Full Length Research Paper

Evaluation of fluoride enrichment processes in groundwater of Chimakurthy granitic pluton complex in Prakasam District India

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Hydrogeochemical evaluation of aquifers belonging to Chimakurthy granitic pluton complex reveals wide spatial and temporal variation in F^- distribution. F^- concentration in groundwater of different aquifers varies from < 0. 50 to 9.84 mg/l. Among three sampled episodes, the mean value of F^- is high in July 2010 and 61% of samples have values above maximum permissible limit as per the Bureau of Indian Standards. In April 2008, 44% and in February 2009, 41% of samples were not fit for drinking purposes due to enrichment of F^-. Northern half of the area is almost free from F^- but south central part, which has witnessed igneous activity with mafic intrusive form the core area of F^- mineralization. Cent percent testing of all the groundwater structures in fifteen villages show uneven distribution of F^- even within limited terrain. F^- show close positive correlation with pH (0.57), Na^+ (0.68), HCO_3^- (0.61) and distinct negative correlation (-0.31) with Ca^{2+}. The groundwater facies is of sodium bicarbonate chloride type, sodium magnesium bicarbonate type and calcium magnesium bicarbonate type. Among 23 analyzed trace elements, Zn is the most dominant (mean 3200 μmg/l). Trace elements concentrations do not exhibit any distinct control over F^- contribution to groundwater. F^- content in rock samples varies drastically from below detectable limit (BDL) to 492 ppm whereas in soil it varies between (BDL) and 612 ppm. F^- concentration of rock-soil-groundwater does not synchronize depicting latter enrichment of F^- into formation water. Ratios, indices and plots indicate multiple mechanisms were responsible in F^- absorption into groundwater. Water-rock interactions, ion exchange followed by evapotranspiration have facilitated the F^- mineralization of groundwater. Na^+/Cl^- ratio of >1in almost all the samples of three sampling sessions establish silicate weathering. Ca^{2+}/Mg^{2+}, Na^+/Ca^{2+}, Ca^{2+}, Mg^{2+} and HCO_3^- ratios authenticate carbonate dissolution is responsible for alkali earths addition. Sodic rich and calcium depleted water together with balanced alkalinity has enabled F^- enrichment. Presence of fluorite as accessory mineral apart from occurrence of F^- in mineral lattice of biotite, hornblende, muscovite, and pyroxene were the potential sources of F^- to the percolating pore waters. Though F^- was abundantly available in solid solution the receptive hydrochemical character of solute was governing the F^- adsorption which could be one of the strong reasons for uneven distribution of F^- with in similar petrological setup.

Key words: Water-rock interaction, fluoride, groundwater, Chimakurthy, gabbro, hydrogeochemistry.

INTRODUCTION

Fluoride rich groundwaters were attracting the attention of wide spectrum of scientists' world over for the past four decades. Since supplementing F⁻ to toothpaste or food products was stopped in late seventies due to the availability of F⁻ in water as well as edible food items, the studies on enrichment processes of F⁻ in groundwater has taken a quantum leap (Handa,1975; Chinoy, 1991; Nawlakhe et al., 1995; Sumalatha et al., 1999; Ray et al., 2000; Dass et al., 2003; Sreedevi et al., 2006; Madhnure et al. , 2007; Gupta et al., 2005; Raju et al., 2009; Rizwan and Gurdepp2013).

Though drinking water often targeted for high ingestion of F⁻ by human beings, food is also an important source of F⁻ which goes unnoticed due to lack of serious studies in this direction. But of-late the research on F⁻ has become a multi-disciplinary topic involving not only geologists and hydrogeochemists but also biochemists, medical professionals and nutrition experts (Susheela and Das, 1991; Dobaradaran et al., 2008; Takahashi et al., 2001; Sharma and Sharma 2004; Shin et al., 1998; Bouaziz, 2006; Toi et al., 2009). Inadequate F⁻ in drinking waters (< 0.5 mg/l) is also a major challenge in many countries as water is the primary source of F⁻ intake. The nationwide mean fluoride level in the groundwater resources in Iran was found to be lower than the minimum permissible level of 0.5 mg/L (Mesdaghinia et al., 2010). In some parts of India, fluoride levels are below 0.5 mg/L, while in other places, fluoride levels are as high as 30 mg/l (Sharma et al., 2011). Excess concentration of F⁻ either in water, beverages or in food is a matter of concern to all public health organizations Elevated fluoride content in drinking water resources have been reported in a number of countries, but in developing countries because of inadequate financial and technical supports, dealing with this issue have been found problematic and sophisticated (Fawell et al., 2006; Siddique et al., 2006; D'Alessandro, 2006).

Drinking water is the major source (75%) of daily intake of F⁻. The severity of injury is determined by duration of fluoride exposure and concentration (Sharma et al., 2011). Growing number of disabilities among people consuming F⁻ rich groundwater, which often encompass hitherto unknown areas, has made the scientists as well as administrators to focus on genesis of F⁻ into water in an urge to search suitable remedial measures (Grandjean et al., 1992; Gupta, 2011; Ayoob and Gupta, 2006; Brunt et al., 2004; Currell et al., 2011; Edmunds and Smedley, 2005; Kumar and Saxena, 2011; Pillai and Stanley, 2002; Rafique et al., 2009; Shaji et al., 2007; Subba, 2003). Keen assessment of water quality

scenario of rural and underdeveloped areas reveal that groundwater in the virgin or less exploited hinterlands of Indian sub-continent are also highly contaminated in many hydrological environments both from geogenic and anthropogenic sources (Reddy, 2014). Excess fluoride affects plants and animals also. The effect on agriculture was also evident due to inhibition on plant metabolism leading to necrosis, needle scratch and tip burn diseases. In animals also, prominent symptoms of fluorosis were observed (Brindha et al., 2011). Having understood and accepted the fact that enrichment of F⁻ in groundwater is a natural process; the multi-dimensional research is polarized on envisaging the absorption processes and isolate F⁻ inflicted waters.

Though distribution of F⁻ groundwater in space and time is very erratic and unpredictable, it is predominant in tropical zones and its adverse impact is distinct in undernourished people and those who are below poverty line (BPL) especially in third world countries. The southern India, being predominantly occupied with peninsular gneissic complex, is wreaked with F⁻contaminated waters which occasionally include surface waters too. Wide spectrum of scientists is engaged in sustained research on these stressed, fractured granitic aquifers for the past few decades. These efforts have resulted in uninterrupted flow of information, creation of baseline data and publications. Institutional effort to mitigate the problem and for better understanding of the F⁻ enhancement process is also evident as many premier institutions and NGOs are continuously engaged in research on F⁻ groundwater adopting latest technology.

F⁻ rich groundwater, though available in almost all the geological horizons even in alluvial phreatic aquifers, but its concentration is immensely felt in igneous rocks. The Prakasam district of Andhra Pradesh is well known for plutonic complexes which have some of the rare rock assemblages including alkaline rocks, grano-diorite and norite, gabbro etc. Occurrence of F⁻ minerals in mafic rich plutonic rocks or migmatites is rare. A chance finding of F⁻ rich aquifers amidst complex igneous rocks is explored further to bring to light the intricacies of F⁻ assimilation in groundwater where the F⁻ is present to the extent of 9mg/l.

Preliminary study in and around Chimakurthy pluton revealed the presence of F⁻ concentrated aquifers which has called for detail hydrogeochemical studies. On the basis of the previous publication (Reddy, 2014), the present study has been extended to 15 villages surrounding Chimakurhty, in order to investigate the extent and degree of groundwater pollution, and to

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evaluate the principal geochemical factors controlling the F⁻ contamination. All the groundwater structures in hydrogeochemical processes that are involved are selected villages were subsequently tested for F⁻ content which revealed that F⁻ rich aquifers occur in isolated patches confining to peripheries of the plutonic complex which is occupied by migmatites and granite gneisses. Presence of F⁻-rich groundwater in hitherto unknown rock assemblages has fueled the fascination for more in-depth studies. Rather than just reporting the extent of F⁻ contamination in groundwater, efforts were made to elucidate the solute transport and adsorption processes. Source of F⁻, role of formation water chemistry and explored to establish the link with rock and soil groundwater. F⁻ concentration in groundwater, soil and rock, is studied in relation with other associated element constituents and trace elements to understand and evaluate geochemical processes that are involved in F⁻ enhancement.

Physiography, climate and hydrogeology

The study area covering 280 sq. km lies in North latitudes 15°29′ to 15°42′ and East longitudes 79°46′ to79°58′ and is bounded by Musi river in west and south, hills and forest in northwest and villages of neighboring *Mandals* like Podili, Santhanuthalapadu, Thallur, Kandapi etc, (*Mandal* is an administrative unit) in north and east (Figure 1). The area is characterized by denudational hills and pediplain. Denudational hills are scattered in western part, they strike in N – S direction reaching an elevation of 638m amsl (above mean sea level). Pediplain is characterized by low lying flat terrain with gentle slope of less than 6° from NW to SE. The general elevation in NW is about 73 m amsl and in SW it is 30 m amsl.

The terrain experiences semiarid and subtropical continental climate is characterized by severe summers and moderate winters. The mean annual maximum temperature recorded from May to June is 41°C and the mean annual minimum temperature from December to January is 14°C. The average normal rainfall for the entire area is 875 mm, and in general it is decreasing from east to west and north to south. Half of the area received less than normal rainfall in half of the observed years from 1990 to 2007 (HBS, 2007).

The area is underlain by the rocks of Khondalite group, Charnockite group, unclassified metamorphics and Dharwar Super Group rock assemblages belonging to Archaean age along with mafic intrusives like gabbros, norite and anorthosites (GSI, 2002; Figure 2). The thickness of weathering is limited to 8 to 10 m. Groundwater occurs under water table conditions in the weathered zone, which is developed through open wells down to 8 to 12 m bgl (below ground level). The fracture zones extend from 20 to 80 m but potential fractures are largely confined to 30 to 50 m depth. The water levels are

deeper in bore wells than open wells as they mostly tap groundwater from semi-confined and partly from confined aquifers (Reddy 2008).

MATERIALS AND METHODS

Groundwater samples were collected in three different sampling episodes to assess spatial and temporal variation of F⁻ content in complex granitic aquifers. The samples were subjected to major element analysis to obtain the concentration of various important parameters. The samples of one sampling episode were analyzed of twenty trace elements and metals to facilitate critical interpretation of underlying process in F⁻ enrichment with reference to micro-content of specific chemical constituents of groundwater. Apart from water, soil and rock samples were also collected from some selected locations to establish the source and pathways of F⁻.

Sampling procedure

After carrying out brief hydrogeological survey and collecting basic hydrological data, the sampling locations were finalized to initiate periodic water quality monitoring. The water samples were collected from domestic wells which include both dug wells representing phreatic aquifers and hand pump fitted bore wells (HPBW) which tap semi-confined, fractured as well as hydrologically stressed multifaceted plutonic aquifers. The groundwater was sampled after sufficient purging or pumping out of stagnant water for 10 to 15 min until physiochemical features of the water were stabilized. Groundwater samples were collected in different episodes for analysis of different parameters which are labeled as Group A, B and C. The details of sampling and analytical procedures adopted are mentioned in following paragraphs:

Group A: 318 water samples (100 ml) were collected in February, 2009 from almost all the domestic wells of 15 villages for carrying out spot analysis for EC and F⁻ to demarcate the fluoride rich zones and assess the distribution and variation of F⁻ within limited terrain (Figure 2).

Group B: The water samples were collected in three events roughly representing pre-, monsoon-, post=monsoon seasons in the months of April, 2008, February, 2009 and July, 2010. The area is bestowed with both south west and north east monsoon seasons spread over from June to December. Efforts were made to collect samples from same sources in all the sampling episodes. On a few occasions, samples were gathered from nearby groundwater structures to enhance the data density. The samples were obtained from different wells representing all the hydrogeological conditions depending on the availability of wells. The total numbers of samples collected were 36 in April, 2008, 39 in February, 2009 and 26 in July, 2010. The exact location of samples pertaining to each sampling event is shown in Figures 3a to 3c. Groundwater samples from the study area were collected in pre-cleaned one-liter or 200 ml polyethylene bottle following APHA (2005) method.

Group C: In February, 2009 twelve representative samples were gathered from selected wells which have highly variable F⁻ content for carrying out trace element analysis. These samples were collected in pre-cleaned and rinsed 1000 ml PVC bottles and were acidified to pH<2 by adding the solution of 6 M HNO₃ to retain all chemical constituents (Figure 1).

Ten representative rock as well as soil samples (ten each) was collected from different locations. The samples of about 300 to 500 g containing homogeneous rock material and soil samples (at
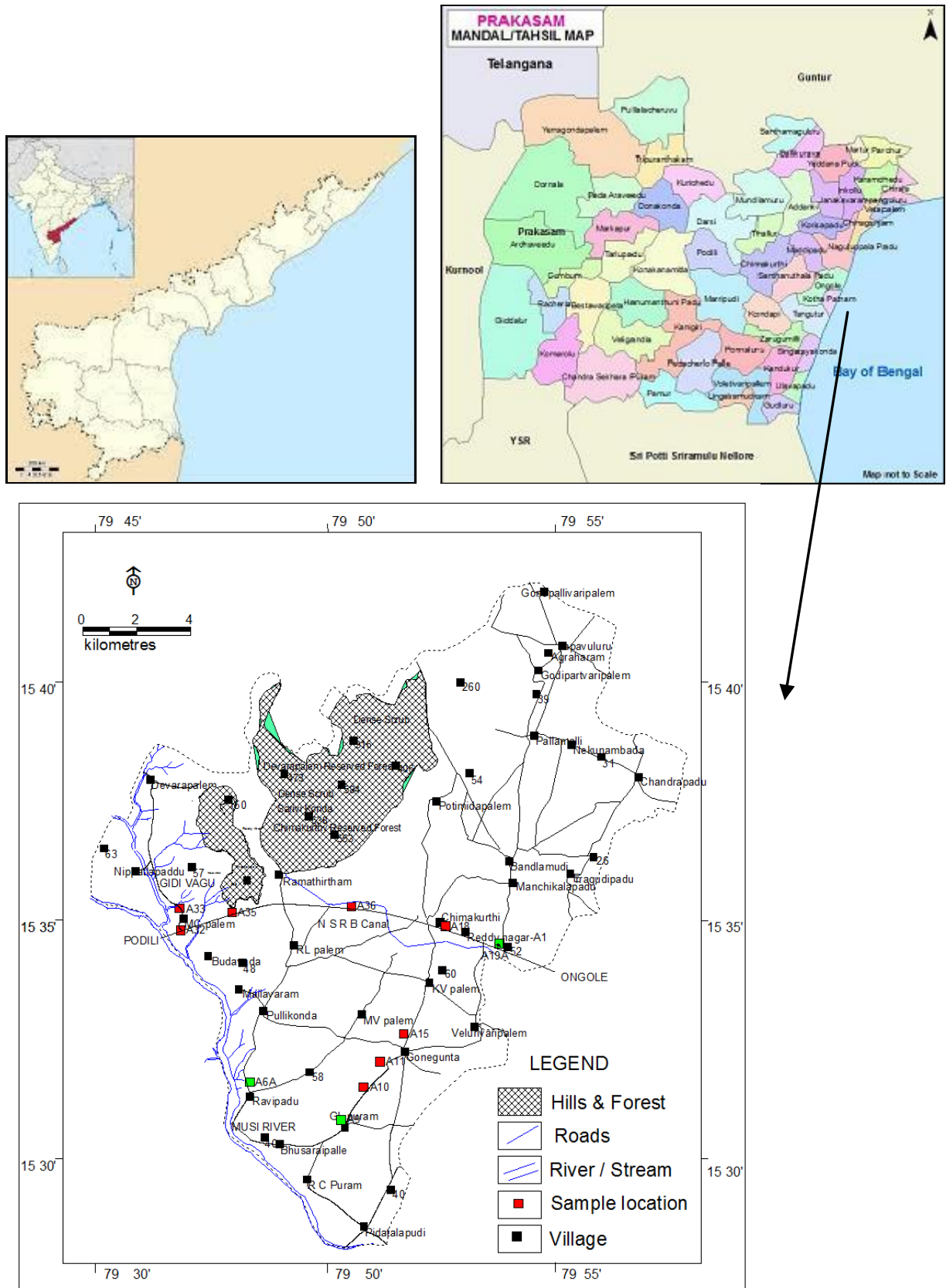
Figure 1. Key map (top), study area (above) with physiography and locations of groundwater samples for trace metal analysis. (Green color squares represent groundwater having < 1.5 mg/l F⁻ content and red > 1.5 mg/l).
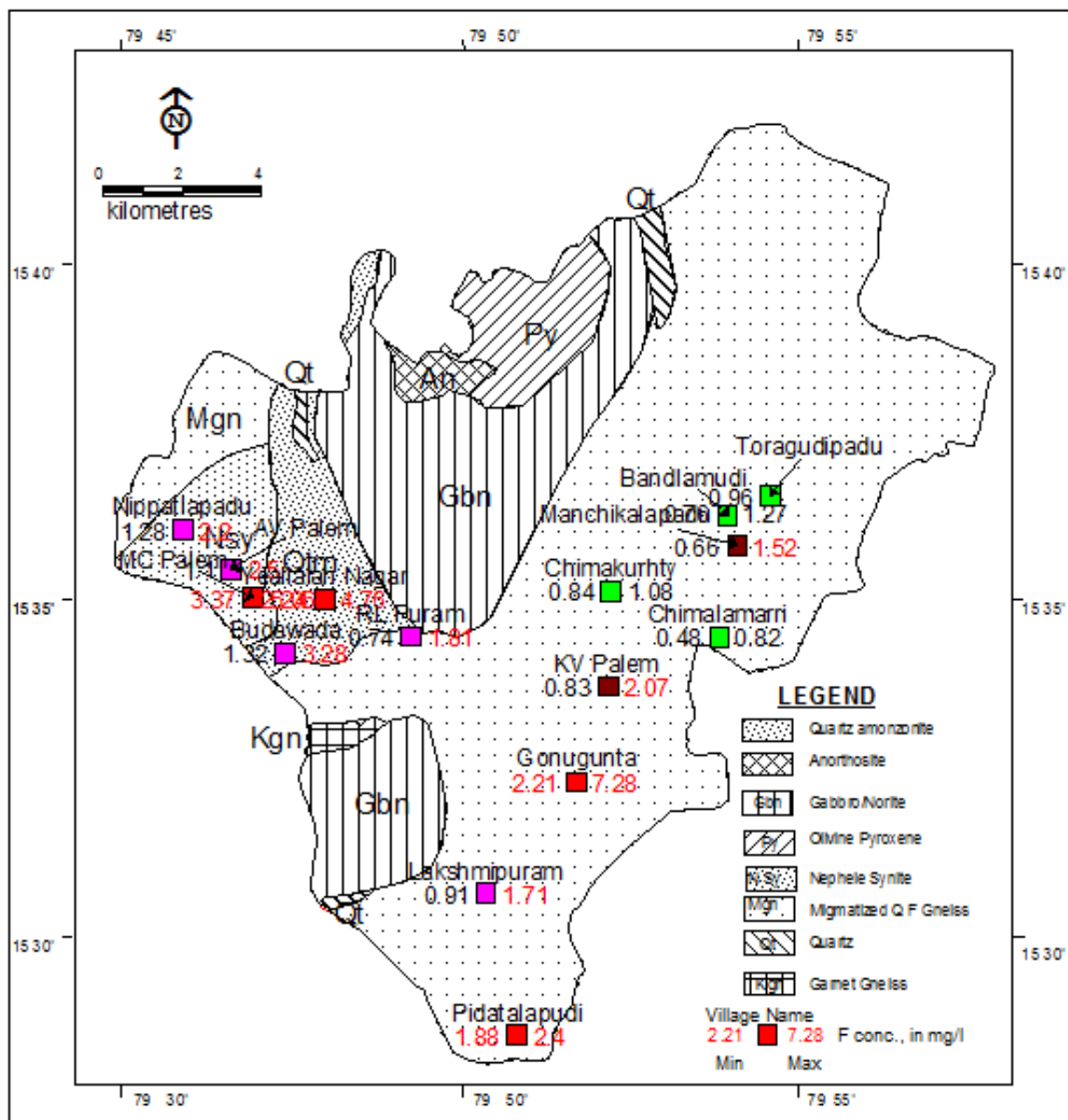
Figure 2. Range of F⁻ concentration (mean of all domestic wells) in villages of study area.

different vertical profiles) from 1 to 3 m depth below ground surface were gathered to analyze for mineral composition as well as their F⁻ content.

Analytical procedures

Three sets of hydrochemical measurements viz partial analysis, major analysis and trace element analysis were carried out on different group of groundwater samples. Water temperature, pH and electric conductivity (EC) was measured insitu during Group B and C sampling events apart from laboratory estimate. For the 318 water samples (Group A), the EC was estimated by EC/TDS analyzer, CM 183 model (2007) of ELICO make and F⁻ using the ion selective electrode of Orion 290A + (Thermoelectron

Corporation).

All the samples of Group B were subjected to major element analysis adopting APHA (2005) method. The April, 2008 samples were analyzed in the Regional chemical laboratory of Central Ground Water Board, Hyderabad. The pH was measured by using the Digital pH meter and EC by the EC/TDS analyzer, CM 183 model. The classical methods of analysis were applied for the estimation of Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^- and Cl^-. Na^+ and K^+ were analysed by flame photometry method using CL- 345 model. SO_4^{2-} was estimated by the turbidity method with the Digital Nephelo-Turbidity meter 132 model. NO_3^- was analysed applying the UV-Vis screen method by UV- visible spectrophotometer UV-1201 model. F⁻ was tested by the ion selective electrode method using Orion 290A+ model. The samples gathered in February 2009 and July 2010 was analyzed using Ion-chromatography (I C) and titration at
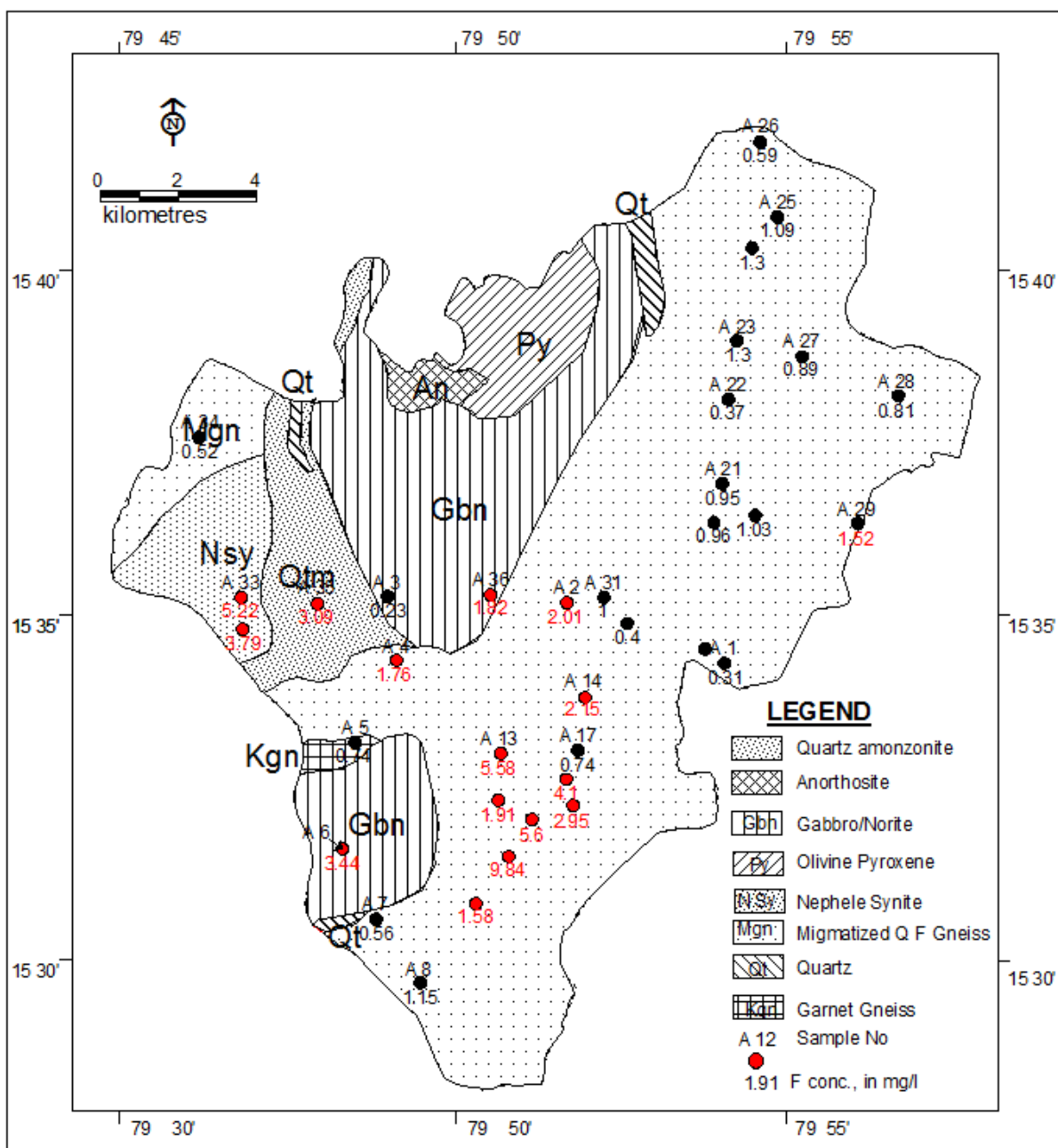
Figure 3a. Groundwater sample locations (April 2008) along with F⁻ concentration (F > 1.50mg/l are in red).

the CSIR-National Geophysical Research Laboratory (NGRI), Hyderabad. pH and electrical conductance of the water samples were measured using the Consort C533 portable multi-parameter analyzer. Carbonate alkalinity was measured by titration. Other anions and cations were measured using I C, Dionex. The quality of the analysis was ensured by standardization using blank, spike and duplicate samples. The total hardness (TH) and total dissolved solids (TDS) were estimated by calculation method (Hem, 1991). The obtained results were tested for accuracy by calculating the Normalized Inorganic Charge Balance (Huh et al., 1998). The majority of analysed samples had ionic charge balances of < +/-5%. The Group C samples were tested for 23 trace elements/metals by

inductively coupled plasma (ICP-MS) method at the CSIR-NGRI, Hyderabad in July, 2009. The soil and rock samples were analysed for major elements and total F⁻ by XRF spectrometry at the CSIR-NGRI using a Philips MagiX PRO PW2440, wavelength-dispersive XRF spectrometer coupled with a PW 2540 auto-sampler. The MagiX PRO is a sequential instrument with a single goniometer-based measuring channel encompassing the entire spectral range from F to U in the concentration range of a few mg/kg to % levels. International reference materials from United States Geological Survey (USGS), Canadian and NIST standards (SO-1, SO-2, JB-2, JP-1, G-2, and JG-1A) were used in the preparation of calibration graphs.
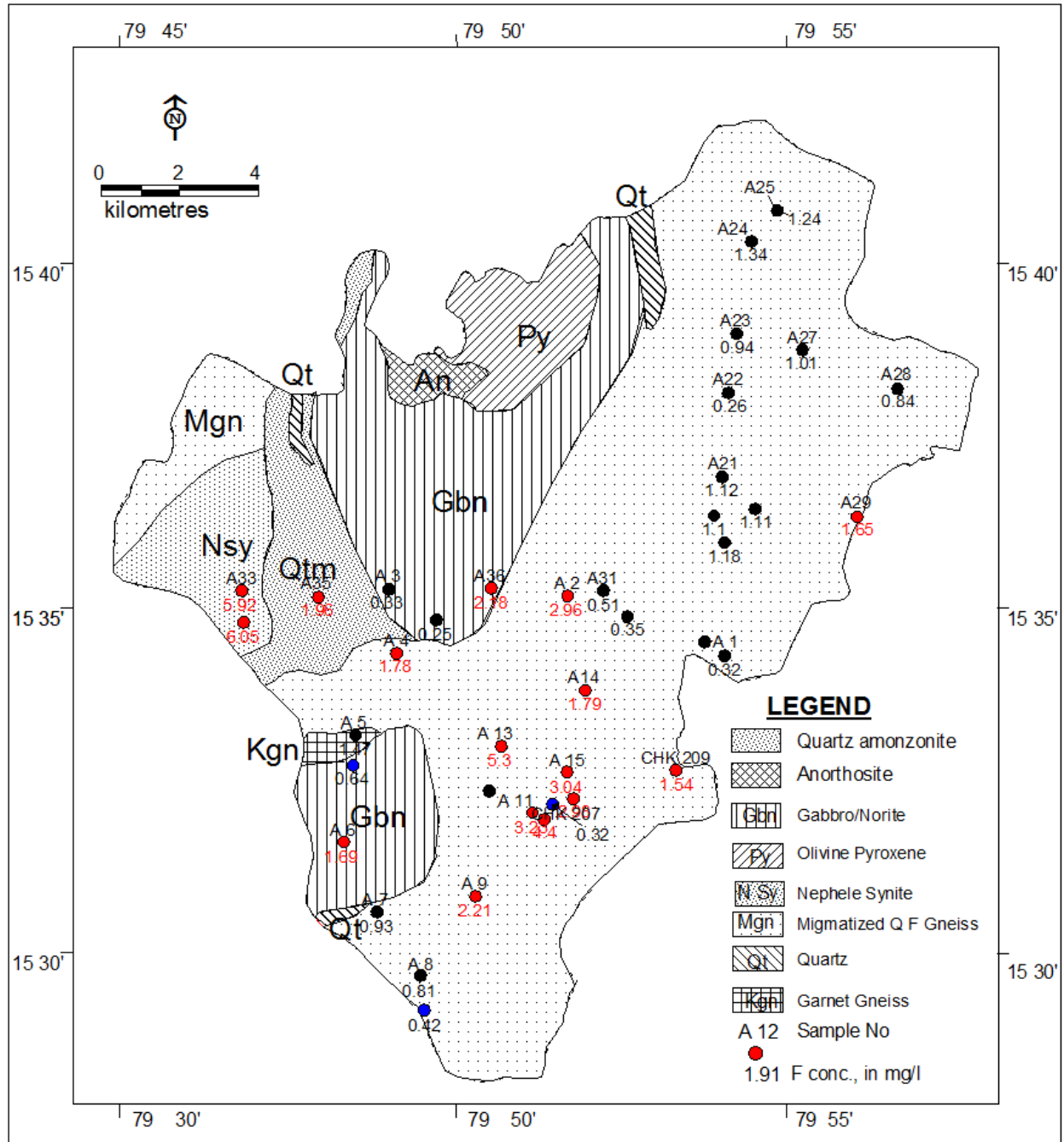
Figure 3b. Groundwater sample locations (February 2009) along with F⁻ concentration (F > 1.50mg/l are in red)

RESULTS AND DISCUSSION

April, 2008

Majority of the important chemical constituents were normal in groundwater during April, 2008 except for high F⁻ and NO$_3^-$ content. The mean values were 2.01mg/l and 118mg/l respectively. The HCO$_3^-$ was also very high (503 mg/l); more than the double value of the mean content of Na$^+$ (242mg/l). Very high standard deviation (SD) value for Cl⁻ as well as TH, SO$_4^{2-}$ and NO$_3^-$ decipher high variability of chemical constituents among analyzed samples (Table 1). The analyzed parameters data arrangement in decreasing order of F⁻ content exhibit that the results does not show any specific ionic assemblage pattern with reference to F⁻ concentration. The TDS is
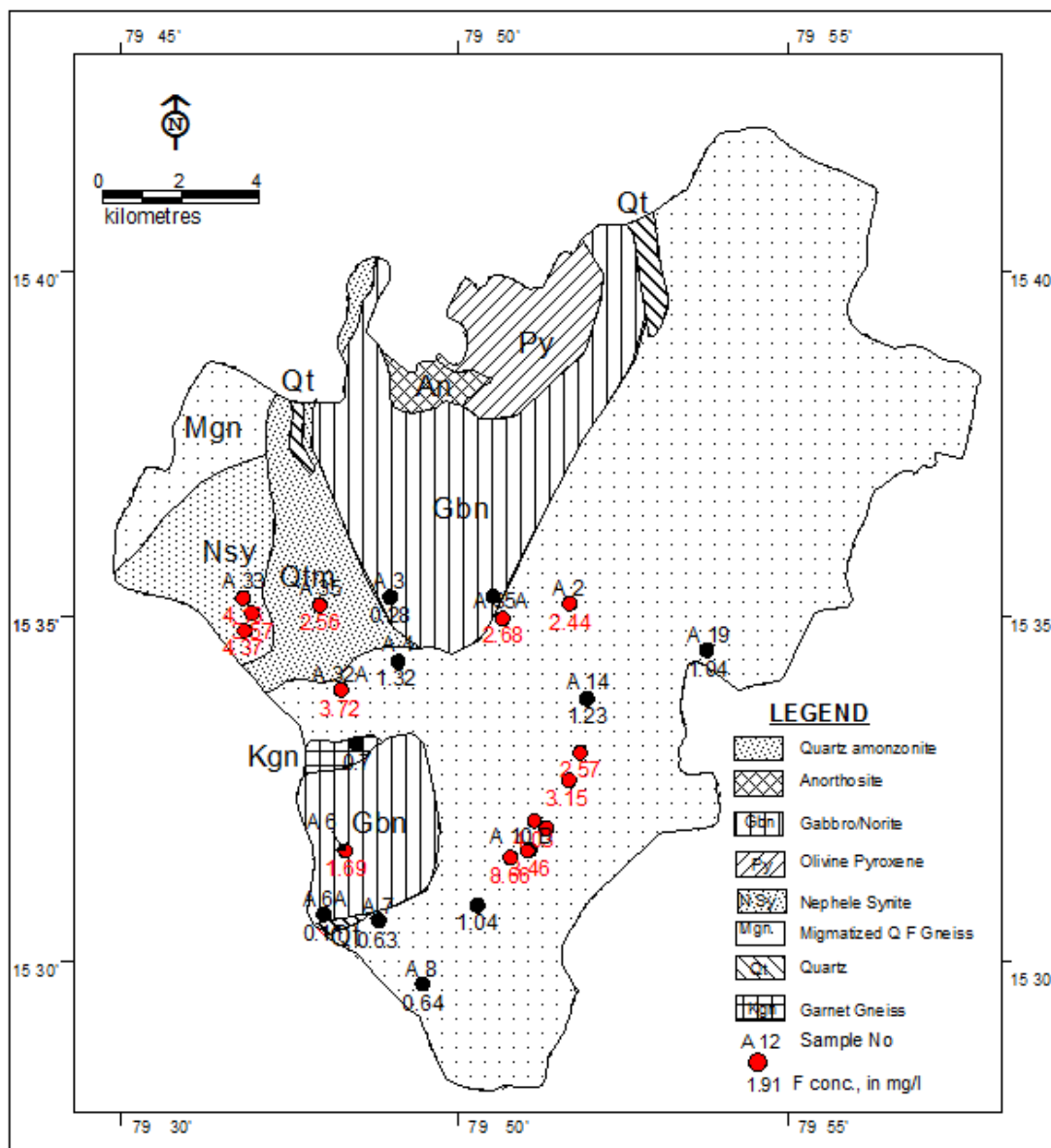
Figure 3c. Groundwater sample locations (July 2010) along with F$^-$ concentration (F > 1.50mg/l are in red).

>1000 mg/l in 31% of analyzed samples. The full results of the analysis for all sampling episodes are presented in supplemental Table 1a to c.

February 2009

The major chemistry is akin to that of April, 2008 except that F$^-$ content reduced marginally (1.71mg/l) whereas NO$_3^-$ has increased to 149mg/l and more than 50% of samples have NO$_3^-$ in above maximum permissible limit (MPL) of BIS (2012) drinking water standards (DWS). The HCO$_3^-$ content has also reduced significantly (Table 1). The variation in ionic strength among samples with

respect to Ca^{2+}, Na$^+$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$ and F$^-$ has increased substantially indicating multiple sources of ionization and solute is in thermodynamic state. The TDS is >1000 mg/l in 38% of analyzed samples which could be due to presence of extraneous elements.

July 2010

In concurrence with preceding analytical results, the groundwater in July, 2010 has high NO$_3^-$ and F$^-$ content. The mean F$^-$ being at its peak 2.44mg/l and NO$_3^-$ is above MPL of BIS (2012) DWS in >50% of analyzed samples. HCO$_3^-$ is comparatively higher than that of

Table 1. Summarized results of majour ion chemistry of groundwater in three sampling episodes.

Variable	April 2008 (n=36)				February 2009 (n=39)				July 2010 (n=26)			
	Mean	Minimum	Maximum	SD	Mean	Minimum	Maximum	SD	Mean	Minimum	Maximum	SD
pH	7.67	7.17	8.24	0.25	7.36	6.72	8.36	0.33	7.73	6.95	8.81	0.45
EC	1521	537	4610	998	1653	450	4580	1001	1589	645	3480	782
TH	385	33	1459	332	352	24	1148	277	394	17	1335	349
Ca^{2+}	67	5.72	382	75	66	4.99	292	64	82	3.04	304	79
Mg^{2+}	53	4.24	201	48	46	2.56	150	36	46	2.27	173	42
Na^+	242	39	800	157	238	36	880	200	269	46	587	155
K^+	12	0.65	137	27	15	1.20	130	26	9.24	0.92	51	10
CO_3^{2-}	20	0.00	84	10	18	0.00	63	15	21	0.00	207	50
HCO_3^-	503	262	1024	173	451	162	936	182	495	238	894	158
Cl^-	200	25	995	240	207	23	922	216	217	36	670	185
SO_4^{2-}	87	26	302	71	89	11	325	84	109	29	320	80
NO_3^-	118	1.00	837	198	149	0.21	838	176	119	0.00	500	151
F^-	2.01	0.23	9.84	0.70	1.71	0.25	6.05	1.52	2.44	0.11	8.66	1.97
TDS	1042	333	3372	740	1026	247	3432	728	1112	427	2655	588
% of samples*	44				41				61			

*Percentage of samples having F^- in > maximum permissible limits of BIS Drinking water standrads; SD: Standard Deviation. Units: EC in µ S/cm, TH to TDS in mg/l.

previous sampling episode (Feb, 2009). The deviation among concentration of different constituents is very high especially with respect to TH, Ca^{2+}, Mg^{2+}, NO_3^- and F^- (Table 1). The TDS is >1000 mg/l in 46% of analyzed samples which underline that the groundwater is more mineralized and its chemistry is altered by local and season-specific physiochemical conditions.

Ionic dominance pattern

Na^+ is the dominant cation in all the three sampling sessions constituting >50% of total cations. HCO_3^- takes similar position among anions followed by Cl^-, SO_4^{2-}/NO_3^-. The relative abundance of both cations and anions is in the order of $Na^+=HCO_3^-> Cl^-= Mg^{2+}> Ca^{2+}> SO_4^{2-}= NO_3^-> CO_3^-> K^+> F^-$. The ionic dominance pattern for groundwater resembles that of leachable ions from the soils, suggesting a lithogenic origin of minerals in the groundwater (Reddy et al., 2010; Raju et al., 2011). In April 2008, the percent ionic content of both Na^+ and HCO_3^- is same (26.55%) but Na^+ precede HCO_3^- in February, 2009 and vary significantly in July, 2010 showing fluctuating in chemical makeup of groundwater over a period or season due to change in recharge and discharge conditions (Table 2).

Occurrence and distribution of F^-

Variable distribution of F

Distinct variability can be seen in F^- content of different

samples in each sampling episode (Figure 4). F^- in sampled groundwater of all three episodes is very high (>6 mg/l) in a few (3%) samples and is low (< 0.50 mg/l) in 12% of samples but most (80%) of the samples fall in 0.50 to 6.00 range. The 20% of samples falling in the threshold level of 1 to 1.5 mg/l range could turn into potential contaminant if left unchecked. The mean F^- content of April 2008 is 2.01 mg/l and 44% of samples have it above MPL of BIS DWS. Among three sampled episodes, F^- content is high in July, 2010 (mean 2.44 mg/l) and 60% of samples have it in MPL. F concentration is marginally low in February 2009 (mean 1.71 mg/l) and a fewer (41%) samples have it in MPL when compared to other samples sessions. In general, majority of the samples except one have F^- content within 6mg/l and is very high (9.84 mg/l) at only one location (A 10) in an isolated domestic dug well which is situated far off from village in agriculture area. Consistently, high (>8 and <10 mg/l) F^- value is observed in this well. Reasons for this anomaly could not be ascertained straightaway as no distinct local hydrological or surface geological leads were visible. Apparently it can be reasoned to continuous accumulation of F^- in this perched aquifer over a long period and lack of flushing and discharge conditions as the well is on water-divide and is rarely put to use.

Spatial distribution of F

The distribution of F^- within 15 villages encompassing the study area show that it varies from 0.48 to 7.28 mg/l whereas the mean values range from 1.31 to 2.60

Table 2. % of mean ionic content in different sample episodes.

Sample episode	% conten to total cations (meq/l)				% conten to total anions (meq/l)					
	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^-	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-
April, 2008	20.82	25.06	52.82	1.30	4.45	52.94	24.31	9.35	8.31	0.65
February, 2009	22.00	23.23	52.75	2.02	4.30	46.50	28.24	9.40	11.01	0.54
July, 2010	20.77	18.21	59.74	1.28	4.02	47.11	28.43	11.27	8.47	0.71
% conten to total ion content										
April, 2008	10.27	12.42	26.55	0.65	2.24	26.54	12.15	4.68	4.18	0.32
February, 2009	10.85	11.45	26.40	1.00	2.17	23.38	14.19	4.73	5.57	0.27
July, 2010	10.62	9.31	29.94	0.65	2.08	23.41	13.95	5.55	4.14	0.36
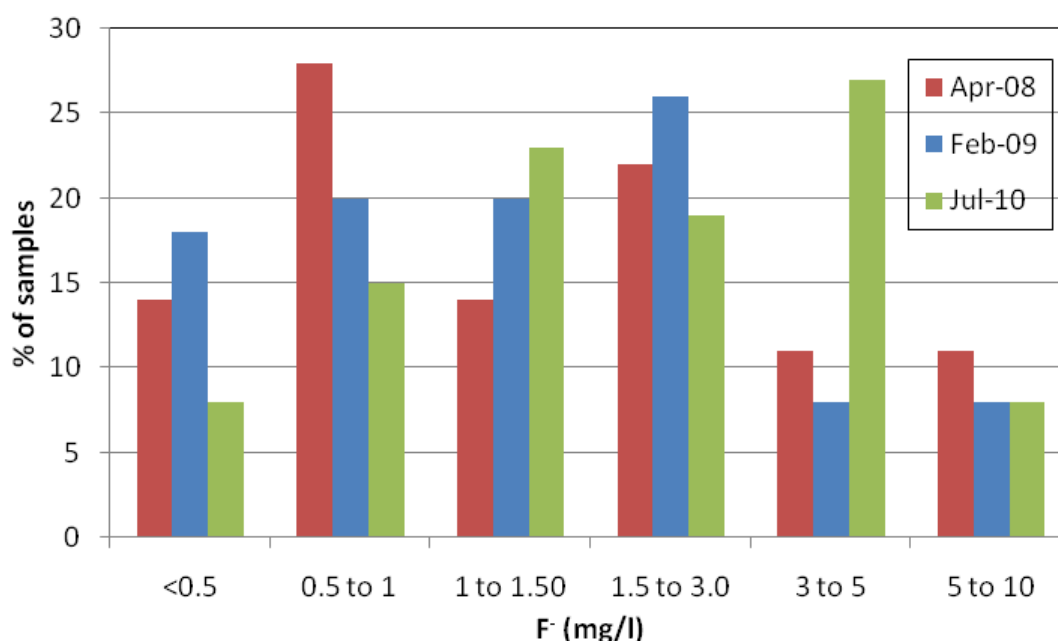
Figure 4. Frequency distribution of F^- in groundwater.

emphasizing the significant F^- enrichment (Table 3 and Figure 2). Considering the mean maximum F^- concentration in wells among 15 studied habitations, it is evident that only 4 villages have F^- content within permissible limit (1.50mg/l) of BIS drinking water standards (2012). The mean minimum data set show that eight villages have >1mg/l content of F^- and all the wells (except one) have F^- concentration >0.50mg/l indicating the groundwater in the areas is on the verge of reaching contaminant limit. Uneven distribution of F^- within an aquifer is distinctly evident as within a village F^- varies very widely (for example. from 2.10 to 7.28 mg/l in Gonegunta). In the western part, all the wells in two villages have high F^- (mean minimum is >1.50 mg/l) whereas those in adjacent villages have < 1.50 mg/l (Figure 2). Presence of varied rock types and

heterogeneous hydrogeological conditions contributes the dissimilar distribution of F^- within close proximity. The F^- content does not show any relation with specific electrical conductance (EC) of groundwater (Table 3) which emphasize that the F^- enrichment is independent of groundwater mineralization. The detail water chemistry study reveals that F^- is low in all the tested sources of northern part of the area. The southern part, which has experienced high intrusive activity, has fluoride rich groundwaters in many wells. Amidst these wells few safe sources also occur which have ~ 0.50 mg/l fluoride (Figure 3a-c). Contrasting F^- distribution can be noticed within very short distance in mid-southern part near G Lakshmipuram - Gonegunta village where the samples A 9 to A17 have F^- concentration varying from 1.58 to 9.84 mg/l (Figure 3a). As also in central part of the area F^- is very

Table 3. Results of partial analysis (EC and F⁻) of all the wells in select villages.

S/N	Broad location of village		Village	No. of samples analysed	EC (µS/cm)		Fluoride (mg/l)	
	X	Y			Min	Max	Min	Max
1	79.89750	15.57440	Chimalamarri	13	391	1670	0.48	0.82
2	79.87000	15.56243	KV Palem	67	995	340	0.83	2.07
3	79.86213	15.53874	Gonugunta	21	1090	3900	2.21	7.28
4	79.82116	15.57485	RL Puram	16	995	3450	0.74	1.81
5	79.87064	15.58593	Chimakurhty	11	655	1125	0.84	1.08
6	79.84744	15.47603	Pidatalapudi	14	530	2860	1.88	2.40
7	79.78189	15.58408	MC Palem	27	1320	4560	3.37	5.06
8	79.77660	15.59123	AV Palem	24	967	2510	1.10	2.50
9	79.76453	15.60102	Nippatlapadu	18	1435	4060	1.28	2.20
10	79.79995	15.58400	Yeallaiah Nagar	15	682	1075	2.24	4.76
11	79.79005	15.57055	Budawada	19	1195	3120	1.32	3.28
12	79.90186	15.59714	Manchikalapadu	24	769	3480	0.66	1.52
13	79.89938	15.60476	Bandlamudi	31	1329	3630	0.76	1.27
14	79.91007	15.60960	Toragudipadu	6	772	976	0.96	1.25
15	79.83972	15.51086	Lakshmipuram	12	1097	2770	0.91	1.71
-	-	1.71	F⁻ >1.50mg/l	-	-	-	-	-

Temporal variation of F

The mean content of F⁻ is fluctuating between 1.71 to 2.44mg/l whereas percent of samples above MPL vary from 41 to 60% among the three sampling episodes (Table 1). The mean F⁻ concentration is low in February 2009 and high in July 2009 among the monitored months. But the April 2008 samples show the highest F⁻ concentration (9.84 mg/l) in a dug well and also has 44% of samples above MPL of BIS DWS. The F⁻ content of samples collected from same source in three sampling episodes show mixed trend, many samples exhibit distinct variation (rise or fall) but few do not show much difference over a year (supplemental Table 2). The negative percentage variation in February 2009 and July 2010 is distinct as many samples show reduced F⁻ concentration which can be attributed to dilution due to fresh influx of monsoon recharge waters but a contradicting phenomenon was noticed in Wailpally watershed having similar hydrogeological conditions (Reddy et al., 2010). The unique feature of erratic occurrence and distribution of F⁻ both geographically and over a period even with short span is making the task of demarcating the contaminated zones very difficult or near impossible. But the silver-lining is that few isolated potable water sources can be located within the F⁻ infested areas due to this uneven distribution character. Apart from the groundwater chemistry, hydrological

properties (for example, residence time) as well as climatic conditions (for example, evapotranspiration, precipitation) and soil conditions (for example, pH, soil type) have an influence on fluoride concentration. Hence, the spatial and temporal heterogeneities of fluoride concentrations in groundwater are particularly large (Manouchehr et al., 2008).

Inter-relationship of F⁻ with co-chemical constituents

Correlation matrix

The summarized results of correlation (limiting to F⁻) of three samples episodes ascribe a fairly significant positive relation of F⁻ with pH, Na⁺, HCO₃⁻ and negative correlation with Ca²⁺, TH, Mg²⁺. The positive relation, with pH and bicarbonate indicates an alkaline environment, as a dominant controlling mechanism for leaching of fluoride from the source material (Subba, 2009, 2011). Positive correlation between HCO₃⁻ and F⁻ suggests that this may be an additional control factor on F⁻ enrichment (Mondal et al., 2014). Similar relationship is observed in each of the sampling episode among select parameter pairs (Table 4). These correlations are in tune with proven F⁻ groundwater chemistry. F⁻ is more aligned with pH (r=0.57) in April, 2008 than those of others. Similarly, February 2009 samples show high positive relation among F⁻-Na⁺ (r=0.68) and F⁻-HCO₃⁻ (r= 0.61) whereas in July 2010 it is reduced to ~ 0.44, correspondingly the F⁻-SO₄²⁻ relation is distinctly different (r= 0.03) than that of April 2008 (r= 0.38) and February 2009 (r= 0.32). Mixed correlation of F⁻-CO₃⁻ among three observed periods is

Table 4. Summarized results of correlation matrix for F- and other parameters.

Parameter	April, 2008	February, 2009	July, 2010
pH	0.57	0.37	0.31
EC	0.16	0.25	0.13
TH	*-0.34*	*-0.16*	*-0.25*
Ca^{2+}	*-0.28*	*-0.22*	*-0.31*
Mg^{2+}	*-0.32*	*-0.06*	*-0.14*
Na^+	0.55	0.68	0.44
K^+	*-0.08*	*-0.09*	*-0.09*
CO_3^{2-}	0.41	0.53	*-0.02*
HCO_3^-	0.44	0.61	0.43
Cl^-	0.06	0.28	0.10
SO_4^{2-}	0.38	0.32	0.03
NO_3^-	*-0.18*	*-0.03*	*-0.17*
F^-	1.00	1.00	1.00

0.68 Pasitive correlation (r=>0.60); (-) *0.28* Negative correlation (r=<0).

incongruent. Though F⁻ is feebly correlated with many ions, the correlation does not follow any particular pattern or alignment as its genesis into groundwater is independent and governed by geochemical environment and host rock mineralogy.

Cross-plots

Cross plots of F⁻ with selected analyzed parameters exhibit similar behavior of associated chemical species with respect of F⁻ in all the sampled episodes. F⁻ is showing distinct positive trend with pH (Figure 5a), EC (Figure 5b), Na⁺ (Figure 5e) and HCO₃⁻ (Figure 5f) and a scattered or uneven behavior is noticed in F⁻ vs Cl⁻ (Figure 5g) as well as Mg²⁺ (Figure 5d) plots. F⁻ concentration having the near linear relationship with Cl⁻ validate fluoride concentration in groundwater in arid and semiarid regions promoted by evaporation and evapotranspiration (Jacks et al., 2005).

The relation of F⁻ with pH is in agreement with general trend substantiating pH has a greater control on water soluble F⁻ content and confirms that much greater F⁻ was desorbed at pH 10, than those in pH 5 (Mondal et al., 2014). High F⁻ in the groundwater (>1.20 mg L⁻¹) is characterized by pH more than 8.0 (Subba, 2011). The positive trend between EC and F⁻ especially within 1000 to 2000 µS/cm range (Figure 5b) substantiates that F⁻ is aligned with other anions and multiple hydrogeochemcial processes have favored the enrichment of F⁻ in aquatic medium in association with co-related species. Water samples with higher F⁻ concentrations observed to have higher pH and EC values leading to the increase of F⁻ solubility in groundwater (Rose et al., 1979; Perel'man, 1977; Rafique et al., 2009).

The influence of aqueous ionic concentrations of groundwater in the solubility of F⁻ can be deduced from Figure 5b, c, d and e. Weakly positive correlations are observed in regression plots of F⁻ versus Na⁺ and HCO₃⁻ (Figure 5e and f) in the presence of excessive sodium bicarbonates in groundwater the dissociational activity of fluoride will be high (Saxena and Ahmed 2003). The high HCO₃⁻ bearing water has alkaline nature, which favours the higher mobility of F⁻ ions in the groundwater (Mondal et al., 2014). A moderate positive trend of F⁻ with SO₄²⁻ (Figure 5h) points out that the gabbro, norite, pegmatite and migmatized granite gneiss could have contributed these ions as the intrusive rocks are rich in pyrite and apatite, mica etc. Ca²⁺ and Mg²⁺-F⁻ (Figure 5c and d) is negatively aligned with proven concept. Such negative correlations suggest that the low Ca²⁺ and Mg²⁺ concentrations lead to occurrence of highly F⁻ containing groundwaters. High F⁻ and very low Ca²⁺ and Mg²⁺ in water may be due to prior precipitation of CaCO₃ from water and only limited incorporation of F⁻ in the CaCO₃ structure, so that there is always a net balance of F⁻ in solution (Kundu et al., 2001). Low Ca²⁺ and high Na⁺ concentrations could be explained by the cation exchange reaction in which Ca²⁺ originally in the water has been exchanged by Na⁺, or removed due to precipitation of carbonate minerals under high alkalinity (Nickson et al., 2005).

A unique feature in the cross plots is that the behavior of F⁻ with respect of the tested parameters is dissimilar in samples having higher F⁻ concentration (>6mg/l-Fig. 5a-h). These samples does not follow the general trend and are seclude specifying that the higher F⁻ concentration in groundwater could be due to later addition because of ascending water-weathered mantle/soil interaction as the solute is in un-saturation and hydrodynamic state
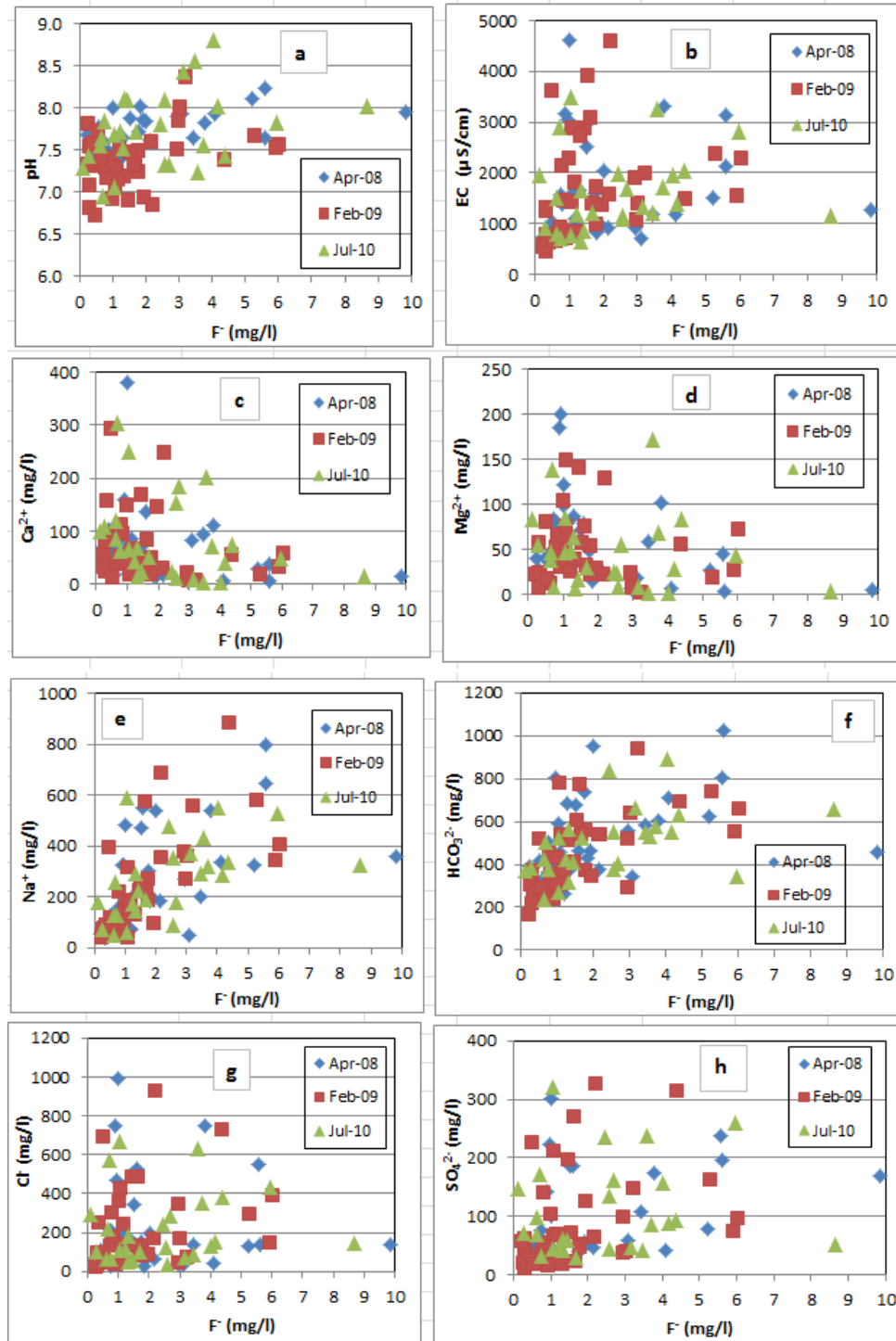
Figure 5a-h. Scatter plots of F- vs paramaters.

facilitating absorption of more F-.

Water facies

Groundwater is evaluated for water facies classification

by plotting all the three episode samples in Piper plot (Hill 1944). The samples of can be distributed into five distinct groups (Figure 6 and Table 5). Majority of samples (mean of three episodes 29%) belong to Na^+-HCO_3^--Cl^-/CO_3^{2-} type followed by Na^+-Mg^{2+}-Ca^{2+}-HCO_3^--Cl^-/SO_4^{2-} type (26%). About 18 to 15% of samples belong to
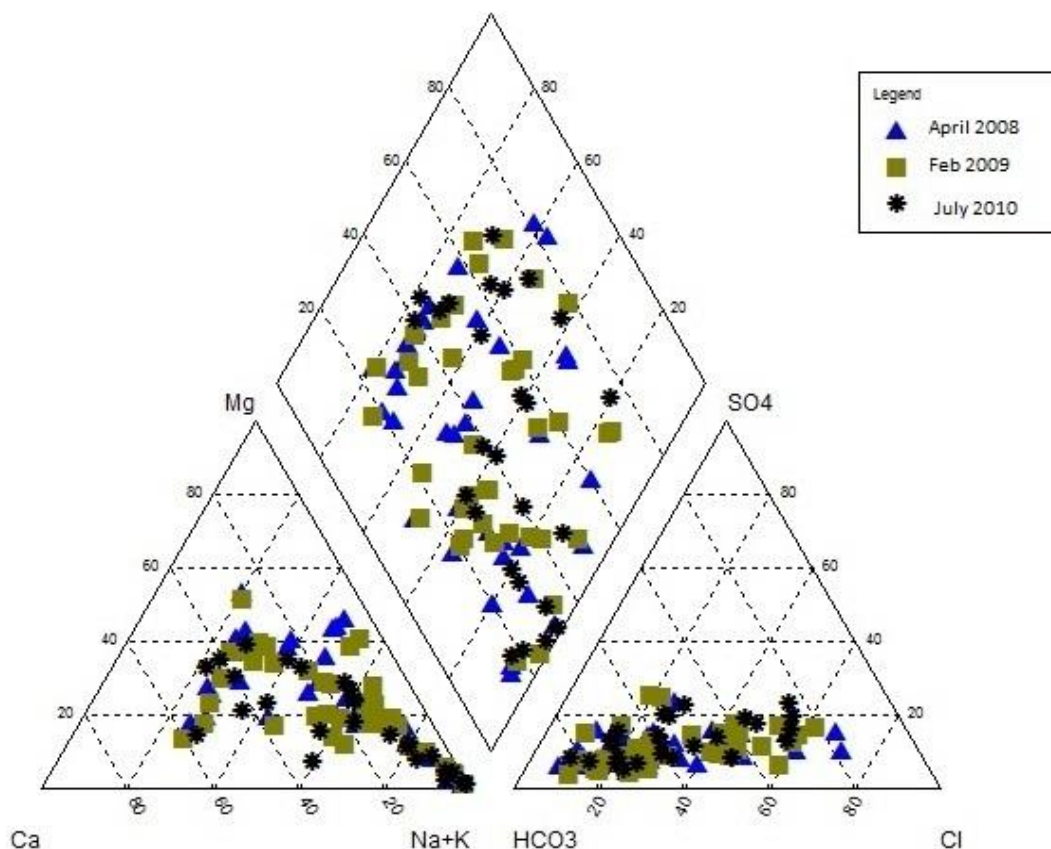
Figure 6. Groundwater samples of three sampling episodes plotted in piper diagram.

Table 5. Classification of groundwater based on Piper plot.

S/N	Water types	% of samples			
		April, 2008	February, 2009	July, 2010	Mean
1	Na^+-HCO_3^--Cl^-/CO_3^{2-}	25	23	38	28.67
2	Na^+-Mg^{2+}-Ca^{2+}-HCO_3^--Cl^-/SO_4^{2-}	28	26	23	25.67
3	Ca^{2+}-Mg^{2+}/Na^+-HCO_3^-/Cl^-	19	13	23	18.33
4	Na^+-Ca^{2+}/Cl^--HCO_3^-/NO_3^-	9	23	12	14.67
5	Mg^{2+}-Ca^{2+}/Na^+-HCO_3^-/Cl^-	19	15	4	12.67

Ca^{2+}-Mg^{2+}/Na^+-HCO_3^-/Cl^- and Na^+-Ca^{2+}/Cl^--HCO_3^-/NO_3^- water facies. The water specie classification is in conjunction with F^- concentration in different episodes. In July 2010, 38% of samples fall in sodium-bicarbonate-chloride category and 31% of samples have F^- concentration in 3-6 mg/l range. Similar inter-dependent relation is evident in other sampling episodes implying active role of Na^+-HCO_3^--Ca^{2+} in F^- enrichment. Na^+-HCO_3^--Cl^- type water could confine to the area as a discharge zone (supplemental Fig. 1). High-fluoride groundwaters are mainly associated with a sodium-bicarbonate water type and relatively low calcium and magnesium concentrations (Brunt et al., 2004).

Trace element study

Trace element and metal composition of groundwater samples having variable concentrations of F^- is measured to have an insight into the source of contaminant and geochemical processes involved in the enrichment of F^- in entrapped water. Among 23 trace elements that are analysed for, Zn is the most dominant having a mean content of 3200 µmg/l followed by Al and Sr (Table 6). Fe, the most common constituent of mafic rich rocks is 627 µmg/l, whereas Cu is 142 µmg/l, and Pb 85 µmg/l. Many rare earth elements are in <10 µmg/l concentration. The variation in trace element content among samples

Table 6. Trace elements and metals content along with F⁻ of select groundwater samples.

Sample No.	Li	B	Be	Al	Si	V	Cr	Mn	Fe	Ni	Co	Cu
						μmg/l						
A6A	0.28	154	0.34	2042	30.27	61.39	7.27	99.87	631	32.12	11.22	83.26
A9	26.98	909	0.60	2884	35.83	74.43	14.13	55.43	1153	77.20	4.63	106.35
A9A	3.22	162	0.06	852	31.54	10.56	6.72	31.26	708	76.46	1.39	615.41
A10	7.92	387	0.38	2065	21.44	16.01	7.99	47.58	539	35.50	2.41	98.21
A11	3.88	734	1.03	2978	28.20	367.09	14.41	141.38	979	73.89	12.27	122.88
A15	4.19	393	0.18	1169	23.19	622.12	10.93	45.46	547	32.26	2.37	64.26
A18	7.47	311	0.34	1398	34.94	219.77	11.00	50.13	687	33.58	1.64	134.45
A19A	5.87	149	0.56	1619	32.76	109.89	12.76	79.20	522	50.75	3.26	130.09
A32	9.79	301	0.14	1268	36.41	44.69	14.99	39.08	463	35.56	1.49	118.57
A33A	8.07	257	0.18	1743	35.57	52.78	9.60	56.73	472	48.39	2.81	106.95
A35	7.41	117	0.16	1276	24.92	19.00	9.34	30.21	500	43.89	1.47	72.50
A36	3.83	170	0.14	1095	29.29	306.09	7.39	23.73	328	26.94	0.88	52.43

Sample No.	Zn	As	Se	Rb	Sr	Mo	Ag	Cd	Sb	Ba	Pb	F⁻
						μmg/l						mg/l
A6A	2333	2.64	5.61	8.30	856	1.77	2.07	1.76	0.62	406	76.76	0.11
A9	2468	8.98	50.50	14.83	7310	3.65	2.68	2.18	1.00	329	92.73	2.11
A9A	13779	2.38	5.89	5.04	1565	1.22	0.53	0.34	0.70	314	129.03	0.74
A10	2486	2.59	3.83	7.86	685	20.77	1.28	1.79	0.50	320	80.26	8.66
A11	1675	72.04	8.15	8.01	231	38.32	0.82	2.43	0.35	150	107.64	3.23
A15	1472	16.89	5.49	6.22	374	11.57	1.57	1.45	0.41	165	65.04	3.04
A18	1574	5.33	9.03	8.57	861	8.59	1.14	1.71	0.54	582	69.18	0.35
A19A	2818	3.85	5.01	6.47	1267	2.20	2.48	2.07	0.43	368	86.70	1.04
A32	4744	5.96	13.64	13.75	1981	2.80	1.20	1.85	0.66	455	68.94	6.05
A33A	2739	5.93	9.50	7.89	1081	5.79	4.31	1.95	0.60	257	130.13	4.16
A35	1575	2.67	5.41	7.35	753	3.10	2.38	2.44	0.72	200	65.86	1.96
A36	736	13.06	4.47	4.94	563	2.25	1.29	1.07	0.41	140	43.43	2.18

having low F⁻ (<1.50 mg/l; mean 0.56 mg/l) and those having high F⁻ content (>1.50 mg/l mean; 3.92 mg/l) is distinct in about half of the tested trace elements. The mean concentration of Li, B, Al, V, Cu, Zn, As, Se, Sr, Mo and Ba in two sets of samples (Table 6) varies widely indicating F⁻ enrichment is independent of many trace elements. Influence of trace element content on F⁻ absorption is further probed by plotting three categories of samples based on F⁻ different concentration (Figure 7). Few trace elements for example, Li, V, Co show distinct variation in their strength. But in general the mean concentration of many trace elements is comparable among three sets of samples. Similar concentration of certain trace elements in both sets of samples could be due to fact that the groundwater F⁻ adsorption into formation water is the latest geochemical process. Groundwater might have gained F⁻ from host rock during sluggish transit though feebly fractured pathways. Capillary upward movement followed by influence of evapotrapiration could have facilitated enhancement of F⁻ in groundwater.

Geochemistry of rocks and soils

Chemistry of country rocks indicates that silica, aluminiun, iron, manganese, calcium are present in order of abundance (Table 7). Oxides of Na and K are unusually in low concentration since fluoride is expected to be contributed from feldspar rich rocks like pegmatites, pink granites, migmatites etc. The rock chemistry does not exhibit any relation between its fluorite and constituent mineral composition. But fluorite varies from very high (258 ppm) to as low as (12.82 ppm). Similar concentration is noticed in groundwater samples collected from nearby wells, ensuring that fluoride in water originated from associated country rocks. Incomparable content of fluorite with other minerals in tested rocks point out that F- mineral present as accessory minerals must have crystallized in later stages of magma consolidation thus occur as an independent entity. Prominent presence of F⁻ rich groundwater at contact zones further indicates that migmatization and intrusive rock reaction with country rocks resulted in
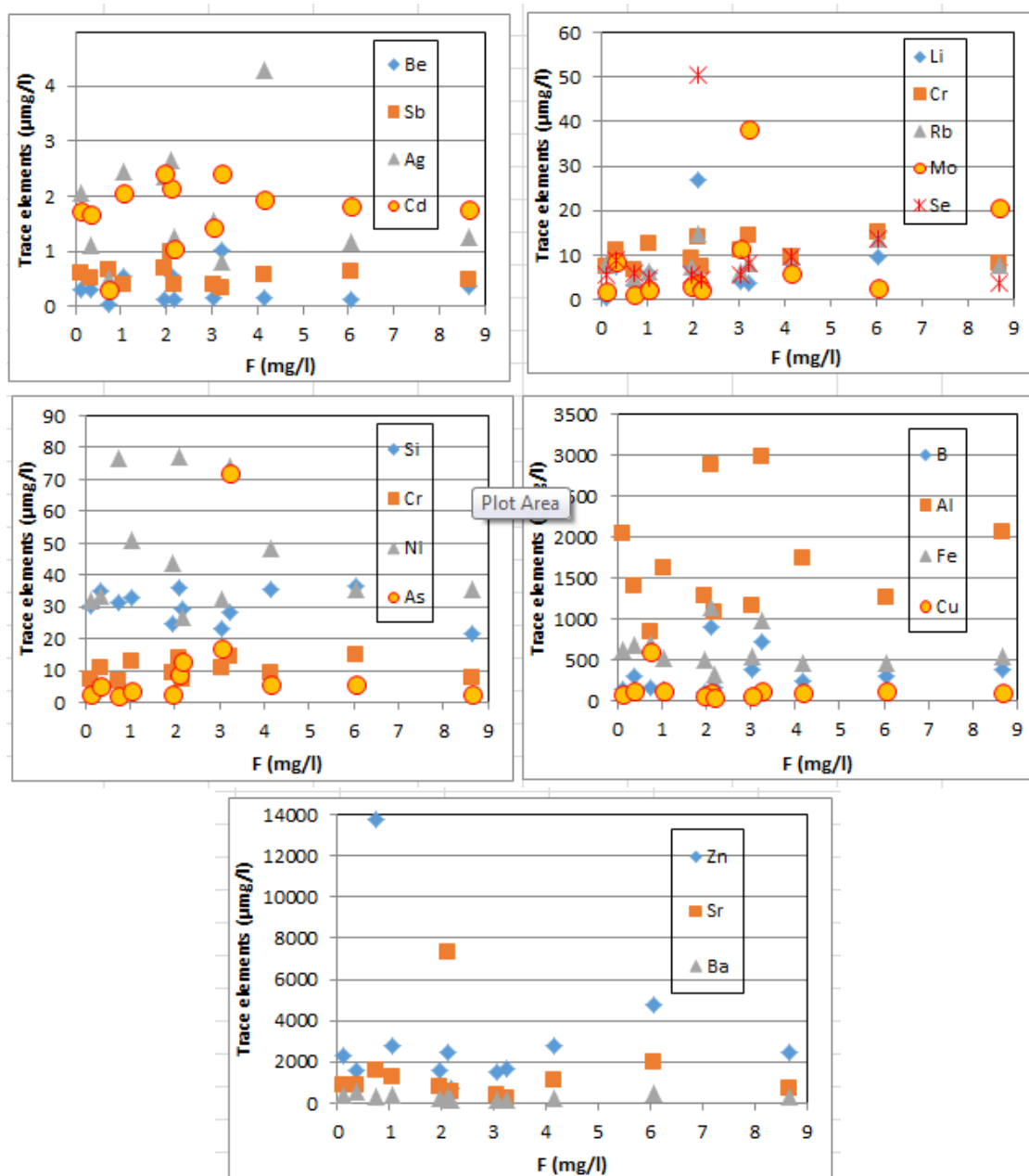
Figure 7. Scatter plot of F- vs trace elements and metals.

development of F- minerals. The fluorine got accumulated in hydrothermal solutions. These fluids may form hydrothermal fluorite deposits and veins (Allmann and Koritnig 1974; Brunt et al., 2004). Preliminary statistical analysis showed that fluoride concentrations decreased with increasing distance from intrusive felsic rocks or extensional tectonic activities (Manouchehr et al., 2008). Low alkali metals especially potassium (mean K_2O - 2.43%) substantiate that intrusive and melanocratic rocks have also added fluorite to interstitial water. Apart from associated rocks, the origin of F- into groundwater could

be from deep meteoric sources as fluorite is not detected in some rocks samples collected near the wells having high F- content. Conflicting occurrence of F- in some water and rock samples also confirms that groundwater is getting saturated with F- in deeper horizons under confined hydrological conditions if adequate F- minerals are available in aquifer material. Dissimilar distribution of F- in water and associated rocks even in close proximity (Table 7 sample No A 15/1 and A15/2) might be due to variations in solute chemistry which control the ion adsorption capabilities.

Table 7. Chemical composition of rock, soil along with F⁻ content of closeby groundwater samples.

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	U	Th	F⁻	F⁻
	(%)												ppm	
Rock samples														GWS
A10	55.22	16.73	7.59	0.11	4.04	3.00	4.03	6.12	0.77	0.42	6.66	13.79	258.25	9.84
A33	44.87	15.55	7.01	0.10	15.13	12.14	2.83	0.38	0.61	0.10	3.35	ND	ND	5.22
A15/1	44.62	11.19	12.93	0.18	15.02	8.96	2.40	1.45	1.25	0.18	5.21	ND	285.08	4.10
A15/2	56.22	16.16	7.53	0.11	4.27	2.84	3.88	6.07	0.78	0.42	3.58	16.55	201.85	4.03
A6	44.01	16.20	7.78	0.10	15.70	11.25	2.71	0.44	0.39	0.07	3.35	ND	ND	3.44
A35	62.78	16.54	5.48	0.12	0.34	1.79	4.54	6.54	0.54	0.16	1.47	ND	492.08	3.09
A9	47.12	22.83	6.68	0.08	6.19	12.29	2.57	0.38	0.69	0.03	3.70	ND	ND	2.21
A36	49.84	16.83	8.32	0.11	8.87	10.59	2.69	0.60	0.79	0.26	5.36	ND	13.31	2.18
A36/A	48.88	16.85	8.82	0.12	8.72	10.79	2.78	0.59	0.74	0.14	7.76	ND	12.82	1.82
A8	44.82	14.35	8.16	0.15	14.85	7.91	3.67	1.73	2.24	0.73	2.98	ND	ND	1.15
Soil samples														GWS
A10	41.89	8.06	2.05	0.06	0.17	6.90	1.37	3.08	0.15	0.06	0.09	ND	56.51	9.84
A11/2	21.89	1.76	1.16	0.08	0.11	45.30	0.36	0.17	0.10	0.03	2.16	ND	ND	6.60
A32	47.85	6.48	1.69	0.06	ND	4.71	1.62	2.50	0.48	0.02	7.80	7.45	ND	6.05
A11/1	31.05	4.10	2.17	0.21	0.70	26.03	1.08	0.67	0.34	0.05	4.54	ND	14.28	5.60
A33	43.49	6.67	2.50	0.09	1.19	6.41	0.99	1.36	0.63	0.05	2.91	ND	383.20	5.22
A15	33.53	4.79	3.14	0.06	1.68	23.90	0.26	0.26	0.46	0.03	1.76	ND	278.90	4.10
A6	33.51	8.97	5.93	0.09	2.11	9.24	1.25	0.27	1.74	0.04	1.83	ND	299.68	3.44
A35	43.41	9.93	3.53	0.07	ND	1.09	1.48	2.91	0.47	0.04	1.10	ND	611.78	3.09
A9/1	21.35	2.59	1.54	0.02	0.15	43.19	0.18	0.08	0.15	0.02	0.49	ND	ND	2.21
A36	38.63	6.50	4.13	0.13	2.31	10.22	0.82	0.50	1.02	0.07	5.70	ND	91.04	2.18
A9/2	15.36	0.48	0.69	0.01	ND	0.41	0.53	0.01	0.03	0.00	ND	25.03	ND	1.58
A8	23.92	2.41	2.04	0.05	0.63	37.99	0.18	0.31	0.33	0.04	1.93	ND	276.06	1.15

ND: Not detected; GWA: Groundwater samples collected close to rock/soil samples.

Soil chemistry is in conflict to that of rock composition and many constituent ion oxides are present in reduced concentration except CaO which is >100% than that of the rock samples (Table 7). Significantly lesser content of many metallic oxides in soil than those of associated rocks could be due to deferential weathering pattern and many minerals in rocks are resistant to prevailing weathering process. MgO is distinctly low (1%) in soil samples though the associated rocks have it to the tune of ~9% of whole rock composition. It could be due to resistant Mg minerals and up taking by plants. Favorable carbonate dissolution geochemical environment might be responsible for Ca^{2+} enrichment in soils than rocks. Semi-arid climate and severe summer could be supporting dissipation of carbon minerals leaving remnants of silicate mineral residue.

Occurrence of lime nodules beneath the top soil indicates prevalence of high carbonate dissolution. Higher F⁻ content in soil can be
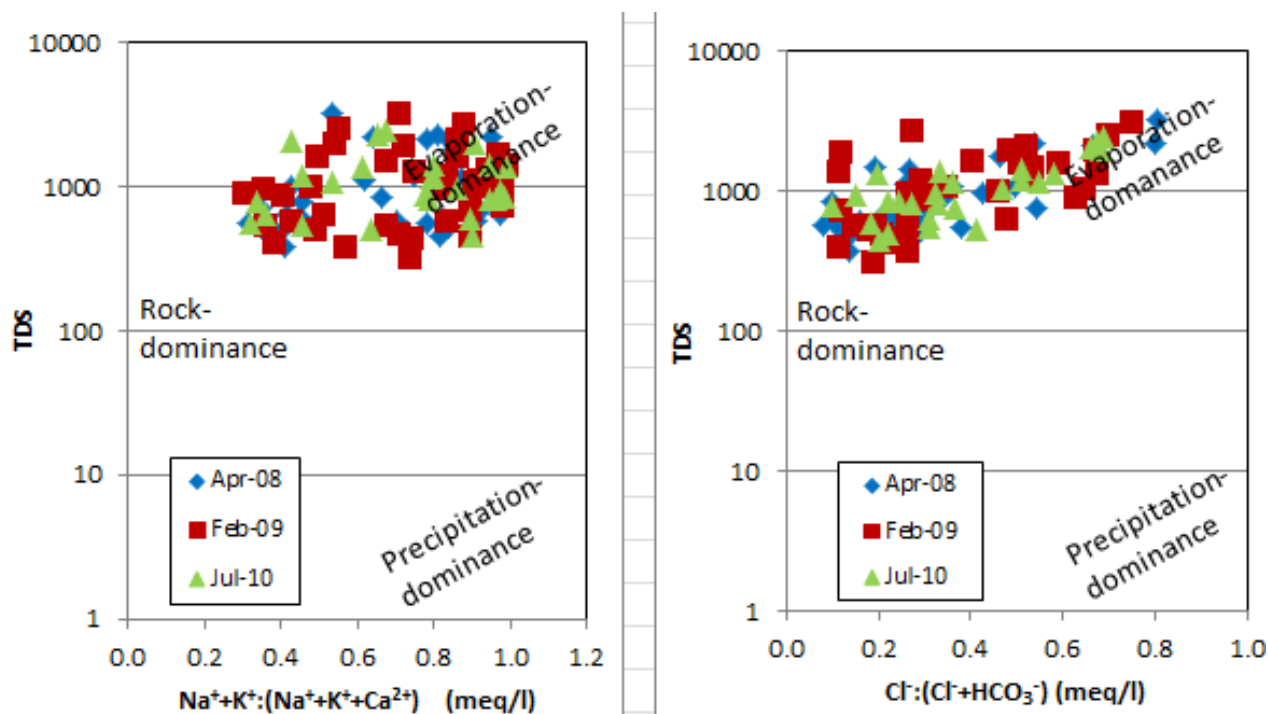
Figure 8a and b. Gibbs plots.

accounted for active weathering process and also redistribution and subsequent deposition of F$^-$ by percolating water. Fluorides are very immobile in soil and are not easily leached from it (http://www.greenfacts.org). Discordant content of F$^-$ in soil and nearby groundwater samples specify that groundwater is gaining F$^-$ from aquifer material in deeper horizons and attaining saturation. Intermixing of percolating water is adding F$^-$ to groundwater which was further enhanced by evapotranspiration (Reddy et al., 2009; Reddy 2012). High fluoride and EC in shallow aquifers originate from evaporative enrichment (Gupta et al., 2005). Sample 10 is classic example of this assumption. Its F$^-$ concentration in groundwater is 9.84 mg/l, rock sample is 285 ppm whereas for soil it is 56 ppm. On the contrary, the sample 33 has 5.22 mg/l for groundwater, and is not detected in rock sample but in soil the F$^-$ is 383 ppm. Similarly, close examination of chemistry of rock-soil samples show contradictory relation (% variation range from +98 to 0 to -380) validating soil chemistry in evolving stage also is receives mineral load from surface runoff. Lack of sequential distribution of F$^-$ in different geological media (rock-soil-groundwater) underlines erratic behavior of F$^-$ and multiple processes are involved in its enrichment (Mondal et al., 2014). It also signifies that solute chemistry is one of controlling factors in F$^-$ captivation into interstitial waters (Habes et al., 2014). The process of adsorption and dispersion of fluoride species in the soil as well as lateral mixing of groundwater along specific flow-paths control the groundwater fluoride and ^{18}O composition

(Datta et al., 1996).

Hydrogeochemical process

Gibbs (1970) plots substantiate that aquifer material played a dominant role in genesis of F$^-$ into groundwater which was further aggravated by evaporation process as evident in TDS vs select cations plot (Figure 8a). In the Figure 8b, where TDS vs select anions were plotted, the sample points spread over rock dominance to evaporation dominance fields but more inclined towards rock dominance zone. All samples points belonging to three episodes follow the similar pattern and confirm that country rock mineralogy contributed F$^-$ to entrapped groundwater (Figure 8a and b). Sluggish flow in these relatively flat regions enables sufficient rock-water interactions (Sajil, 2013). Role of aquifer material in F$^-$ enrichment can be further illustrated by calculating chloro-alkali indices (CAI-1 and CAI-2; Schoeller 1977) which relates the ion exchange process between groundwater and aquifer material. Contrasting values are obtained for CAI 1 and CAI 2 indicating multiple processes were involved in evolution of groundwater chemistry. More than half of the samples have positive CAI-1 values whereas CAI-2 is negative in more than 80% of samples in all the observed seasons (Figure 9a and b). The indices indicate that both ion exchange and reverse exchange processes were involved between Na$^+$-K$^+$ in water with Ca^{2+}-Mg^{2+} in host rock and vice-versa.
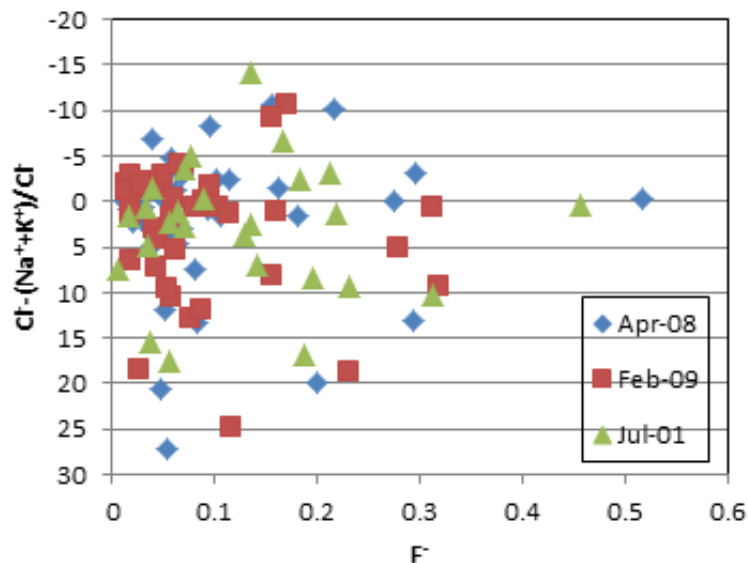
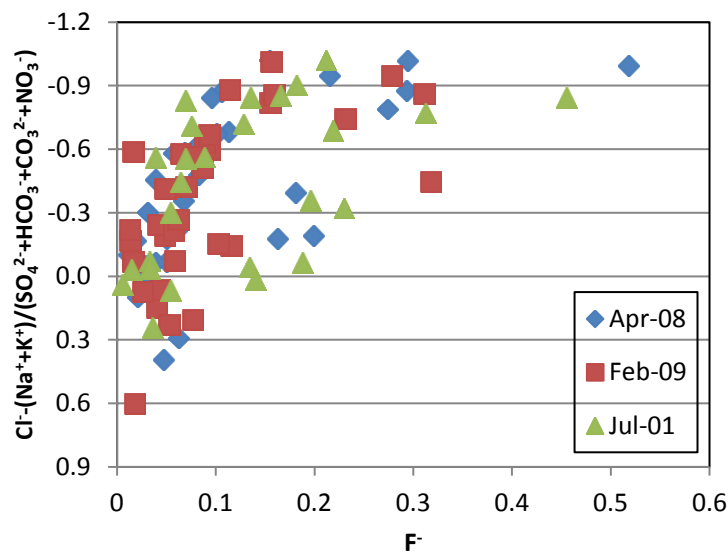**Figure 9a.** Cross plot of F⁻ vs CAI-1 (meq/l).

Figure 9b. Cross plot of F⁻ vs CAI-2 (meq/l).

The CAI-2 ratio has stabilized at 0.80 meq/l after F⁻ attaining 0.01 meg/l and sample points run parallel to x-axis (Figure 9b) and in Figure 9a similar situation can be seen at CAI-1 ratios of O (zero) expressing the F⁻ enrichment is independent to other ionic species and is added to aqueous solution directly from host rock. The negative indices specify the prevalence of secondary leaching process also. The Gibbs plots and the varied CAI values establish that the after reaching a saturation state the F⁻ mineralization of groundwater is further facilitated by ion exchange and evaporation activity. Above all, favorable geochemical environment played a catalyst role in F⁻ enhancement. Weathering of rocks and evaporation of groundwater are responsible for high fluoride capture in groundwater of Agra (Sharma et al., 2011).

Hydrogeochemical properties which govern the groundwater mobilization mechanism of F⁻ are further deliberated upon to demonstrate the hypothesis. The scatter plot of Na^+/Cl^- versus EC where most of the samples were plotted in a horizontal line parallel to x axis, reflect evapotranspiration process played crucial role in increasing the concentration of all the species in the water (Figure 10). The Na^+/Cl^- molar ratio (Table 8) is >1
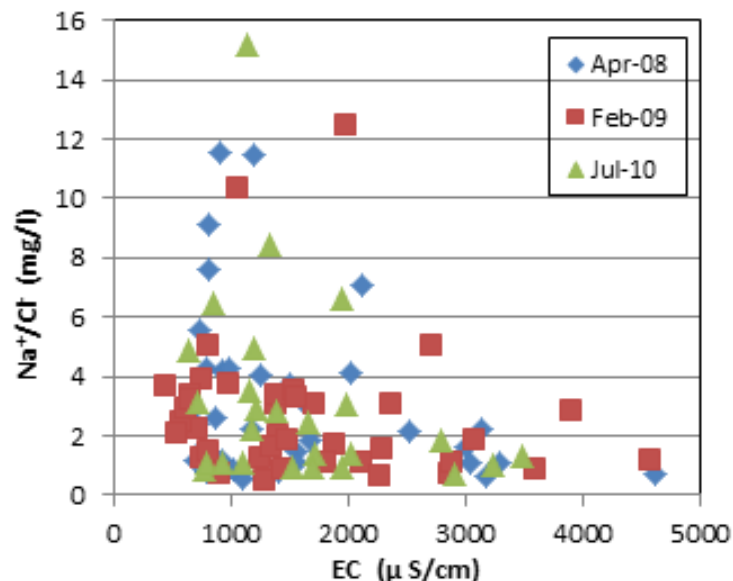
Figure 10. Cross plot of EC vs Na$^+$/Cl$^-$.

Table 8. Mean ionic ratios for different Groups of samples.

Ionic ratios and Indices	April, 2008	February, 2009	July, 2010
CAI-1, % of samples having + values	56	68	77
CAI-2, % of samples having + values	6	18	19
Na$^+$/Cl$^-$ meq/l	3.17	2.72	3.12
Ca^{2+}/Mg^{2+} meq/l	0.91	1.01	1.28
Ca^{2+}+Mg^{2+}/HCO$_3^-$ meq/l	1.08	1.04	1.09
Na$^+$+K$^+$/Tz$^+$ meq/l	0.54	0.57	0.61
Ca^{2+}+Mg^{2+}/Tz$^+$ meq/l	0.46	0.43	0.39
Ca^{2+}+Mg^{2+}/Na$^+$+K$^+$ meq/l	1.31	1.13	1.02
Ca^{2+}/Na$^+$ meq/l	0.651	0.585	0.581
(Na$^+$/Ca^{2+})/ (F$^-$) mqe/l	20.68	20.27	17.81
(Na$^+$/Ca^{2+}) mg/l	0.651	0.585	0.581
Mg^{2+}/Na$^+$ meq/l	0.71	0.59	0.47
Mg^{2+}/HCO$_3^-$ meq/l	0.59	0.53	0.51
Mg^{2+}/Ca^{2+} meq/l	1.72	1.56	1.09
SO$_4^{2-}$/Cl$^-$ meq/l	0.50	0.42	0.46
% of samples with F$^-$ <0.50 mg/l	11%	18%	8%
F$^-$/Ca^{2+} meq/l	0.116	0.089	0.165
F$^-$/Na$^+$ meq/l	0.651	0.585	0.581
F$^-$/K$^+$ meq/l	33.92	29.39	34.69
F$^-$/HCO$_3^-$ meq/l	0.490	0.507	0.575
F$^-$/SO$_4^{2-}$ meq/l	0.0726	0.0732	0.0834
Na$^+$/Cl$^-$% of samples with >1.00 meq/l	83%	84%	81%
Tz$^+$: HCO$_3^-$ meq/l	2.29	2.46	2.51
EC:F$^-$ correlation (r^2) meq/l	-0.952	-0.787	-1.307

in almost all the samples of three sampled seasons,indicating that silicate weathering was the primary process responsible for the excess release of Na$^+$ into the groundwater (Stallard and Edmond 1983; Meybeck 1987; Pophare and Dewalkar 2007). Higher Na$^+$ content (26 to 30%) than Ca^{2+} (10 to 11%) resulted in
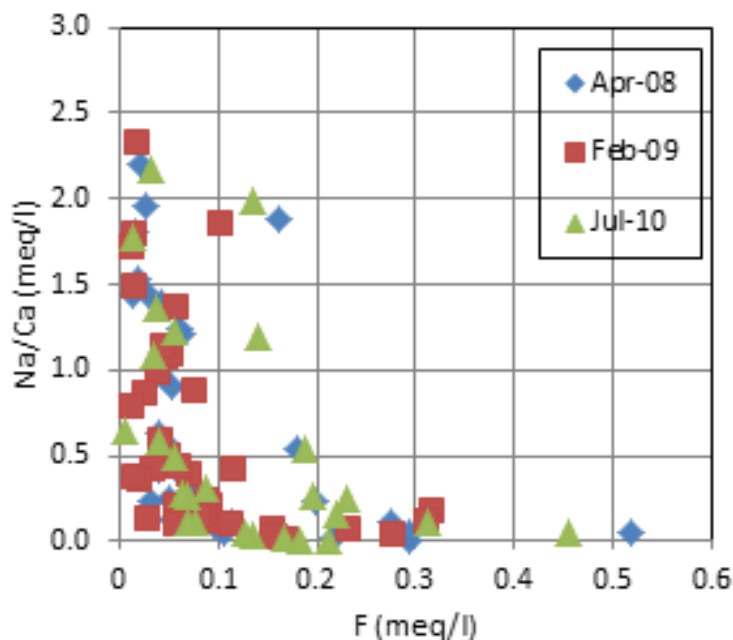
Figure 11. Cross plot of Na^+/Ca^{2+} vs F^-.

Ca^{2+} deficit groundwater facilitating increase in F^- concentration. The equivalent Na^+/Ca^{2+} ratio is also high in samples having high F^- (Table 8) indicating that the Na^+ and Ca^{2+} content of water have a control on the release of F^- from parent rocks (Mondal et al., 2014). If there is more sodium in the sample, the lesser would be the calcium content and consequently an increase in the levels of fluoride (Shaji et al., 2007). The Na^+/Ca^{2+} and F^- do not exhibit distinct relationship as the mean values are incomparable but broadly confirms to the general contention of negative affiliation between Ca^{2+} - F^- and positive trend of F^- and alkaline pH (Figure 11 and Table 8). The dissolution of dolomite was one of the prime processes involved in enrichment of Ca^{2+} and Mg^{2+} in the groundwater as the Ca^{2+}/Mg^{2+} ratio varies between 1 and <2 in most of the samples in all the three episodes (Table 8; May and Loucks 1995). The Ca^{2+}, Mg^{2+}, and HCO_3^- ratio of ~ 1 indicates that Ca^{2+} and Mg^{2+} are added to the solution at a lesser rate than HCO_3^-, and Ca^{2+}-Mg^{2+} originated from the dissolution of carbonate minerals in the aquifer material (Sami 1992). It also point out diminution of Ca^{2+} felicitating F^- mineralization of groundwater and existence of recharge conditions keeping the formation waters at higher pace of hydrodynamics. The very low Ca^{2+}/HCO_3^- in most of the samples (Table 8) in all the three sample sessions shows availability of conductive geochemical environment for F^- inclusion in formation water. High fluoride is also related to residual alkalinity ($Ca^{2+} < HCO_3^-$) and saturation with respect to fluorite (Jacks et al., 2005). The plot of calcite and gypsum equilibrium solubility (Figure 12) exhibits that the water is supersaturated with respect to both gypsum

and calcite. The F^- concentrations of groundwater are continuously enriched even after the groundwater reaches an equilibrium state with respect to fluorite (CaF_2) due to removal of Ca^{2+} by precipitation of calcite ($CaCO_3$).

Bivariant plot of $(Ca^{2+}+Mg^{2+})$-$(HCO_3^- $-$ SO_4^{2-})$ versus (Na^++K^+)-Cl^- (Figure 13) of the groundwater samples display a scattered distribution of sample points but majority are closely aligned with a slope of -1 (McLean et al., 2000). This point out that most of the Ca^{2+}, Mg^{2+} and Na^+ are added to the solute by ion exchange reactions (Garcia et al., 2001). Whereas scattered dispersion away from slope line, especially in February 2009 samples, indicate ion species are evolved from sodic plagioclase and/or saline salts (Jankowski et al., 1998; Benony 2007; Tirumalesh et al., 2010). Low (1to1.3) mean molar ratios of $(Ca^{2+}+Mg^{2+})/(Na^++K^+)$, similarly the ratio of HCO_3^-:Ca^{2+} (~2 to 2.5) suggest that weathering of silicate minerals and carbonate dissolution could be contributing the cations. Almost equi-proportions of $Ca^{2+}+Mg^{2+}/HCO_3^-$ substantiate the role of silicate weathering in cation addition. The Na^+/HCO_3^- mean ratios vary from 1.27 to 1.44 authenticating dominance of silicate weathering.

Sodic rich country rocks (Nephelene syenite, anorthosite, grey granite gneiss) might be facilitating this geochemical mechanism. <1 mean molecular ratios of Ca^{2+}/Na^+ and Mg^{2+}/Na^+ also supports the active role of silicate weathering (Table 8). About 1 mean ratio of Ca^{2+}/Mg^{2+} substantiates that aquifer matrix is contributing the ions through carbonate dissolution. Variation in the ratio between 0.91 and 1.28 among three sampling sessions signify the role of physico-chemical properties of
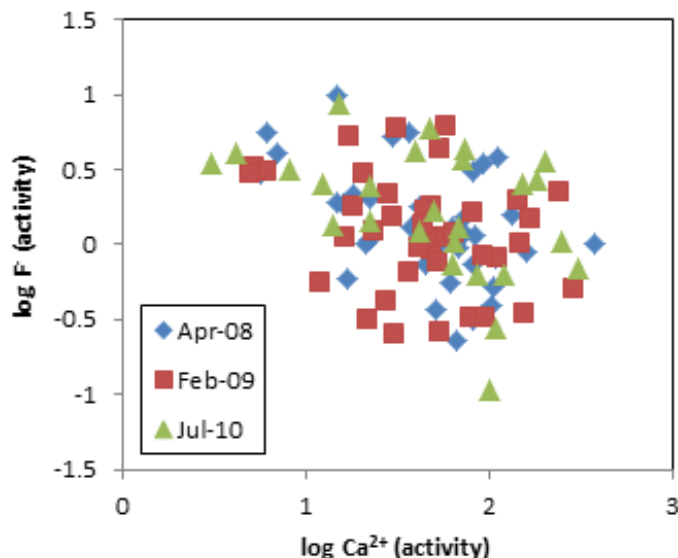
Figure 12. Log F$^-$ - Log Ca^{2+} activity.
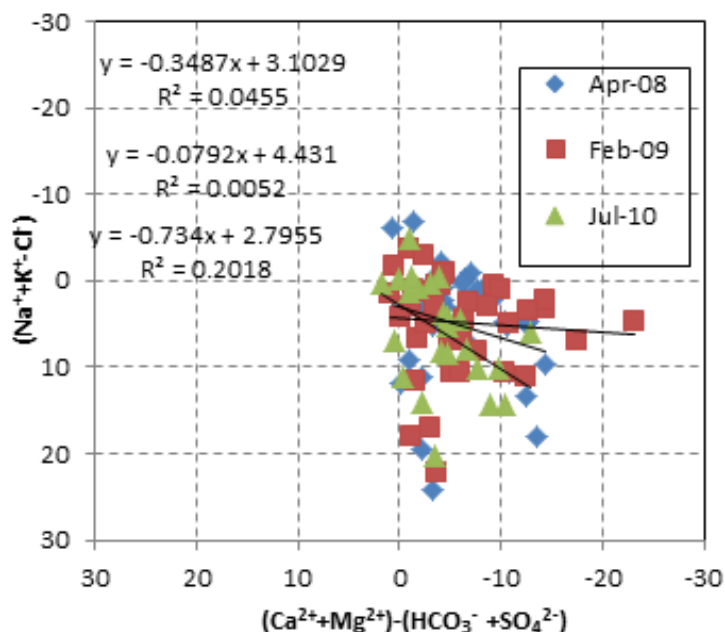
Figure 13. (Ca^{2+}+Mg^{2+})-(HCO$_3^-$ +SO$_4^{2-}$) vs Na$^+$ + K$^+$ + Cl$^-$ (meq/l).

aquatic medium in water-rock interaction. The indices of Mg^{2+}/Ca^{2+} and Ca^{2+}/SO$_4^{2-}$ which are mostly >1.5 indicate that alkaline earths are added by carbonate precipitation aided with chemical weathering. About 0.80 mean molecular ratio of (HCO$_3^-$ /HCO$_3^-$ +SO$_4^{2-}$) in three sets of samples signify active role of the carbonic acid weathering and sulphide oxidation in proton inclusion (Brown et al., 1996; Raju et al., 2012). Sulphide solutions could be produced by leaching of pyrite which evidently

high in gabbros. Dominance of Ca^{2+}+Mg^{2+} over Na$^+$+K$^+$ and HCO$_3^-$ (mean ratio vary from 1.02 to 1.31) could be due to multiple sources of calcium apart from aquifer material, like atmosphere, rainwater and soil. High (~3) Na$^+$/Cl$^-$ ratio indicates dissimilar sources as well as hydrogeochemical processes for absorption of these ions in to formation water. Over view of the various indices and plots indicate that multiple operating mechanisms were governing the solute acquisition processes.
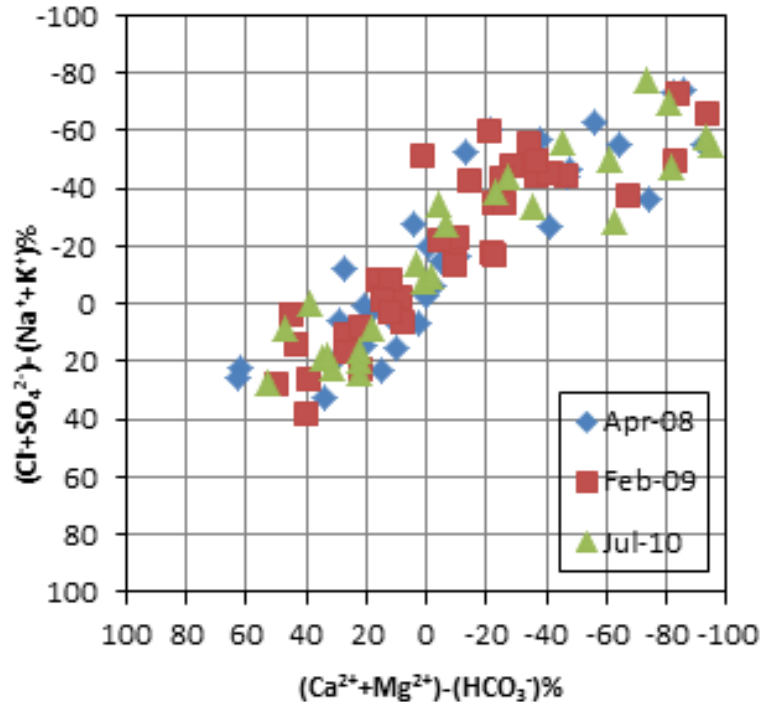
Figure 14. Langelier and Ludwing diagram (modified).

The Langelier and Ludwing diagram (modified – Figure 14) plot explicitly depicts the lithogenic origin of F^- as majority of samples fall in negative zone aligned to unit line of $(Ca^{2+}+Mg^{2+})-(HCO_3^-)$% versus $(Cl^-+SO_4^{2-})-(Na^++K^+)$%. The average r^2 value of three sample sessions is 0.80 showing bicarbonate - alkali affinity acting as catalyst in F^- dissolution. Dispersion in the extreme negative end (>-0.60) could be due to influence of later anthropogenic alterations incidentally these samples have high F^- content. F^- enrichment could be a later phenomenon due to prolonged pore water entrapment fractured aquifer matrix followed by evapotranspiration leading to $CaCO_3$ precipitation leading to more F^- absorption. But for this abnormality, samples with low to moderate F^- occupied potions between 40 to -81 and show distinct trend exhibiting F^- genesis into groundwater is due to direct petrogenic interaction. $(Ca^{2+}+Mg^{2+})-(HCO_3^-)$% mean value is -029% in samples having more (>1.50mg/l) F^-, whereas it is 16.32% in samples with low (<1.50mg/l) F^- indicating prevalence of low calcium and high bicarbonate environment. But in July 2010, 36% of F^- rich (>1.50 mg/l) samples have higher $(Ca^{2+}+Mg^{2+})$ than (HCO_3^-) which could be due fresh influx of recharge water as the sampling is done amidst monsoon period. Similarly the $(Cl^-+SO_4^{2-})-(Na^++K^+)$% mean value is also -033% in samples having more (>1.50mg/l) in concurrence with proven theory. But $(Cl^-+SO_4^{2-})$% is high in 50% of samples with low (<1.50mg/l) F^-. Influence of SO4 is negligible as it is more than Cl in only few (<10%) of samples and Cl is more

than double that of SO4 which vindicate impact of evaporation and anthropogenic activity. This assumption is substantiated by very high (mean 97%) Na content of among (Na^++K^+)%.

Source and genesis of F^- into groundwater

The Archaean crystallines are the major rock types encountered in the district. Charnockites, hornblende gneiss, migmatites and gneisses occupy a major part of study area and they contain fluorine in their mineral lattice. Igneous and volcanic rocks have a fluorine concentration from 100 ppm (ultramafic) up to >1000 ppm (alkalic) (Frencken, 1992). Granitic rocks which are a typical source of fluoride rich rocks contain fluoride ranging between 500 and 1400 mg/kg (Koritnig, 1978; Krauskopf and Bird, 1995), which is much higher than any other rock type. The world average content of fluoride in granitic rocks is 810 mg/kg (Wedepohl 1969).

Granite and granitic gneisses in Nalgonda, India contain fluoride rich minerals such as fluorite (0 to 3.3%), biotite (0.1 to 1.7%) and hornblende (0.1 to 1.1%) (Ramamohana et al., 1993). Mondal et al. (2009) reported from the same area that the rocks contain 460 to 1706 mg/kg of fluoride. Presence of alkaline rocks (Nephlene synite) and Gabbro in western part could be the potential sources of F^- as groundwater samples from these areas have high fluoride content. In general, apatite and fluorite, besides replacement of hydroxyl by
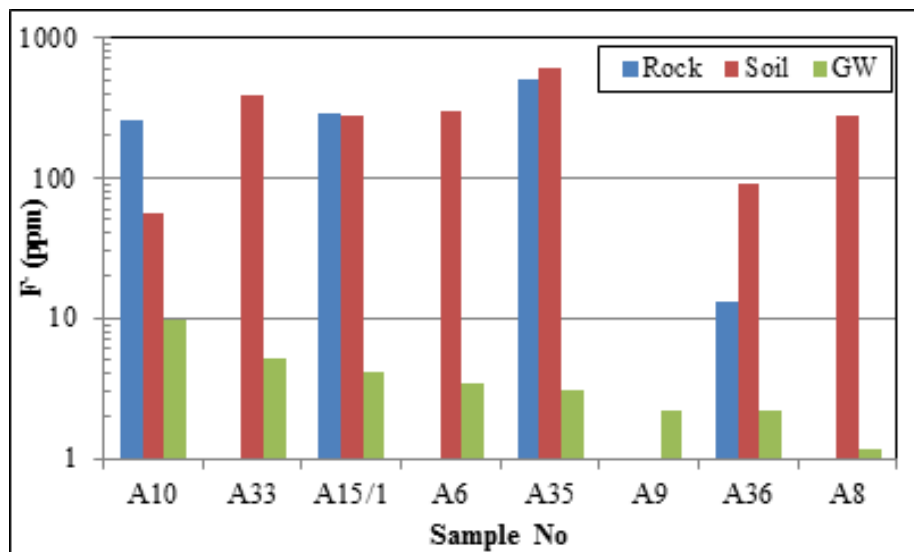
Figure 15. F⁻ content in rock, soil and groundwater samples.

fluoride ions in mica, hornblende and soil that mostly consists of clay minerals, are major sources of F⁻ in circulating water. The country rocks contain apatite (0.2 to 1.20%), fluorite (0.1 to 1.49%) and biotite (0.21 to 8.22%), which could be the possible provenance of fluoride in groundwater. But even if the country rock/soil has abundant with F⁻ minerals, fluoride enrichment processes in groundwater depends on fluid kinetics and inter-connectivity of aquifers. Sporadic distribution of F⁻ in rock-soil-groundwater even close proximity substantiates the contention (Figure 15). The source of fluoride might be related to the geology, but the geochemical behavior is controlled by the chemistry of the groundwater (Chae et al., 2007). Normally, biotite in granite gneissic rocks may contain as much as 0.91% fluorine; hornblende contains 0.17% fluorine; and fluor-apatite has a fluorine concentration of 3.72% (Deer et al., 1985). Lithogenic sodium (LNa^+), that is, the net Na^+ acquired by groundwater from the chemical weathering of rock-forming minerals, is used as an index of the weathering of minerals (Ramesam, 1985). Fluoride minerals such as fluorite and cryolite are not readily soluble in water under normal pressure and temperature. But under alkaline conditions and range of specific conductivity between 750 and 1750 µS/cm, dissolution rate of fluorite minerals increase. Sodium bicarbonate type water (Na^+-HCO_3^-) 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 (Saxena and Ahmed, 2003). The weathering activity characterized by alternate wet and dry conditions of the semiarid climate is responsible for leaching of fluoride from the minerals present in the soils and rocks.

Laboratory studies conducted by Chae et al. (2006) showed that leaching of fluoride from granitic rocks contributed 6 to 10 mg/l of fluoride to water. Jacks et al. (2005) reported that in Coimbatore District, Tamil Nadu, dark-coloured minerals in rocks contain 180 to 2600 mg/kg F⁻ and the relative stability of flourapatite during the weathering process indicates that the main source of fluoride in groundwater is from micas, hornblende and pyroxene. The country rock in the fluoride affected areas of Palghat and Coimbatore is hornblende biotite gneiss. Irrigation increases the sodicity of the soil. Also, the fertilizers used for irrigation purpose are expected to contribute for high fluoride concentration in the aquifers. It is as well possible that long-term continuous irrigation practice could affect the fluoride content of groundwater (Brindha et al., 2011). Contribution of F⁻ to groundwater or top soil due to the fertilizers contained soluble F⁻ is ruled out as F⁻ distribution is even in different land uses for example, in village as well as agriculture. It can be further supported by poor correlation of F⁻ with K^+, SO_4^{2-}, NO_3^- which form part of chemical fertilizers (UREA, NPK, DAP, phosphate/potash-fertilizers) that is most commonly applied in the area (Farooqi et al., 2007).

Conclusion

High geogenic contamination in the form of fluoride among melenocratic intrusive rocks is a rare phenomenon. Confinement of F⁻ rich groundwater near structurally disturbed and area of high igneous activity point out F⁻ mineralization has occurred along contact zone during intrusive magma consolidation period. Volatile rock in direct interaction with felsic rich granites might have resulted in crystallization of fluoride based minerals. Multiple magma intrusive episodes with diverse molten rock varying from mafic rich (gabbro, anorthosite,

dolerite) to felsic rich (pegmatite, pink granite) material into granite gneiss country rocks has resulted in F⁻ mineralization. Presence of Sodic rich rocks like nepheline synites and other alkaline rocks confirm F⁻ crystallization during magma consolidation. Conduit water with receptive chemical composition has led to the F⁻ dissolution. Aquifer hydraulics in the form of sluggish mobility, prolonged residency period has facilitated F⁻ capture into formation waters. Subsequently, water underwent thermodynamic reactions to attain super saturation with F⁻. Water chemistry and kinetics could be controlling the F⁻ absorption mechanism even though free F⁻ was available in solid solution. Groundwater having specific chemistry is gaining F⁻ due to water-rock interaction in deep meteoric horizons and is getting enriched with F⁻ during its transit in inter aquifer zones.

Conflicts of Interests

The authors have not declared any conflict of interests.

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Supplemental Table 1a. Major ion groundwater chemistry of Chimakurthy - April 2008.

S/N	Sample	Village	pH	EC (μ S/cm)	TH – calculated (mg/l)	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	CO$_3^-$	HCO$_3^-$	Cl$^-$	SO$_4^{2-}$	NO$_3^-$	F$^-$	TDS- calculated
1	A 10	G Lakshimipuram (Forest)	7.96	1260	55	15	5	358	2	21	456	136	169	10	9.84	943
2	A 11	Gonegunta (Forest)	8.24	2120	33	6	4	645	4	84	1024	140	196	7	5.60	1563
3	A 13	Muvarripalem	7.65	3140	275	37	44	800	9	42	805	547	237	175	5.58	2278
4	A 33	M C Palem - GLSR	8.11	1510	186	30	27	323	4	27	625	134	79	20	5.22	949
5	A 15	Gonegunta - Opst church	7.94	1190	46	7	7	334	4	33	714	45	43	27	4.10	844
6	A 32	M C Palem - SC Colony	7.83	3300	699	112	101	537	30	24	601	750	173	82	3.79	2102
7	A 6	ChinnarajPalem	7.65	1180	476	93	59	199	21	12	586	137	108	79	3.44	999
8	A 35	Yelliaah Nagar - Nr School	7.93	710	285	83	19	50	3	18	345	33	59	1	3.09	432
9	A 16	Gonegunta - Peduripalle	7.89	912	44	6	7	266	4	3	558	35	39	24	2.95	665
10	A 14	K V Palem	7.62	930	140	18	23	181	6	15	378	67	47	83	2.15	624
11	A 2	Chimakurthy-Jr Colg	7.85	2030	170	23	28	539	6	42	949	200	54	158	2.01	1504
12	A 12	Gudipudivaripalem	7.86	990	135	15	24	197	6	15.6	464	71	56	42	1.91	652
13	A 36	Chimakurthy - Mines area	8.03	820	100	16	15	185	2	15	428	31	45	5	1.82	523
14	A 4	R L Puram	7.71	1610	301	41	48	301	30	18	738	149	39	118	1.76	1106
15	A 9	G Lakshimipuram	7.49	3010	659	135	78	551	6	27	461	529	187	428	1.58	2158
16	A 29	Lakshmipuram -S N Padu Mandal	7.88	2520	480	74	72	469	14	12	680	341	187	178	1.52	1682
17	A 23	Pallamalli - Sub St	7.64	788	233	37	34	151	4	15	372	55	26	99	1.30	601
18	A 24	Gadiparthyvaripalem (R S Puram)	7.44	1670	514	63	86	208	21	21	686	175	50	2	1.30	960
19	A 19	Chimalamarri	7.38	1100	436	73	62	69	3	15	262	182	43	78	1.19	650
20	A 8	Ramachendrapuram	7.51	873	372	85	39	79	2	12	420	46	32	131	1.15	631
21	A 25	Illapavalluru - SC colony	7.63	744	168	22	27	133	7	12	454	37	28	1	1.09	489
22	A 30	Tharagudipadu	8.00	1560	461	21	99	188	13	18	589	192	100	1	1.03	918
23	A 31	Chimakurthy- NE end	7.17	4610	1459	382	123	484	39	0	421	995	302	837	1.00	3372
24	A 20	Bandlamudi - Bus Stand	7.25	3050	999	69	201	324	137	18	805	473	223	355	0.96	2194
25	A 21	Bandlamudi - SC clny	7.43	821	388	52	63	44	2	12	375	47	33	131	0.95	565
26	A 27	Nekullambgh	7.36	3170	1160	159	185	325	7	9	326	752	142	545	0.89	2285
27	A 28	Chendarpadu	7.50	1400	600	108	80	89	6	12	406	176	41	205	0.81	915
28	A 17	Gonegunta Fields N end	7.50	808	268	45	38	124	1	42	505	25	29	5	0.74	542
29	A 5	Pulikonda	7.60	1560	548	83	83	152	6	27	366	211	76	226	0.74	1034
30	A 26	G V Palem	7.77	636	219	17	43	84	4	24	328	54	56	1	0.59	435
31	A 7	Busurpalle (Malapalle)	7.46	920	330	62	43	49	2	0	265	65	53	129	0.56	536
32	A 34	Devarapalem	7.74	1025	422	106	38	63	4	15	418	107	40	47	0.52	622
33	A 18	Chimakurthy- E end	7.33	792	339	103	20	54	2	21	304	108	35	33	0.40	517
34	A 22	Pallamalli - Fields	7.67	537	225	52	23	39	4	15	303	27	27	1	0.37	333
35	A 1	Reddy Nagar	7.49	701	314	82	27	52	2	18	300	69	29	1	0.31	421
36	A 3	Ramathirtham	7.68	749	334	67	40	54	1	18	387	53	56	1	0.23	475

2.01 Highlighted: samples having F$^-$ in > maximum permissible limits (MPL) of BIS Drinking water standrads n. a Not analysed; n. c Not calculated.

Supplemental Table 1b. Major ion groundwater chemistry of Chimakurthy - Feb 2009.

S/N	Sample No.	Village	pH	EC (µ S/cm)	TH – calculated (Mg/l)	Ca²⁺	Mg²⁺	Na⁺	K⁺	CO₃⁻	HCO₃⁻	Cl⁻	SO₄²⁻	NO₃⁻	F⁻	TDS- calculated
1	A 28	M C Palem - SC Colony	7.55	2290	443	58	72	401	9.8	48	656	390	97	36	6.05	1421
2	A 29	M C Palem - GLSR	7.53	1540	185	31	26	340	5	42	552	148	73	33	5.92	958
3	A 11	Muvarripalem	7.66	2370	119	17	18	576	8.3	21	738	290	163	113	5.3	1571
4	A 38	Chimakurthy-3	7.38	1480	361	54	55	880	14.7	30	690	727	314	338	4.4	2748
5	A 10	Gonegunta (Forest)	8.36	1980	24	5	3	556	4.2	63	936	69	147	n.a.	3.23	n. c
6	A 13	Gonegunta - Opst church	8.01	1390	47	6	8	360	5.5	30	634	164	38	51	3.04	968
7	A 14	Gonegunta - Peduripalle	7.84	1060	37	5	6	270	4	30	515	40	37	22	2.98	661
8	A 2	Chimakurthy-Jr Colg	7.51	1890	148	21	23	374	6.8	18	287	346	99	49	2.96	1074
9	A 9	G Lakshimipuram	6.85	4580	1148	246	129	687	13	0	540	922	325	838	2.21	3432
10	A 31	Chimakurthy - Mines area-1	7.6	1560	159	28	21	355	1.6	51	537	167	63	24	2.18	956
11	A 30	Yelliaah Nagar - Nr School	6.93	1360	484	146	29	91	3.2	0	345	85	126	160	1.96	814
12	A 12	K V Palem	7.48	978	139	18	22	183	6.1	21	369	76	47	75	1.79	625
13	A 4	R L Puram	7.24	1710	340	48	53	266	17.5	9	555	134	53	206	1.78	1062
14	A 6	ChinnarajPalem	7.3	1380	243	46	31	218	22.7	12	534	110	23	84	1.69	809
15	A 25	Lakshmipuram-S N Padu Mndl	7.33	3080	517	81	76	573	17.5	0	769	487	270	272	1.65	2163
16	A 39	Chimakurthy- 4	7.46	3900	310	29	57	237	17	21	604	130	72	27	1.54	884
17	A 5	Pulikonda	6.9	2860	996	168	140	223	7.3	0	409	481	195	457	1.47	1878
18	A 21	Gadiparthyvaripalem (R S Puram)	7.19	2720	268	44	38	129	5.2	21	507	39	17	98	1.34	637
19	A 22	Illapavalluru - SC colony	7.5	817	162	24	25	135	6.9	15	409	41	28	39	1.24	512
20	A 35	Chimakurthy - 7	7.15	1810	419	65	62	175	80.1	15	372	240	70	177	1.18	1063
21	A 18	Bandlamudi - SC clny	7.23	816	333	47	52	39	2.1	24	303	42	24	92	1.12	463
22	A 26	Tharagudipadu	7.29	1410	355	17	76	185	13.4	0	537	141	65	n.a.	1.11	n. c
23	A 17	Bandlamudi - Bus Stand	7.04	2880	752	55	150	311	130	21	778	425	211	308	1.1	1989
24	A 23	Nekullambgh	6.92	2280	800	148	104	156	17.1	0	433	362	103	235	1.01	1344
25	A 20	Pallamalli - Sub St	7.39	764	256	42	37	98	5.1	27	308	39	16	101	0.94	505
26	A 7	Busurpalle (Malapalle)	7.34	722	248	49	31	52	2.3	12	238	36	48	102	0.93	446
27	A 24	Chendarpadu	7.16	1440	502	93	65	95	5.7	24	354	175	54	184	0.84	862
28	A 8	Ramachendrapuram	7.38	2120	489	111	51	216	88.8	18	451	303	139	114	0.81	1258
29	A 16	Chimalamarri	7.29	905	309	53	43	62	2.6	15	244	129	36	55	0.77	511
30	A 32	Chimakurthy - 5	7.41	659	141	36	12	100	1.7	18	289	45	22	n.a.	0.64	0
31	A 37	Chimakurthy- 2	7.72	650	98	12	16	115	3.9	21	287	56	17	n.a.	0.55	n. c
32	A 27	Chimakurthy- NE end	6.72	3600	1061	292	80	392	31.8	0	515	688	226	527	0.51	2495
33	A 33	Chimakurthy - Mines area-2	7.57	618	130	27	15	89	3	18	271	48	27	n.a.	0.42	0
34	A 15	Chimakurthy- E end	7.31	1290	474	155	21	77	1.4	0	250	245	36	64	0.35	725
35	A 3	Ramathirtham	7.08	1250	469	95	56	73	1.2	0	369	91	61	152	0.33	715
36	A 1	Reddy Nagar	7.54	760	298	81	23	52	1.3	30	311	64	39	6	0.32	437
37	A 34	Chimakurthy - 6	6.81	450	82	22	7	68	2.7	0	217	29	11	0	0.32	247
38	A 19	Pallamalli - Fields	7.32	576	227	54	23	36	4.1	21	303	23	21	4	0.26	326
39	A 36	Chimakurthy- 1	7.8	537	167	31	22	45	2.1	18	162	33	58	24	0.25	305

Supplemental Table 1c. Major ion groundwater chemistry of Chimakurthy - July 2010

S/N	Sample No.	Village	pH	EC	TH - calculated	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	CO$_3^-$	HCO$_3^-$	Cl$^-$	SO$_4^{2-}$	NO$_3^-$	F$^-$	TDS - calculated
				µ S/cm							mg/l					
1	A 10	G Lakshimipuram (Forest)	8.03	1160	54	15	4	326	4.2	0	656	143	51	20	8.66	900
2	Chrk 207	Chimakurthy-3	7.82	2800	303	48	44	529	13.2	0	344	432	259	213	5.95	1716
3	A 32	M C Palem - SC Colony	7.44	2030	527	74	83	337	10.7	0	631	382	93	42	4.37	1343
4	A 33	M C Palem - GLSR	8.02	1390	217	39	29	282	4.5	15	552	152	88	26	4.16	910
5	A 11	Gonegunta (Forest)	8.81	1940	20	4	2	548	4.4	57	894	128	158	6	4.03	1329
6	A 32A	M C Palem - SC Colony (alt)	7.55	1710	461	72	68	318	12.7	0	576	348	85	62	3.72	1258
7	A 33A	M C Palem - GLSR (alt)	7.23	3240	1216	202	173	431	20.3	0	528	634	238	500	3.57	2465
8	A 10B	G Lakshimipuram (Forest-alt2)	8.56	1200	17	3	2	290	4.2	30	549	90	41	26	3.46	749
9	A 15	Gonegunta - Opst church	8.44	1330	57	8	9	372	5.4	119	665	68	48	64	3.15	970
10	A 35A	Yelliaah Nagar - (alt)	7.32	1690	685	183	55	176	4.6	0	403	284	161	151	2.68	1219
11	A 17	Gonegunta Fields N end	8.10	1140	69	12	9	351	4.0	207	553	36	44	12	2.57	852
12	A 35	Yelliaah Nagar - Nr School	7.32	1100	481	154	23	89	3.2	0	375	126	135	0	2.56	721
13	A 2	Chimakurthy-Jr Colg	7.80	1990	158	23	25	476	6.5	0	836	241	235	63	2.44	1490
14	A 6	ChinnarajPalem	7.71	1220	248	50	30	187	20.1	0	525	98	29	75	1.69	753
15	A 36	Chimakurthy - Mines area	8.10	843	125	22	17	224	2.7	110	408	54	59	9	1.44	649
16	A 10A	G Lakshimipuram (Forest-alt1)	8.11	645	64	14	7	146	4.5	0	317	46	41	8	1.33	427
17	A 4	R L Puram	7.52	1660	428	68	63	290	23.3	0	564	185	61	242	1.32	1214
18	A 14	K V Palem	7.71	1170	303	42	48	175	7.4	0	421	119	51	122	1.23	776
19	A 19	Chimalamarri	7.69	767	352	64	46	61	2.9	0	271	111	45	45	1.04	512
20	A 9	G Lakshimipuram	7.05	3480	972	249	85	587	9.8	0	525	670	320	471	1.04	2655
21	A 9A	G Lakshimipuram (alt)	7.84	719	194	64	8	126	5.7	0	375	62	33	2	0.74	490
22	A 5	Pulikonda	6.95	2900	1335	304	139	257	4.5	0	506	570	171	493	0.70	2193
23	A 8	Ramachendrapuram	7.65	1520	496	121	47	128	51.1	0	421	216	98	139	0.64	1011
24	A 7	Busurpalle(Malapalle)	7.55	794	372	86	38	46	2.0	0	238	63	68	146	0.63	568
25	A 3	Ramathirtham	7.44	922	497	108	55	70	0.9	0	381	99	71	89	0.28	684
26	A 6A	ChinnarajPalem (alt)	7.29	1950	598	101	84	178	7.4	0	369	296	147	56	0.11	1054

Supplemental Table 2. Varaition in F⁻ content among samples collected in three different sampling episodes.

April 2008		February 2009		July 10			
A 1	0.31	A 1	0.32	-	-	-	-
A 2	2.01	A 2	2.96	A 2	2.44	-	-
A 3	0.23	A 3	0.33	A 3	0.28	-	-
A 4	1.76	A 4	1.78	A 4	1.32	-	-
A 5	0.74	A 5	1.47	A 5	0.70	-	-
A 6	3.44	A 6	1.69	A 6	1.69	AO6A	0.11
A 7	0.56	A 7	0.93	A 7	0.63		
A 8	1.15	A 8	0.81	A 8	0.64		
A 9	1.58	A 9	2.21	A 9	1.04	AO9A	0.74
A 10	9.84	-	-	A 10	8.66		
A 11	5.60	A 11	3.23	A 11	4.03	AO10A	1.33
A 12	1.91	-	-	-	-	AO10B	3.46
A 13	5.58	A 13	5.30	-	-	-	-
A 14	2.15	A 14	1.79	A 14	1.23	-	-
A 15	4.10	A 15	3.04	A 15	3.15	-	-
A 16	2.95	A 16	2.98	A 16	-	-	-
A 17	0.74			A 17	2.57	-	-
A 18	0.40	A 18	0.35	A 18	-	-	-
A 19	1.19	A 19	0.77	A 19	1.04	-	-
A 21	0.95	A 21	1.12	-	-	-	-
A 22	0.37	A 22	0.26	-	-	-	-
A 23	1.30	A 23	0.94	-	-	-	-
A 24	1.30	A 24	1.34	-	-	-	-
A 25	1.09	A 25	1.24	-	-	-	-
A 27	0.89	A 27	1.01	-	-	-	-
A 28	0.81	A 28	0.84	-	-	-	-
A 29	1.52	A 29	1.65	-	-	-	-
A 30	1.03	A 30	1.11	-	-	-	-
A 31	1.00	A 31	0.51	-	-	-	-
A 32	3.79	A 32	6.05	A 32	4.37	A 32A	3.72
A 33	5.22	A 33	5.92	A 33	4.16	A 32A	3.57
A 34	0.52	-	-	-	-	-	-
A 35	3.09	A 35	1.96	A 35	2.56	A 35A	2.68
A 36	1.82	A 36	2.18	A 36	1.44	-	-
-	-	CHK 203	0.25	-	-	-	-
-	-	CHK 205	0.55	-	-	-	-
-	-	CHK 207	4.40	CHK 207	5.95	-	-
-	-	CHK 209	1.54	-	-	-	-
-	A 32A	Samples from alternate/close by wells					