose prescribed as 1500 microseimens/cm [1]. Total dissolved solids values of all samples exceed highest desirable limit of 500 mg/l [22].Total Hardness values of all samples exceed the highest desirable limits. Hardness of water is primarily due to the result of interaction between water and the geological formations [23].The limit of total hardness for drinking water is specified as 300 mg/l [22]. Nearly 92% of the groundwater of the area during pre- monsoon and post-monsoon exceeds the desirable limits of calcium, magnesium and sodium [1]. The fluoride concentration of the groundwater in the study area ranges from 1.7 mg/l to 6.8 mg/l with an average of 4.2 mg/l during pre-monsoon period and from 1.5 to 6.8 mg/l with an average of 3.3 mg/l during post-monsoon period. The permissible limit of fluoride in drinking water is 1.5 mg/l [22]. It is observed that nearly 95% of the groundwater of the area exceeds the desirable limits during pre monsoon and post-monsoon periods. Majority of the study area appears to have high concentrations of nitrate. The upper limit of nitrate concentration for drinking water is specified as 45 mg/l [22].

Significance of Fluoride

Impact of fluoride on human health

Fluoride is important for the development of teeth and the bones [24]. Small doses of fluoride have beneficial effects on the teeth by hardening the enamel and reducing the increase of caries, but excessive intake of fluoride results in dental and skeletal fluorosis [24,25] and other disorders may also occur [27]. The maximum tolerance limit of fluoride in drinking water specified by the World Health Organization [1] is 1.5 mg/l. There are an estimated 8700 villages in India which have problems of excessive fluoride in water; affecting 2.5 million people. Fluorine in the exogenic cycle of this fluorosis belt is almost entirely derived from granitic and pegmatitic rocks. There is no evidence of any addition of fluoride into the environment by artificial means either by industry or by any other sources. The principal fluorine bearing minerals such as fluorite and fluorapatite are responsible for a high concentration of fluoride under normal pressure and temperature conditions. The factors that govern the distribution of fluoride in natural waters are dependent on amount of fluorine in the source rocks and soils, and the duration of contact of water with the rocks and soils. It may be noted that the high incidence of fluorosis is because of a variety of factors such as geological, climatological, social and economic conditions. The natural occurrence of high fluorine content in groundwater is an environmental hazard.

The main source of fluoride in the groundwater is fluoride bearing rocks from which it get weathered and/or leached out contaminates the water. 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). Concentration of fluorides is five times higher in granite than in basalt rock areas. Similarly, Shale has a higher concentration than sandstone and limestone. Alkaline rocks contain high percentage of fluoride (1200 to 8500 mg/kg) [28]. All the water sources collected from ten villages of the Uravakonda revenue mandal revealed fluoride in the range 1.8 to 7.2 mg/l. The lowest value of the fluoride level in peddachinnapyapili Village was 1.8 mg/l and the highest was 7.2 mg/l in uravakonda Village. A total of 795 school children were screened from ten villages of this block, of whom 470 (59.11%) were found to be affected by dental fluorosis. Stages of dental fluorosis among these individuals were chalky white (26.18%), yellowish brown (27.17%), and brownish black (11.64%) with 23.13% showing horizontal streaks, 28.25% spots, and 13.61% both spots and streaks. Few cases of skeletal fluorosis were also noticed in the uravakonda village (Table 3).

Nitrate and Human Health

Fears have been expressed that high nitrate levels in drinking water may cause methacmoglobinaemia or well water cyanosis, in bottle-fed infants. Circumstantial proof has also been postulated that amines and nitrite react in the human body to form carcinogenic nitrosamines, the nitrite resulting from the reduction of ingested nitrate[29]. Whenever nitrate limits in water are exceeded, it is recommended that infants up to the age of one year be supplied with low-nitrate water from other sources. The World Health Organization (WHO) 1984 has established maximum permissible limits for nitrates in water used for drinking purposes at 45 mg/l NO_3^-. Nitrate contamination or the world's ground water supply poses a serious human health threat. High nitrate levels found in drinking water have been proven to be the cause for numerous health conditions across the world. If we intend to provide for the future survival of man and life on planet earth, we must take action new to assure the quality or one of our most precious resources, our ground water supply. Protection of groundwater from nitrate contamination is an often-overlooked health concern. Leaching of nitrate from agricultural land and from other sources to groundwater is a global phenomenon. Nitrates in drinking water is associated with a number of health problems such as other gastrointestinal cancers, methaemoglobinaemia, alzheimer's disease, vascular dementia, multiple sclerosis in human beings [30,31]. Nitrate contamination leads to Eutrophication of water bodies. In the context of facing the challenge of increasing food production from decreasing cultivable land, issues concerned with nitrate pollution in this country can be reviewed and policy options available for combating the problem can be studied. A study in Spain found increased mortalility rates from gastric and prostate cancer with increasing exposure to nitrates in the drinking water [32].

A cluster of spontaneous abortions was identified in Indiana among women with nitrate-contaminated wells [33]. In USA and Europe, approximately 2000 cases or methaemoglobinaemia were reported during the period 1945-1960 and about 7-8% of the infant, died [34]. Elevates levels of methaemoglobinaemia concentrations were found in Russia, in children who drank water containing as much as 182 mg / l NO_3^- [34]. In Columbia and Italy, high levels of nitrate in well water were associated with an increased risk of gastric cancer [35]. In a cross-sectional study in an area with a high incidence of gastric cancer in northeastern China, an association was observed between high levels of nitrate in drinking water supplies and neoplastic changes in the stomach. A critical evaluation of the existing status suggests the need for a systematic investigation of the occurrence and mechanism of nitrate to design effective mitigation and management techniques. Hence the study of nitrate in potable water assumes a great importance. The present study indicates that nitrate concentrations of groundwater are over 100 mg/l in several places in the study area and concentrations as high as 140 mg/l have been observed whilst a maximum permissible limit of 45 mg/l is suggested by W.H.O. Nitrate salts usually have a high solubility and are not absorbed by the clays present in the soils of the area. Nitrate content in groundwater serves as a basis for detecting pollution. Most of the samples of groundwater drawn from the bore wells showed an occurrence of nitrate ranging from 1.7 to 140 mg/l. These wells located near to the cultivable lands where large quantities of inorganic fertilizers and pesticides are used. These chemicals pollute the well- water through percolation. The high level of nitrate should be considered a serious problem for further future development of drinking water.

Probable Sources of Nitrate Contamination

Nitrate (NO_3^-) contamination of the groundwater, due to the intensive use of fertilizers has become a serious ecological problem in the study area. Detailed study of the groundwater in the study area revealed that the nitrate levels are exceeding the prescribed limit of 50mg/l. Leaching of nitrate to groundwater is mainly due to excessive application of N- fertilizer, the absence of proper soil and water management practices, septic tanks, improper disposal of domestic wastes.

Conclusion

Hydrogeochemical studies of Uravakonda area, Anantapur District reveal that the concentration of EC, TDS, TH, Na^+, K^+ , Ca^{2+} nitrate and fluoride are exceeding the permissible limit for drinking purpose. Groundwater quality is strongly influenced by bedrock geology and climate, but may also be attributed to the impacts of agricultural pollution. The present water availability situation in the study area is under great threat. The chief sources of fluoride in groundwater are the fluoride-bearing minerals in the rocks and the sediments. The high fluoride content in the groundwater of this area has affected villagers in the form of primary level of fluorosis resulted in stained and darkened tooth enamel. The source of fluoride in the natural water can be traced to the occurrence of fluorine-rich granitic rocks and soils derived from those rocks. The high fluoride content in the drinking water should also be given attention and defluoridated water should be provided for drinking purposes in the rural areas. The prime sources of nitrate enrichment are leaching from the sewage effluents being utilized extensively for irrigation, leakage from sewerage systems, septic tanks and natural drains carrying municipal wastes, and application of fertililizers. Due to the detrimental biological effects, treatment and prevention methods must be considered to protect groundwater aquifers from nitrate leaching and high concentrations. Many Defluoridation devices and techniques, which includes Activated Alumina, Red mud, Nalgonda technique, Magnesia & Montmorillonite have been referred with various limitations. Treatment through ion-exchange and other processes can rehabilitate already contaminated water, while prevention, such as reduced dependence on nitrogen-rich fertilizers can lower the influx of nitrates. Regular monitoring of water quality is recommended to improve understanding of nitrate pollution in the groundwater in these villages and in surrounding region

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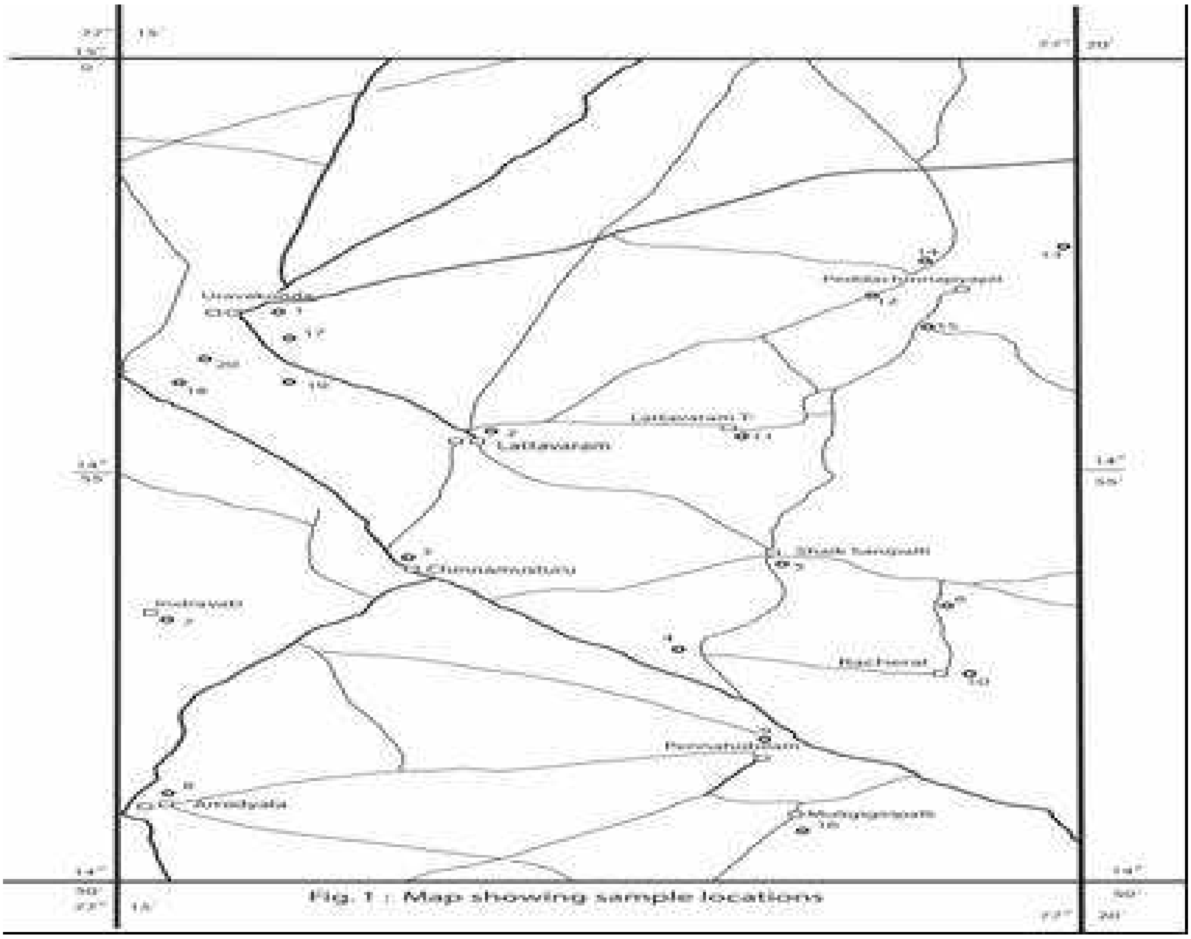

Fig. 1 : Map showing sample locations

Figure 1: Map showing sample Locations

Table 1: Analytical data of the groundwater of the study area for Pre-monsoon season (mg/l)

S.No.	pH	EC	TDS mg/l	TH mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	HCO_3 mg/l	CO_3 mg/l	SO_4 mg/l	Cl mg/l	F mg/l	NO_3 mg/l
1	8.3	652	1812	600	717	170	200	214	187	Nil	170	235	2.3	60
2	8.4	654	1393	1000	819	90	280	174	227	Nil	360	260	2.3	70
3	7.2	1168	2030	1600	1750	39	230	340	164	Nil	450	270	2.7	70
4	8.1	727	1650	1200	850	43	246	236	270	Nil	430	340	3.1	95
5	7.8	346	926	500	734	70	120	130	274	Nil	70	245	2.5	54
6	9.2	418	987	900	826	10	170	175	185	Nil	65	150	2.7	34
7	7.6	1550	2626	700	1690	28	510	552	157	Nil	600	335	2.1	65
8	8.5	1039	1027	1500	1770	76	280	264	136	Nil	250	260	2.5	70
9	8.3	630	1116	900	735	51	172	170	170	Nil	780	220	1.8	10
10	8.6	878	514	900	810	141	126	130	197	Nil	430	135	3.3	73
11	8.3	726	648	100	824	104	162	168	159	Nil	230	140	7.2	72
12	8.2	368	1191	500	200	34	405	75	216	Nil	90	150	4.4	62
13	8.6	273	1426	300	150	47	214	270	274	Nil	74	130	2.7	47
14	8.5	616	1550	1300	903	36	136	302	274	Nil	132	290	2.6	40
15	7.3	352	1041	400	164	46	152	191	480	Nil	60	230	4.2	48
16	8.1	233	3246	400	177	147	253	660	188	Nil	75	150	3.2	56
17	7.6	1444	4560	2900	844	63	730	700	Nil	290	182	750	3.4	76
18	8.1	2548	1629	4200	4500	15	355	184	330	Nil	700	800	7.2	87
19	7.2	2146	4220	3500	1800	46	760	610	Nil	295	324	900	4.2	88
20	8.2	520	1206	700	726	38	364	60	182	Nil	234	220	4.3	56
21	7.4	2026	2770	3500	3200	23	384	454	167	Nil	560	850	5.2	48
22	8.4	238	1203	300	140	39	250	127	149	Nil	440	150	4.6	98
23	7.4	2580	3151	3500	1900	96	430	351	Nil	244	850	950	4.5	98
24	7.3	1238	2118	2000	821	34	271	331	Nil	341	380	640	4.3	65
25	7.5	243	1120	400	160	125	173	153	Nil	341	60	260	3.6	66

Note: *EC is expressed in µ Siemens/cm

Table 2: Analytical data of the groundwater of the study area for Post-monsoon season (mg/l)

S. No.	pH	EC	TDS mg/l	TH mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	HCO_3 mg/l	CO_3 mg/l	SO_4 mg/l	Cl mg/l	F mg/l	NO_3 mg/l
1	8.2	670	650	1820	720	72	220	220	190	Nil	170	240	2.1	85
2	8.1	664	1010	1340	825	95	280	180	228	Nil	370	270	2.2	96
3	7.0	1172	1650	2020	1800	40	240	360	170	Nil	460	275	2.6	63
4	8.0	732	1250	1670	870	45	250	245	270	Nil	440	340	3.0	90
5	8.2	360	560	930	740	70	110	138	270	Nil	50	260	2.4	90
6	7.8	425	950	990	830	10	175	178	190	Nil	60	160	2.5	85
7	7.8	1600	700	2630	1000	30	520	560	158	Nil	750	330	2.0	80
8	8.8	1042	1400	1030	1800	80	270	270	140	Nil	700	250	2.3	63
9	8.5	610	990	1120	740	60	180	138	175	Nil	550	210	1.5	35
10	8.6	880	960	510	820	150	130	170	160	Nil	440	140	3.0	89
11	8.2	728	90	650	826	100	170	60	210	Nil	240	140	6.8	95
12	8.2	370	550	1200	210	38	420	280	270	Nil	90	140	4.0	58
13	8.6	280	350	1430	158	48	216	308	270	Nil	80	120	2.2	42
14	8.7	620	1350	1560	920	54	140	200	270	Nil	130	270	2.0	50
15	7.8	360	450	1051	165	50	160	670	170	Nil	70	220	4.0	75
16	8.3	240	450	3248	180	150	270	680	Nil	220	180	170	3.0	10
17	7.8	1510	2910	4500	840	67	740	188	340	Nil	160	120	2.7	84
18	8.2	2560	4000	1700	650	18	340	620	Nil	300	650	920	6.0	96
19	7.4	2150	3700	4220	2000	35	750	64	185	Nil	320	900	4.0	68
20	8.4	230	750	1210	740	39	370	460	167	Nil	240	220	4.1	63
21	7.6	2030	3700	2780	3200	25	390	128	150	Nil	600	850	5.0	65
22	8.5	245	350	1210	130	42	250	360	400	Nil	470	160	4.0	58
23	7.6	2585	360	3050	1700	74	440	340	380	Nil	800	820	4.2	75
24	7.7	1300	2020	2120	170	64	280	160	Nil	370	120	620	4.1	90
25	7.8	247	425	1130	120	128	180	140	180	Nil	60	270	3.0	58

Note: *EC is expressed in μ Siemens/cm

Table 3: Statistical parameters of the different chemical constituents of groundwater of the study area during Pre-monsoon period

Parameter	Minimum	Maximum	Average	Standard Deviation
pH	7.2	8.6	7.5	0.47
EC	220	2560	1480	591
TH	90	4000	3691	1224
TDS	510	4500	2500	1028
Na	120	3200	1660	804
K	10	150	80	1034
Ca	110	740	425	643
Mg	78	700	449	535
HCO_3	BDL	400	200	90
SO_4	50	800	455	460
Cl	120	920	520	160
F	1.7	6.8	3.3	1.4
NO_3	10	95	52	25

Table 4: Statistical parameters of the different chemical constituents of groundwater of the study area during post-monsoon period

Parameter	Minimum	Maximum	Average	Standard Deviation
pH	7.0	8.6	7.9	0.5
EC	230	2580	944	723
TH	100	4200	1352	1207
TDS	514	4560	2530	1064
Na	140	4500	2320	812
K	10	170	90	1942
Ca	120	760	440	170
Mg	60	690	214	180
HCO_3	BDL	480	240	55
SO_4	60	850	455	774
Cl	130	950	540	330
F	1.7	6.8	4.2	1.34
NO_3	10	98	54	22

Table 5: Data on incidence and severity of the dental fluorosis in school children surveyed from the study area Anantapur District

S. No.	Name of the village	Fluoride Concentration (mg/l) Range	Mean	Number of individuals examined	No. of affected individuals (%)
1	Uravakonda	3.3-7.2	5.25	100	75 (75)
2	Lattavaram	2.6-3.2	2.9	85	50 (58.8)
3	Chiinamusturu	2.3-3.1	2.7	80	30 (37.5)
4	Shaik saniaplli	2.1-2.7	2.4	50	20 (40)
5	Amidyala	2.6-4.4	3.5	60	35 (58.3)
6	Racherla	2.7-4.2	3.45	75	45 (60)
7	Peddachinnapyapili	1.8-3.0	2.4	90	40 (44.4)
8	Muligiriaplli	2.6-3.2	2.9	65	45 (69.2)
9	Pennahobilam	4.2-5.2	4.7	120	80 (66.6)
10	Indravati	3.6-4.5	4.05	70	50 (71.4)
	Total	-	-	795	470(59.11)