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Influence of Anthropogenic Contamination on Fluoride Concentration in Groundwater

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Abstract. Groundwater contamination is a serious concern in India. Major geogenic contaminants include fluoride, arsenic and iron, while common anthropogenic contaminants include nitrate, metals, organics and microbial contamination. Besides, known point and diffuse sources, groundwater contamination from infiltration of pit toilet leachate is an emerging concern. The study area of this paper is Kolar district in Karnataka that is hot spot of fluoride contamination. The absence of fluoride contamination in Mulbagal town and the alterations in groundwater chemistry from infiltration of pit toilet leachate motivated the author to examine the possible linkages between anthropogenic contamination and fluoride concentration in groundwater of Mulbagal town. Analysis of the groundwater chemistry revealed that the groundwater in Mulbagal town is under saturated with respect to calcite that suppresses the dissolution of fluorite and the fluoride concentration in the groundwater. The slightly acidic pH of the groundwater is considered responsible to facilitate calcite dissolution under saturation.

Introduction

Problems with water quality are often as severe as problems with water availability, but less attention has been paid to them, particularly in developing countries. Water pollution is a serious problem in a growing number of groundwater reserves that have been contaminated by chemical pollutants in the country (Trivedi, 2008). Pollution of groundwater resources are geogenic and anthropogenic in origin (Rao *et al*., 2008). Contamination of groundwater by fluoride, arsenic and dissolved salts are mainly contributed by geological activities. Contamination of groundwater resources by organics, heavy metals, cyanides, aluminum and nitrates are anthropogenic in origin and arise due to uncontrolled discharges from industries, sewage treatment plants and agricultural applications of fertilizers and pesticides (Rao *et al*., 2008). In addition, owing to socio-economic conditions prevalent in India, on-site sewerage system is an option that is practiced by many communities (Chourasia, 2008). A central component of these on-site systems is a pit that facilitates leaching of liquid into surrounding soil and decomposition of solid waste (Garg, 1988; RGNDWM, 2008). Infiltration of pit-toilet leachate imposes unacceptable levels of nitrates and *E.Coli* in groundwater as revealed by Rao (2011) in a recent study in Mulbagal town, Kolar District, Karnataka. Besides anthropogenic contaminants, high levels of fluoride ranging between 1.5 and 3 mg/L are encountered in groundwater of Kolar district (Mamatha and Rao, 2010). Interestingly, groundwater inside Mulbagal town did not reveal excessive fluoride concentration. This paper examines if the infiltration of pit toilet leachate has any effect on the low fluoride concentrations inside Mulbagal town. SI (saturation index) values were computed for calcite and fluorite using the Visual MINTEQ program (http://www.lwr.kth.se/English/OurSoftware/vminteq/#download).

Study area. Mulbagal is a town in Mulbagal Taluk in Kolar district in the state of Karnataka, India (Fig. 1). Mulbagal town is at distance of 95 km from Bangalore. The town geographically lies between 78º 4´ & 78º 24´ E longitude and 13º 17´ & 13º 10´ N latitude and has an average elevation of 827 metres (2713 feet). The geographical area of Mulbagal Taluk is 823 km^2 and of the town is 8.5 km^2. As per the 2001 census the population of Mulbagal Taluk is about 231,000 and the town has population of 44,000 (the town population according to present estimates is roughly 80,000). Temperature varied between 18º C and 35º C in winter and summer respectively; and the area receives an average annual rainfall of 818 mm and on an average receives rain in 72 days per year. The soil of the Taluk is red loam which is well-suited for cultivation. Typical bore-hole data for red soil deposits from Karnataka indicate that the residual soil is about 3-6 m thick and is underlain by dis-integrated rock strata (Rao and Venkatesh, 2012). The Taluk forest area is 21.22 km^2, which constitutes 3% of total area. In the Taluk, net cultivated area is 464.4 km^2 which is about 13% of total net area cultivated in Kolar district.

Materials and Methods

Groundwater samples from 43 drinking water wells located inside Mulbagal town (Fig. 2) were examined from the study area. Majority of the wells were drilled between 2000 and 2005 to depths ranging from 16 to 90 m. Collection of the groundwater samples from the 43 drinking water wells for laboratory testing was

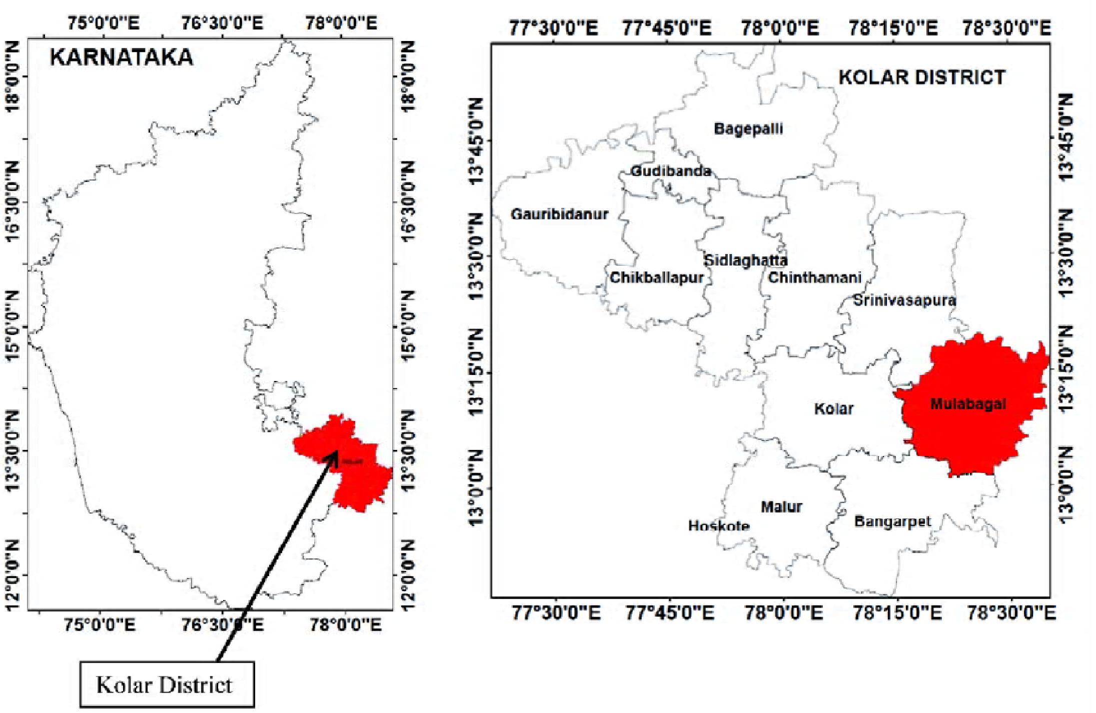

Fig. 1. Location of Mulbagal town

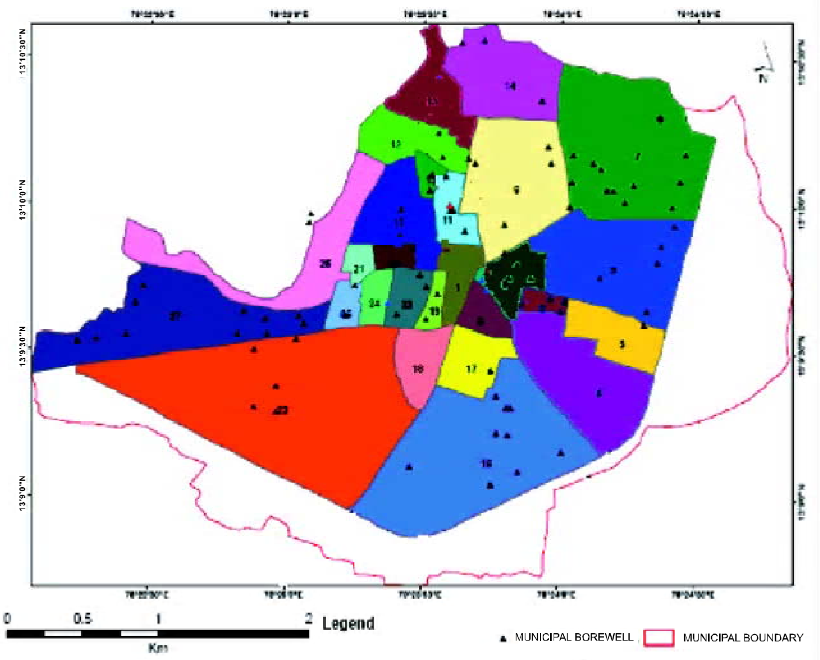

Fig. 2. Location of bore-wells in Mulbagal town: Arabic numerals represent ward numbers in Mulbagal town. Each ward is identified with different color

accomplished in 5 phases between April and June 2009. Twenty groundwater samples were collected on 15th April 2009, ten on 28th April 2009, nineteen on 13th May 2009, eleven on 3rd June 2009 and nine groundwater samples were collected on 25th June 2009 respectively. All drinking water wells were equipped with electrical pumps. The intervals between sampling phases were mainly governed by availability of field personnel who assisted in water collection from the wells. During water collection, the junction between the well and the pipe leading to storage tanks were opened; groundwater was pumped out for about 15 minutes following which samples were collected for laboratory analysis. Water samples for chemical analysis were collected in 1 liter capacity polythene containers and were preserved at 4°C immediately after collection, during transportation and after being received by the laboratory. Mulabagal town is located at distance of 100 km from Bangalore; each round of sample collection and transportation to laboratory (located at Bangalore) required 12 hours. All laboratory testing was initiated within twenty four hours of field collection. Laboratory analysis of water samples collected during each sampling round was accomplished in about 7 days. The pH and electrical conductivity (EC) of the collected water samples were measured in the field using portable pH and electrical conductivity meters. The EC values are converted to total dissolved solids (TDS) using the equation (Todd, 1980).

1 mg/L=1.56 μ Siemen/cm ....(1)

The concentrations of magnesium, calcium, sodium and potassium ions in the groundwater samples were determined using induced coupled Plasma Optical Emission Spectrometer. The concentrations of sulfate, chloride and nitrate ions were determined using ion chromatograph and bicarbonate ion concentration was determined using an automatic titrator. The ionic concentrations of groundwater samples are provided in Table 1.

Table 1. Ionic composition of groundwater samples.

BW No.	pH	TDS, mg/L	Ca, mg/L	Mg, mg/L	Na, mg/L	K, mg/L	HCO_3, mg/L	Cl, mg/L	SO_4, mg/L	NO_3, mg/L	F, mg/L
114	7.13	823	31	12	67	2.5	171	50	70	42	0.78
115	6.31	661	101	31	99	4	234	208	58	67	0.55
116	6.34	1357	205	49	383	12	522	426	111	207	0.7
117	6.24	1110	184	49	356	5	512	422	114	209	0.75
118	6.52	1422	196	45	214	108	517	403	171	277	1.01
119	6.42	1292	246	63	207	10	439	426	124	328	0.77
120	6.57	1229	236	61	184	7	385	440	123	276	0.52
121	6.92	572	96	28	146	2.4	332	149	45	43	0.89
212	6.99	450	54	16	114	4.7	322	70	29	65	1.34
224	6.48	971	135	36	193	7.7	532	312	80	28	0.81
225	6.42	1082	199	48	198	13	407	419	107	55	1.03
227	5.72	1101	177	30	177	11	229	283	77	326	0.55
228	6.42	1054	189	34	188	12	410	257	85	159	1.04
229	6.42	946	196	32	155	8	400	218	64	142	0.49
230	6.72	1093	159	39	243	9	610	272	17	178	0.49
231	6.26	1234	197	58	189	5	375	284	80	197	0.69
233	6.61	948	156	47	140	11	361	203	64	127	0.51
234	6.62	1006	168	40	163	6	361	214	73	143	0.54
235	6.63	804	116	32	160	8	395	224	66	96	0.35
236	6.52	1075	133	35	229	3	454	342	100	96	0.6
239	6.81	1149	172	39	190	3	371	423	145	37	0.36
240	7.21	1112	157	38	186	5	366	412	145	37	0.33
244	6.19	898	133	38	145	5.3	351	328	90	78	0.62
245	7.66	1043	143	32	194	3	249	351	77	5	0.93
300	6.26	403	45	11	75	3	195	71	23	62	0.39
312	6.67	1889	175	55	264	301	634	504	160	266	1.05
313	6.84	1825	170	46	355	149.8	737	540	177	266	1.13
314	6.97	2337	326	88	349	93	532	756	214	105	1.2
400	7.14	812	81	24	142	76	381	218	90	75	1.32
401	6.65	1233	210	40	188	60	444	323	63	146	0.5
402	6.78	1153	119	24	162	211	415	240	95	147	0.64
403	6.41	1325	286	60	186	27	381	474	123	388	0.49
404	6.11	936	146	46	248	2	381	296	66	118	0.57
405	6.22	1338	197	57	421	53	669	449	108	234	1.1
406	6.51	1318	218	50	378	13	600	331	82	195	0.81
407	5.91	974	159	35	238	6	303	325	65	252	0.29
408	5.72	986	197	38	245	6	312	167	42	140	0.29
410	6.52	549	87	23	149	23	347		41	30	1.01
411	6.48	1318	181	41	207	62	473	338	90	139	0.51
413	6.63	1623	196	48	181	275	576	354	110	275	0.29
415	7.37	999	167	35	115	102	424	228	86	124	0.31
419	6.78	1883	225	60	284	177	502	522	134	281	1.29
421	6.41	1422	212	49	203	78	500	462	131	289	0.96

Results and Discussion

Groundwater chemistry. Figure 3 presents the variations between sodium absorption ratio (SAR) as function of total dissolved solids (TDS) concentration in the groundwater samples. The sodium absorption ratio is defined as:

$$SAR = SAR = [Na^+] / \{([Ca^{2+}] + [Mg^{2+}]) / 2\}^{1/2} \qquad (2)$$

where, sodium, calcium, and magnesium are in milliequivalents/liter.

The plot shows that the SAR levels in the groundwater samples range between 1.1 to 4.6 and tend to increase with TDS. The high sodium concentration in the groundwater samples is attributed to enrichment by pit toilet leachate as sodium concentration in human fecal matter ranges between 0.2 to 1 mg/g of wet mass (Nishimuta *et al*., 2006).

Figure 4 plots the variations in nitrate concentrations in the groundwater samples as function of the major (HCO_3 + SO_4 + Cl + NO_3) anion concentration. Conventionally, bicarbonate, sulfate and chloride ions are the major anions in groundwater samples (Younger, 2007). Owing to their predominance in groundwater samples, nitrate is included as anion constituent. The nitrate concentrations in the groundwater samples tend to linearly increase with major anion concentration; 84 % of the samples possess nitrate concentrations in excess of the permissible limit (45 mg/L) and values range from 55 mg/L to 388 mg/L. Apparently, infiltration of leachate from pit toilets into subsurface environment leads to excessive nitrate concentrations in the groundwater, Non carbonaceous matter such as ammonia is produced during the hydrolysis of proteins in the waste water that is oxidized to nitrite and subsequently to nitrate by nitrifying bacteria (Metcalf and Eddy, 2003).

Figure 5 plots the TDS levels in the groundwater samples.

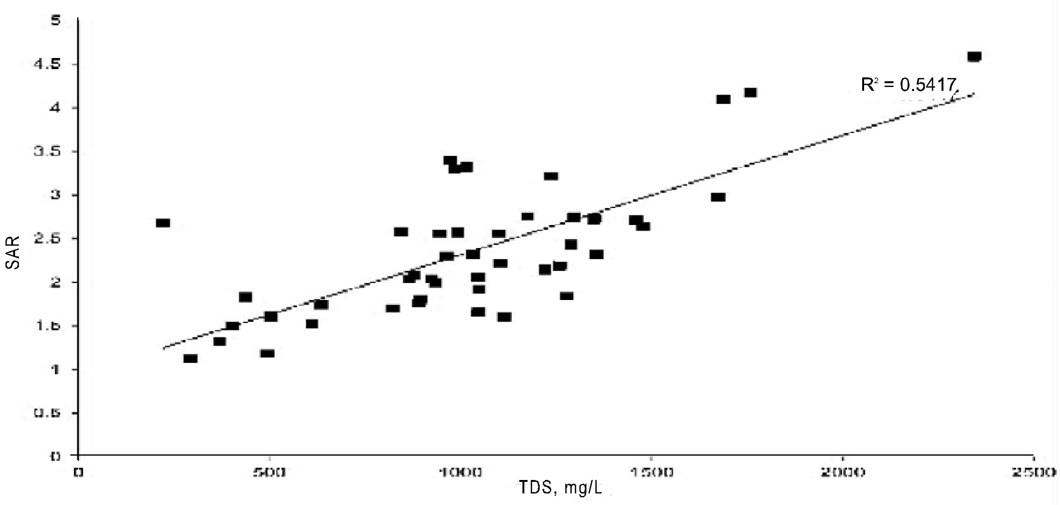

Fig. 3. Variation of SAR with TDS

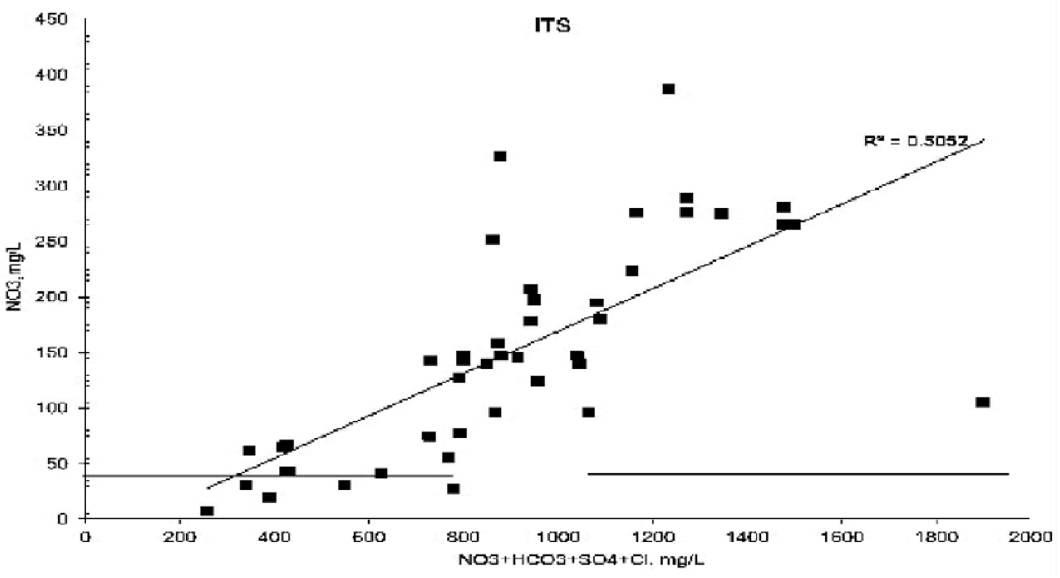

Fig. 4. Variation of nitrate with major anion concentration

Majority (91 %) of groundwater samples have TDS levels in excess of the desirable limit of 500 mg/L and values range from 611 mg/L to 2344 mg/L. Figure 6 plots the average distribution of major cations (calcium, magnesium, sodium and potassium) and anions (bicarbonate, chloride, sulfate and nitrate) in the groundwater. The excess potassium ion in the groundwater samples is attributed to leakage from soak pits as potassium ion is excreted at the rate of 1.8 to 2.7 g/person/d (Schouw *et al.*, 2002). Figure 6 also illustrates bicarbonate to be the predominant anion in the groundwater.

Figure 7 plots variations in calcium ion concentration in the groundwater samples as function of major cation (Ca^{2+}, Mg^{2}, Na^{+}, K^{+}) concentration. The calcium concentration tends to increase with major cation concentration. Also 78 % of the groundwater samples are characterized by calcium ion concentrations in excess of 100 mg/L; the values ranging from 114 to 318 mg/L. The higher calcium ion concentration in the groundwater samples is reflected in the much higher values of total hardness (Fig. 8); 78 % of the groundwater samples are classified as very hard water with the TH concentrations ranging from 413 mg/L to 1150 mg/L. The TH of the groundwater samples is calculated as (Todd, 1980):

$$\text{Total hardness (mg/L as CaCO}_3) = 2.5[Ca^{2+}] + 4.1[Mg^{2+}] \quad (3)$$

In equation 3, the square bracket denotes the concentration of each cation in mg/L. Figure 9 presents the Piper plot for the groundwater samples. The distribution of data

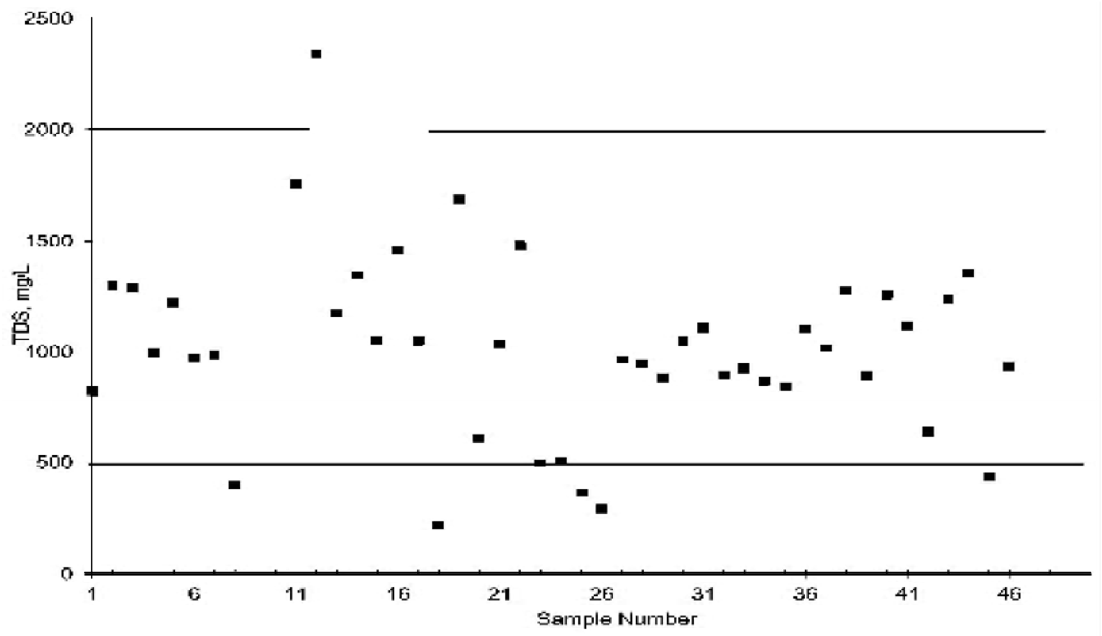

Fig. 5. TDS levels in groundwater samples.

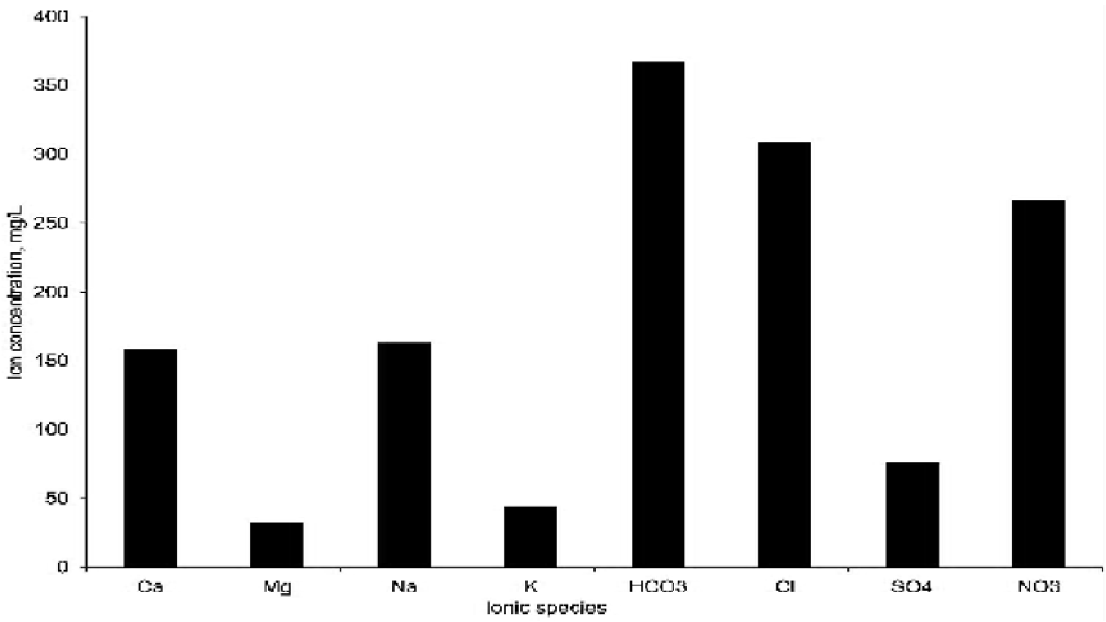

Fig. 6. Ion concentration in groundwater samples.

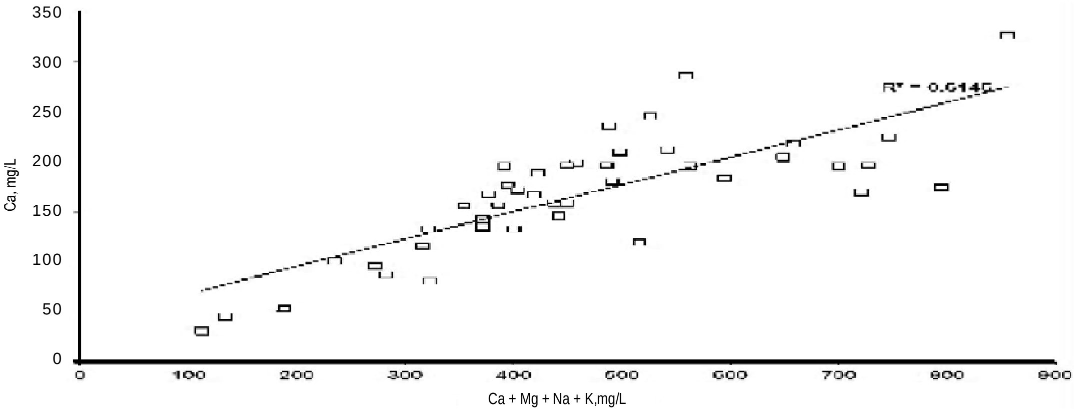

Fig. 7. Variation of calcium with major cation concentration.

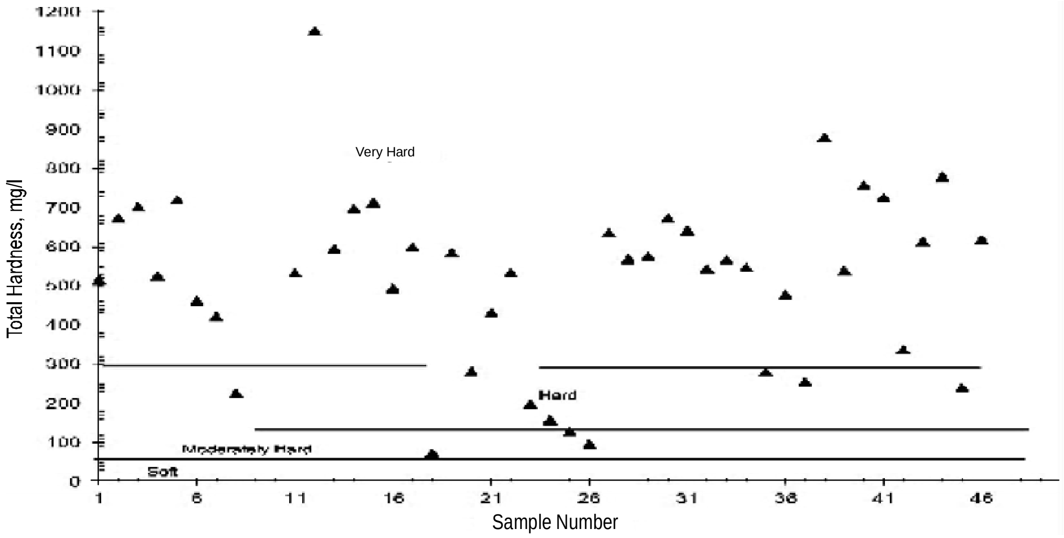

Fig. 8. Hardness classification of groundwater samples.

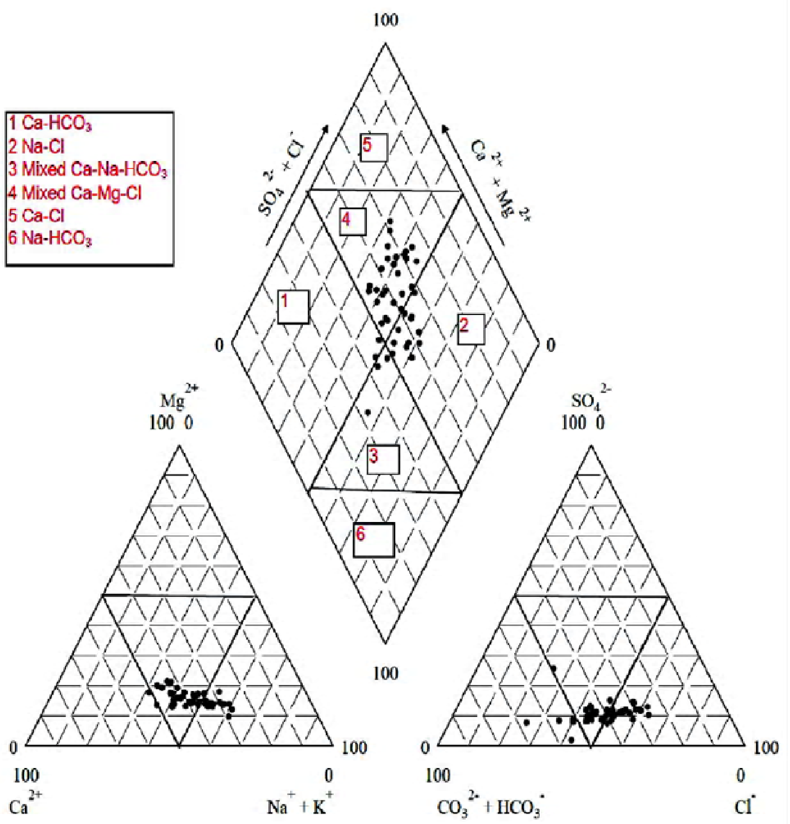

Fig. 9. Piper diagram for groundwater samples.

points in lower base triangles in Fig. 9 reveals that majority of the samples (65 %) do not categorize in any major cation type, while 30 to 31 % categorize as sodium and potassium type and the remainder as calcium type. Majority of samples (around 60 %) fall in Cl type, 28 % categorize under no dominant type and the remainder classified as HCO_3 type. The distribution of data points in rhomboids in Fig. 9 reveals that 60 % of the groundwater samples are classified as mixed Ca-Mg-Cl type, 28 % as Na-Cl type, 7 % as mixed $CaNaHCO_3$ type and the remainder as $CaHCO_3$ type.

Figure 10 presents the fluoride scatter plot of the groundwater samples. Although, Kolar district is known to be hot-spot for fluoride contaminated groundwater (Mamatha and Rao, 2010), none of the 43 samples exceeded the permissible limit of 1.5 mg/L and only 10 samples have fluoride concentrations above the desirable limit of 1 mg/L. The excess (above desirable/permissible limit) fluoride concentration in the groundwater samples of Kolar district is of geogenic origin (Mamatha and Rao, 2010). High calcium concentrations are known to restrict fluoride presence in the groundwater as they react with dissolved fluoride ions to form insoluble fluorite as (Handa, 1975; Hem, 1985):

$$Ca^{2+} + 2F^{-} \longrightarrow CaF_2 \text{ (insoluble)} \qquad (4)$$

Figure 11 shows that the calcium and fluoride concentrations in the groundwater samples of Mulbagal town are poorly correlated ($R^2 = 8\times10^{-6}$). The solubility of fluorite mineral and fluoride concentration in groundwater also increases with bicarbonate ion concentration and at constant pH the fluoride concentration is directly proportional to bicarbonate concentration (Rao and Devadas, 2003). Similar to the trend obtained for F versus Ca concentration (Fig. 11), the bicarbonate concentration has poor correlation ($R^2 = 0.096$) with fluoride concentration (Fig. 12). Table 2 summarizes the correlation coefficients for various parametric relations examined.

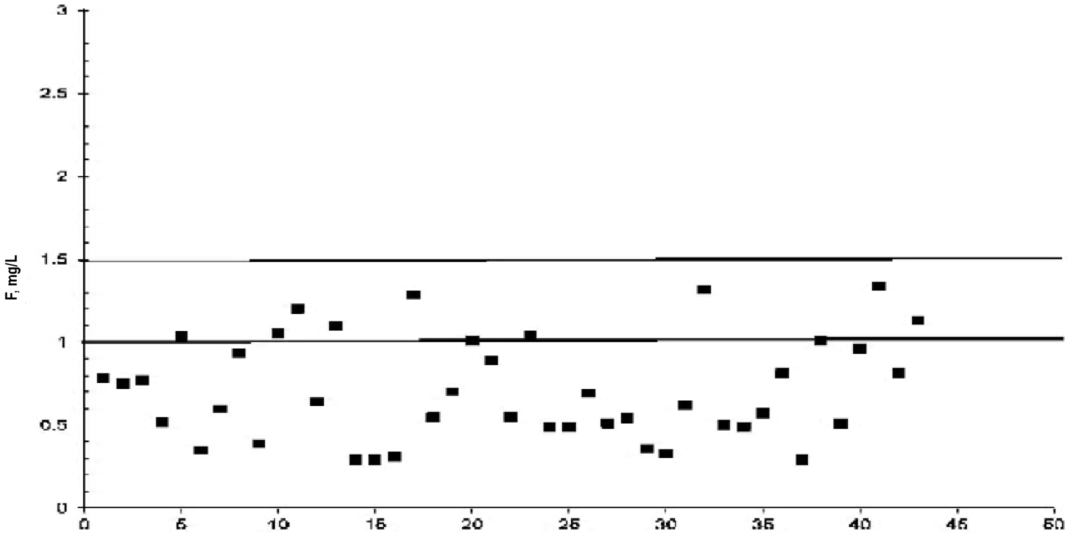

Fig. 10. Scatter plot of fluoride levels.

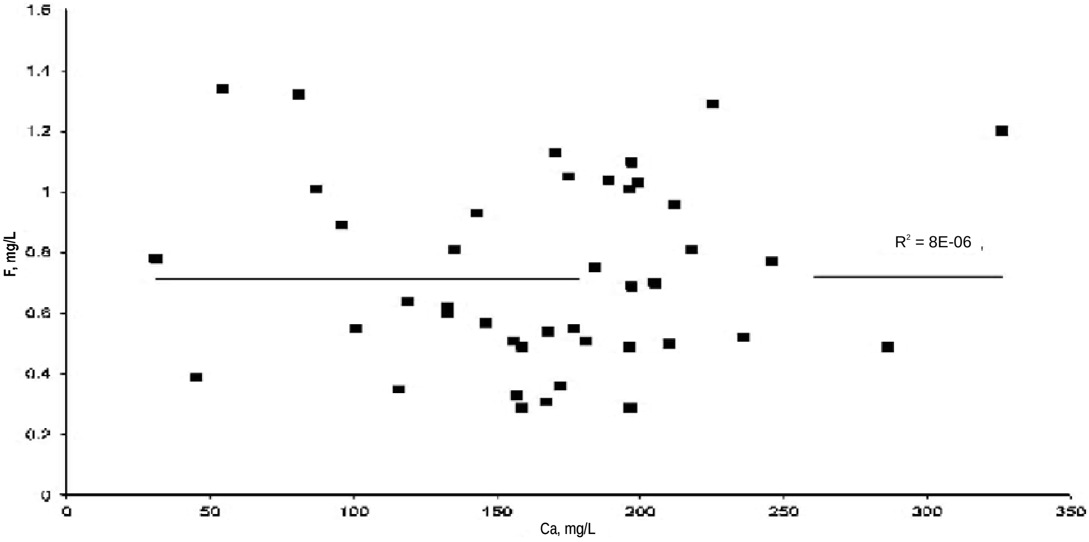

Fig. 11. Variation of fluoride with calcium ion concentration.

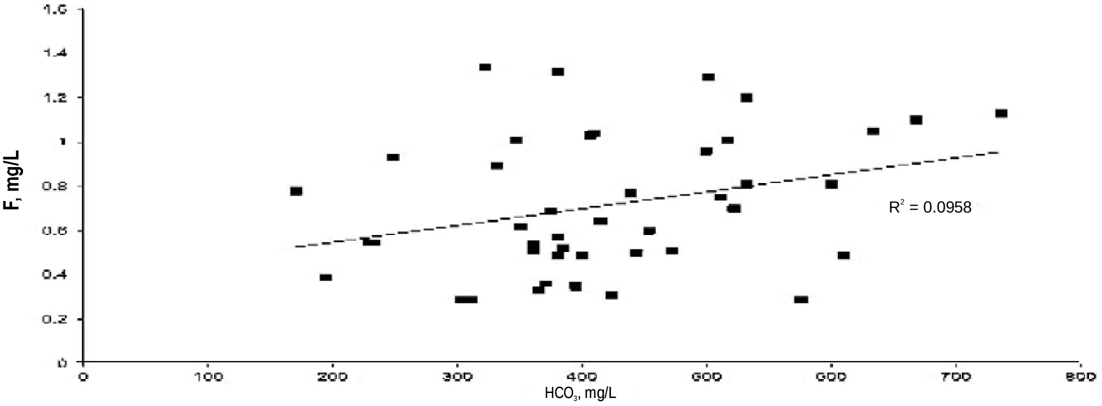

Fig. 12. Variation of fluoride with bicarbonate concentration.

The average calcium ion concentration in the groundwater samples in Mulbagal town corresponds to 167 mg/L, while the minimum and maximum concentrations correspond to 31 and 326 mg/L respectively. The average bicarbonate ion concentration in the groundwater samples corresponds to 421 mg/L, while the minimum and maximum concentrations correspond to 171 and 737 mg/L respectively. Mamatha and Rao (2010) had noted that calcium ion concentrations in the groundwater samples of Kolar district range from 30 to 254 mg/l with an average value of 95 mg/l. The average bicarbonate ion concentration in the groundwater samples of Kolar District corresponds to 364 mg/L, while the minimum and maximum concentrations correspond to 153 and 634 mg/L respectively. The groundwater samples in the study of Mamatha and Rao (2010) were obtained from regions that were free of anthropogenic contamination and are located approximately 100 km towards north of the present study area. Comparison of the data for groundwater samples from Mulbagal town and Kolar district indicate that the groundwater samples are characterized by larger average calcium and bicarbonate ion concentrations. The occurrence of higher calcium and bicarbonate concentrations in the groundwater of Mulbagal town is facilitated by the infiltration of pit toilet leachate in to the sub-soil zone. Decay of organic matter in the leachate enhances the CO_2 concentration in the pores of the geological stratum. The CO_2 in turn reacts with water to form carbonic acid that would dissolve calcite in the geological stratum and contribute to the larger calcium and bicarbonate ion concentrations in the groundwater of Mulbagal town. The poor correlation between calcium and fluoride levels and bicarbonate and fluoride levels in the groundwater of Mulbagal town apparently arise due to interference by anthropogenic activities on the geogenic based calcium and bicarbonate ion concentrations in the groundwater.

Saturation index. The saturation index value calculations indicated the groundwater studied by Mamatha and Rao (2010), in this study the area of Kolar district is oversaturated with respect to calcite and under saturated with respect to fluorite. The deficiency of calcium ion concentration in the groundwater due to calcite precipitation favours fluorite dissolution leading to excess fluoride concentration.

The SI of a mineral is obtained from the equation (Merkel and Friedrich, 2002):

$$SI = \log_{10}\frac{IAP}{K_{sp}} \qquad (5)$$

In equation 5, IAP represents the ion activity product of the dissociated chemical species in solution and K_{sp} represents the equilibrium solubility product of the mineral at sample temperature. If SI = 0; mineral is in equilibrium with solution, SI < 0; mineral is under saturated and if SI > 0; solution is oversaturated with the mineral (Deutsch, 1997). The SI values of calcite and fluorite are plotted for the groundwater samples (Fig. 13). An allowance of ± 0.5 units (dashed lines in Fig. 13) represents the boundaries for equilibrium zone to account for errors involved in field measurement and analytical procedures involved in computation of SI (Nordstorm and Jenne, 1977; Deutsch, 1997; Carrillo-Rivera *et al.*, 2002). The Fig. 13 shows that the groundwater is under-saturated with respect to calcite and fluorite. Groundwater samples collected from Kolar district from regions that were free of anthropogenic contamination, were however observed to be either oversaturated or in equilibrium with calcite (Mamatha and Rao, 2010). The under saturation of the groundwater samples with calcite in the study area (Fig. 13) possibly arises due to the acidic pH of the groundwater environment as illustrated next. Table 1 summarizes the ionic composition of groundwater samples.

Figure 14 plots the pH variation in groundwater samples. About 37 % of the groundwater samples exhibit pH < 6.5 (below potable limit) and 86 % of samples exhibit pH between 6.5 and 7. The average pH of the groundwater samples corresponds to 6.57, while the minimum and maximum pH values are 5.72 and 7.66 respectively. The pH of groundwater samples acquire acidic pH when the major anion (chloride, sulfate, bicarbonate/carbonate, nitrate) concentration (expressed in terms of meq/L) is not balanced by an equivalent quantity of major cations (calcium, magnesium, sodium, potassium) in groundwater (Younger, 2007).

Table 2. Correlation coefficients for relations between groundwater parameters.

Relation	Correlation coefficient (R^2)
Sodium absorption (SAR) versus total dissolved solids (TDS) concentration	0.54
Nitrate versus total anion concentration	0.51
Calcium versus total cation concentration	0.61
Fluoride versus calcium ion concentration	8×10^{-6}
Fluoride versus bicarbonate ion concentration	0.096

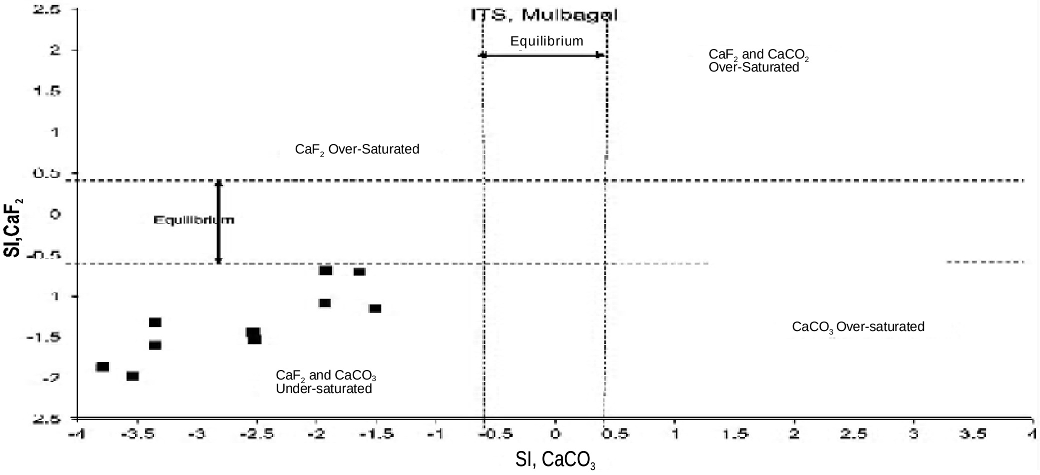

Fig. 13. SI values of calcite and fluorite.

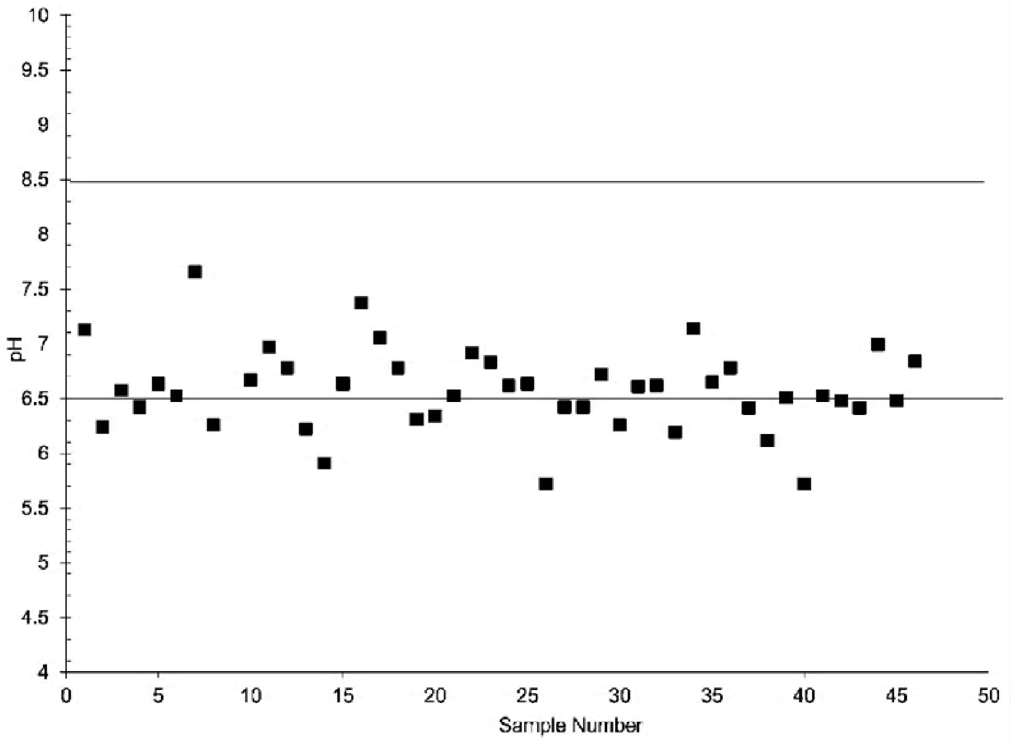

Fig. 14. pH scatter for groundwater samples.

Conclusion

Leachate infiltration from pit toilets imposes large concentrations of sodium, potassium, calcium, bicarbonate and nitrate ions in the groundwater of Mulbagal town in Kolar district, Karnataka. Although Kolar district is hot spot of fluoride contamination, the groundwater samples from Mulbagal town did not exhibit fluoride presence in excess of the permissible limit (1.5 mg/L). Poor correlations between calcium and fluoride ion, and bicarbonate and fluoride ion concentrations are attributed to interference from pit-toilet leachate infiltration on the geogenic derived groundwater chemistry. Computation of saturation index values of calcite and fluorite showed that the groundwater in Mulbagal town is under saturated with respect to calcite that in turn suppresses the tendency of fluorite to dissolve and enhance the fluoride concentration in the groundwater. The slightly acidic pH of the groundwater in Mulbagal town is considered responsible for under saturation of calcite.

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