

1     **Appraisal of salinity and fluoride in a semi-arid region of India using**  
2                     **statistical and multivariate techniques**

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14  
15     **Abstract**

16             Various physico-chemical parameters including fluoride (F<sup>-</sup>) were analyzed to  
17 understand the hydro geochemistry of an aquifer in a semi-arid region of India.  
18 Furthermore, the quality of the shallow and deep aquifer (using tube-well and hand-  
19 pumps) were also investigated for their best ecological use including drinking,  
20 domestic, agricultural and other activities. Different multivariate techniques were  
21 applied to understand the groundwater chemistry of aquifer. Findings of correlation  
22 matrix were strengthened by the factor analysis and this shows that salinity is mainly  
23 contributed by magnesium-salts as compared to calcium-salts in the aquifer. The  
24 problem of salinization seems mainly compounded by the contamination of the shallow  
25 aquifers by the recharging water. High factor loading of total alkalinity and bicarbonates  
26 indicates that total alkalinity was mainly due to carbonates and bicarbonates of sodium.  
27 The concentration of F<sup>-</sup> was found more in the deep aquifer than the shallow aquifer.  
28 Further, only few groundwater samples lie below the permissible limit of F<sup>-</sup> and this  
29 indicate the risks of dental caries in the populace of study area. The present study  
30 indicates that regular monitoring of groundwater is an important step to avoid human  
31 health risks and to assess its quality for various ecological purposes.

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33     **Keywords:** Groundwater, Hydro geochemistry, Fluoride, Salinity, Factor analysis,  
34     Ecological best use.

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## 39 **1. Introduction**

40 Groundwater use has superiority over surface water as it serves as a naturally  
41 occurring reservoir due to less susceptibility to evaporation losses, climate variability  
42 and vulnerability to anthropogenic activities. Because of these advantages and uses, the  
43 significant quantity of groundwater is being used for domestic, agricultural, industrial  
44 and land-use related activities. Monitoring of water quality is one of the important steps  
45 in water resources management. Water quality monitoring has been given the highest  
46 preference in health protection (WHO, 2006) and in environmental protection policies  
47 (Robins, 2002; Kruawal et al., 2005). The routine monitoring of groundwater can assure  
48 the populace about the quality of their drinking water and helps in recommending  
49 remedial action to check further deterioration in quality (Ravindra and Garg, 2007).

50 The chemical characteristics of water govern its suitability for various activities  
51 such as domestic, irrigation and industrial (Wen and Chen 2006). Water chemistry is  
52 very complex because of the association of a large number of measured variables  
53 (Ravindra et al., 2003). This also makes extraction of valuable information from huge  
54 data sets a difficult task. Multivariate statistical methods including factor analysis by  
55 principal component analysis have been used successfully in evaluating water quality,  
56 and the use of such multi-component techniques for the determination of groundwater  
57 quality are very well explained and used in the literature (Lambrakis et al., 2004; Singh  
58 et al., 2005; Mor et al., 2006; Chen et al., 2007).

59 In developing countries, groundwater is extracted without responsible  
60 management as well as without due attention to quality issues (Ravindra and Garg,  
61 2007). In many parts of India, fluoride ( $F^-$ ) is one of the most undesired elements  
62 present in underground water extracted for drinking purposes. Presence of  $F^-$  in  
63 groundwater that is higher than the prescribed permissible limit, significantly affects the  
64 human health and may lead to fluorosis, an endemic disease (Bureau of Indian  
65 Standards (BIS), 1991; Ripa, 1993; WHO, 1997). Recently, Ravindra and Garg (2006;  
66 2007) have highlighted the problem of  $F^-$  and fluorosis in Haryana, India. Prevalence of  
67 fluorosis has been reported mainly due to intake of fluoride rich groundwater over a  
68 long period of time.

69 In the present study, the groundwater quality of Sirsa city was evaluated from  
70 various tube-well (deep aquifers) and hand-pumps (shallow aquifers) to understand the  
71 geochemistry of the aquifer with special attention to  $F^-$  and salinity. Furthermore, its  
72 suitability for domestic, drinking and irrigation purposes was also evaluated. The

73 applications of various multivariate techniques (correlation, factor analysis,  
74 geochemical diagrams) were used to understand the interdependence of various ions and  
75 their groundwater chemistry. The geochemical evaluation of groundwater was  
76 performed using ‘charge balance index’ and ‘Gibb’s plot’, whereas the ‘sodium  
77 absorption ratio (SAR)’ was applied to assess the ecological best use of groundwater.

78

## 79 **2. Material and methods**

### 80 **2.1 Sampling site**

81 Sirsa city is located between latitude 29°14” and 30° North and longitudes 74°  
82 29” and 75° 18” East in Haryana state and climatologically falls under semi-arid zone of  
83 India. The mean daily maximum temperature rises up to 41 – 46 °C during May and  
84 June and the average annual rainfall in Sirsa district varies from 100 to 400mm (Singh  
85 et al., 2006). It is around 250 km far from Delhi and known as “the cotton belt of  
86 Haryana” (Figure 1). The terrain of Sirsa district may be broadly classified from north  
87 to south into three major types i.e. Haryana Plain, alluvial bed of Ghaggar or Nali and  
88 Sand dunes tract. Tube-well and hand-pumps are the main source of groundwater for the  
89 domestic, agricultural and industrial needs in the studied area. These wells also form a  
90 part of municipal water supply system in some limited areas.

91

### 92 **2.2 Collection of groundwater samples**

93 To understand the general variation in groundwater quality a survey of  
94 Sirsa city was conducted in 2006 and representative sampling sites were  
95 identified. Groundwater samples were collected from 28 sites (15 tube well and  
96 13 hand pumps) after flushing water 5-10 minutes in order to remove the interference  
97 of the standing water in the metal casing and to stabilize the Electrical Conductivity  
98 (EC). The details of the sampling sites are presented in Table 1 and Figure 1.  
99 These sites were located in the urbanized part of the city and the main use of the water  
100 was domestic and industrial. Lack of a municipal water supply system has resulted in  
101 the dependency on the groundwater resources. Clean plastic bottle of 500 ml  
102 capacity were used to collect groundwater samples. A separate sub sample was  
103 collected and acidified for the analysis of dissolved metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  
104  $\text{Mg}^{2+}$ ). Groundwater samples were immediately transferred to the lab and were  
105 stored at 4°C to avoid any major chemical alteration.

106

## 107 **2.3 Analytical methodology**

108 The groundwater samples were analyzed using APHA (1995) procedure  
109 and suggested precautions were taken to avoid contamination. The various  
110 parameters determined were pH, EC, total dissolved salts (TDS), total hardness  
111 (TH), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), total alkalinity (TA), carbonate  
112 ( $\text{CO}_3^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ), chloride ( $\text{Cl}^-$ ), sulphate ( $\text{SO}_4^{2-}$ ),  $\text{F}^-$ , sodium  
113 ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ). pH and EC were determined on the spot using  $\mu$ -pH  
114 system-361 (Systronic, India) and conductivity meter Mode-306 (Systronic,  
115 India), respectively, including temperature. The values of TDS were calculated  
116 from EC by multiplying a factor that varies with the type of water (United States  
117 Salinity Laboratory, 1954). TH,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , TA,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  were  
118 estimated by titrimetry, whereas  $\text{Na}^+$  and  $\text{K}^+$  by flame photometry (Systronic-  
119 128).  $\text{F}^-$  was estimated by SPADNS method and  $\text{SO}_4^{2-}$  was estimated using  
120 Perkin-Elmer UV/VIS lambda-2 spectrophotometer. Observed data was  
121 statistically analyzed using SPSS-11.0 software. All the experiments were carried  
122 out in triplicate and the results were found reproducible within  $\pm 3\%$  error limit.

123

## 124 **3. Results and Discussion**

### 125 **3.1 Physico-chemical parameters and health risks**

126 The physiochemical characteristic of groundwater in Sirsa City has been shown  
127 in Table 2. The groundwater of the study area is slightly alkaline in nature. Four  
128 samples were found to deviate from the acceptable limit with pH values in samples  
129 varying from 6.8 – 8.7. The highest value for pH was observed at location number 18.  
130 The hand pump of this location is the newest of all the sampling locations. In general  
131 groundwater pH is slightly alkaline due to the influx of  $\text{HCO}_3^-$  ions in the groundwater  
132 aquifer, which is due to percolation of rain water through soil (Mor et al., 2006; Kumar  
133 et al., 2007). The EC is an indicator of salinity and also signifies the amount of TDS. EC  
134 of collected water samples ranges from 0.4 – 3.7 mS/cm. TDS indicates the inorganic  
135 pollution load. TDS values ranged from 256 mg/l to 2792 mg/l and only one water  
136 sample lies within BIS permissible limit for TDS.

137 Hardness is mainly due to  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in  
138 groundwater (BIS 1991). The higher incidence rate of gallbladder disease, urinary  
139 stones, arthritis and arthropathies has been reported in area supplied with drinking water  
140 harder than 500 mg/l  $\text{CaCO}_3$ . Depending on the interaction with other factors such as

141 pH and alkalinity, water with hardness above 200 mg/l may cause scale deposition in  
142 distribution systems. On the other hand, soft water with hardness less than 100 mg/l has  
143 a greater tendency to cause corrosion of pipe resulting from the presence of heavy  
144 metals such as Pb, Zn, Cu and Cd in drinking water. Durfor and Beckor (1964) have  
145 classified water as soft, moderate, hard and very hard. As per this classification, 20  
146 samples come under the very hard category. Only seven samples fall in category of soft  
147 to moderate as presented in Table 2. The TA in the water samples ranged from 60–728  
148 mg/l. The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are the most abundant elements in the groundwater  $\text{Ca}^{2+}$  may  
149 dissolve readily from carbonate rocks and lime stones or be leached from soils.  
150 However, the dissolved  $\text{Mg}^{2+}$  concentration is lower than  $\text{Ca}^{2+}$  in the groundwater.  $\text{Ca}^{2+}$   
151 is an essential nutritional element for humans and helps in maintaining the structure of  
152 plant cells and soils.  $\text{Mg}^{2+}$  is a constituent of bones and is essential for normal  
153 metabolism of  $\text{Ca}^{2+}$ . Its deficiency may lead to protein energy malnutrition. The  
154 optimum concentration of  $\text{Ca}^{2+}$  is required in drinking water to prevent cardiac disorder  
155 and for proper functioning of metabolic processes. The estimated  $\text{Ca}^{2+}$  contents in water  
156 samples range from 6–106 mg/l, while  $\text{Mg}^{2+}$  concentration varied from 5–140 mg/l.  
157 Only 3 water samples of Sirsa city have  $\text{Ca}^{2+}$  content above the permissible limit.  $\text{Mg}^{2+}$   
158 content in two water samples is beyond the maximum permissible limit and only 8  
159 samples lie within desirable limit.

160 Alkalinity of water is mainly due to the presence of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . It is a  
161 measure of the ability of water to neutralize acids. The alkalinity in natural water system  
162 may be contributed by  $\text{H}_3\text{BO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$ , and  $\text{HS}^-$ . These compounds results from  
163 dissolution of mineral substances in soil. TA of samples ranged from 112-964 mg/l.  
164  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  in water are present mainly in association with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .  $\text{HCO}_3^-$   
165 ranged from 102–777 mg/l, while  $\text{CO}_3^{2-}$  ranged from 10-187 mg/l. High alkalinity does  
166 not pose a health risk but can cause problems such as alkali taste to water. Alkalinity is a  
167 big problem for industries; if alkaline water is used in boiler for steam generation then it  
168 may leads to the formation of scale and embrittlement and the lowered efficiency of  
169 electric water heater.

170  $\text{Cl}^-$  occurs naturally in some sedimentary bed rock layer, particularly shales.  $\text{Cl}^-$   
171 is soluble in water and moves freely with water through soil and rocks.  $\text{Cl}^-$  is more  
172 persistent in nature than nitrate as it is not readily consumed by microorganisms. High  
173 content of  $\text{Cl}^-$  may give a salty taste to groundwater and can corrode pipes, pumps and  
174 plumbing fixtures. People who are not accustomed to high chlorine in drinking water

175 are subjected to laxative effects.  $\text{Cl}^-$  concentration in the study area varied from 28-388  
176 mg/l.  $\text{SO}_4^{2-}$  is a naturally occurring ion in almost all kinds of water bodies and is a  
177 major contributor to total hardness.  $\text{SO}_4^{2-}$  content more than 200 mg/l is objectionable  
178 for domestic purposes, beyond this limit  $\text{SO}_4^{2-}$  causes gastro-intestinal irritation. All the  
179 water samples of Sirsa city had  $\text{SO}_4^{2-}$  content within permissible limits, ranging from 2  
180 – 29 mg/l.

181  $\text{Na}^+$  and  $\text{K}^+$  are naturally occurring elements in groundwater. Industrial and  
182 domestic waste also adds these salts to the groundwater, making it unsuitable for  
183 domestic use. High concentration of  $\text{Na}^+$  in drinking water may cause heart problems.  
184 Further, higher  $\text{Na}^+$  content in irrigation water may cause salinity problems and may  
185 render the soil barren (Kumar et al., 2007).  $\text{Na}^+$  content of the groundwater of Sirsa city  
186 varied from 6–448 mg/l and 24 water samples have  $\text{Na}^+$  content beyond the permissible  
187 limit (WHO, 2006).  $\text{K}^+$  is an important cation and plays a vital role in intermediately  
188 metabolism. It is also important for  $\text{Na}^+ - \text{K}^+$  exchange pump. The  $\text{Na}^+$  content of  
189 groundwater of Sirsa city varied from 2 - 48 mg/l.  $\text{Na}^+$  also regulates the stomatal  
190 activity of leaves and hence plays a very significant role in crop physiology involving  
191 transpiration losses and gaseous exchange in respiration and photosynthesis.

192

### 193 ***3.2 Hydrogeology and salinity in Sirsa***

194 The area in Sirsa district can be divided into two major geomorphic units, viz.  
195 Alluvial plain and Palaeo channels/Sand dune complexes. High levels of TDS indicate  
196 the leaching of natural salts in to the groundwater aquifer and pose a risk of salinization  
197 in Sirsa. The major ions responsible for salinization are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$ .  
198 Moreover, groundwater salinity is also influenced by the quality of the recharging water  
199 (Richter and Kreidler, 1993; Misra and Misra, 2006, 2007a, b). However, leaching of  
200 natural salts is a natural phenomena but the problem is compounded by the  
201 contamination of fresh groundwater by saline water. Such problems are more confined  
202 in the semiarid to arid climatic conditions e.g. in the present case, where the absence of  
203 natural flushing by freshwater makes groundwater prone to enhanced salinization  
204 (Singh et al., 2007a, b). Alluvial Plain consists of clay, sticky clay and fine grained  
205 sand. The sticky clay helps in confining the water under artesian conditions, obstructing  
206 the drainage of the soil (Kumar et al., 2007). This leads to the accumulation of  $\text{Na}^+$  and  
207  $\text{Mg}^{2+}$  -salts and thus gives rise to salt encrustations and renders the soil infertile. This  
208 also explains the higher TDS concentration in the groundwater of Sirsa city. During the

209 course of time and with subsequent rain water recharge, the elution of these salts occurs  
210 and results in the high TDS concentration in the shallow aquifers.

211

### 212 **3.3 Fluoride and fluorosis**

213 The main sources of drinking water in the studied area are hand-pumps and tube-  
214 well. In general, it has been observed that groundwater contains a higher amount of  $F^-$   
215 dissolved from geologic conditions while surface water typically contains lesser amount  
216 of  $F^-$  (Ravindra et al., 2003). Furthermore, usually the  $F^-$  levels are more in the shallow  
217 aquifers in alluvial plains but in the present case the concentration of  $F^-$  was found  
218 relatively high in deep aquifer (tube well) than shallow aquifer (hand-pumps). This  
219 could be due to difference in the geochemical conditions in aquifer. Kim and Jeong  
220 (2005) also reported high fluoride in deep wells than shallow aquifers.

221 A small quantity of  $F^-$  is required for healthy growth of teeth and prevention of  
222 dental caries. High levels of excess  $F^-$  intake cause crippling skeletal  $F^-$ . This is almost  
223 always associated with high  $F^-$  intake from drinking water. Ingestion of excess  $F^-$  during  
224 tooth development, particularly at the maturation stage, may also result in dental  
225 fluorosis (Ravindra and Garg, 2006; 2007). The optimal drinking water concentration of  
226  $F^-$  for dental health generally ranges from 0.5 to 1.0 mg/l and depends upon the volume  
227 of consumption and uptake and exposure from other sources. The BIS permissible limit  
228 of  $F^-$  in groundwater is 1 mg/l. The value of  $F^-$  ranged from 0.10-1.90 mg/l. and 10  
229 samples exceed the permissible limits. As per BIS guidelines the minimum amount of  $F^-$   
230 mandatory for healthy growth of teeth is 0.5 mg/l. One third of groundwater samples  
231 bear  $F^-$  above the desirable BIS limit, indicating the risks of fluorosis for the population  
232 consuming this water over long duration.

233

### 234 **3.4 Ecological best use**

235 Evaluation of groundwater based on various physico-chemical analyses  
236 indicated that 9 (out of 28 samples) are unsuitable for drinking purpose (Table 2 and 3).  
237 Furthermore, more than 50% of the samples fall in the hard to very hard category. The  
238 non availability of the groundwater for daily chorus was found to be related with the  
239 presence of excess  $CO_3^{2-}$  and  $HCO_3^-$  and TDS. Suitability of groundwater for irrigation  
240 purposes was also assessed using the criteria shown in Table 4a and 4b. A comparison  
241 of EC or TDS values with irrigation standards shows that only 35% of samples can be  
242 considered in class I, whereas 65% are in class II. In the absence of other water sources

243 they are suitable with permeable soil (Kumar et al., 2007). Chloride content of 79% of  
244 the samples showed that the groundwater is excellent for irrigation, while it may be  
245 injurious to crops for rest of samples.  $\text{SO}_4^{2-}$  content of all the water samples indicates  
246 that these water samples are of class II (Table 4a).

247 In addition to the EC, TDS,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ;  $\text{Na}^+$  is also an important parameter.  
248 Excess quantities of  $\text{Na}^+$  can cause the soil quality to deteriorate and may cause damage  
249 to the sensitive crops because of sodium phyto-toxicity.  $\text{Na}^+$  in water can be denoted by  
250  $\text{Na}^+$  absorption ratio (SAR) and it was calculated by using following formula

$$251 \quad \text{SAR} = \frac{\text{Na}}{\sqrt{\text{Ca} + \text{Mg}}/2} \quad \text{--- (1)}$$

252 A comparison of SAR and suitability for irrigation has been shown in Table 4b.  
253 It shows that only 10 groundwater wells are suitable for most types of crops and soils. 8  
254 groundwater wells can be used if the organic content in the soil is high or it has a coarse  
255 texture with good permeability reference. The study reveals that 2 groundwater wells  
256 were found harmful for all types of soil and the groundwater quality of 8 wells is not  
257 suitable for irrigation activities. The results also indicated that SAR of the groundwater  
258 should be taken into consideration before its extraction for irrigation. This will be an aid  
259 to protect the sensitive crops from  $\text{Na}^+$  phytotoxicity and to limit the increase of salinity  
260 in the area.

261

#### 262 **4. Multivariate analysis and Groundwater chemistry**

263 Multivariate data can be easily interpreted with the help of statistics and hence  
264 in the present study the understanding of the groundwater chemistry was appraised with  
265 the use of statistical applications. The analytical results shown in supplementary Table 1  
266 were used as input in SPSS software package (version 13.0). The methods of bivariate  
267 correlation analysis [with the Pearson's correlation coefficient (r) at two-tailed  
268 significance level (p)] and principal component analysis (PCA) were applied using the  
269 SPSS software. For PCA, the methods of Varimax-rotation and Kaiser-normalization  
270 were applied. Only principal components (factors) having >10 % of total variance of the  
271 data sets were used as factors.

272

#### 273 **4.1 Geochemical evaluation**

274 The normalized charge balance index (NCBI) was calculated using the following  
275 formula from Kumar et al. (2007):



276

277 
$$NCBI = \frac{\sum Tz^- - \sum Tz^+}{\sum Tz^- + \sum Tz^+} \quad \dots (2)$$

278

279 Where  $\sum Tz^+$  is the sum of total cations (in epm) and  $\sum Tz^-$  is the sum of total  
280 anion (in epm) analyzed in groundwater. It was observed that about 85% of the samples  
281 were in the range of  $\pm 20\%$  error percentage and the charge balance was in favor of  
282 cations (Figure 2). As depicted in the upper graph of Figure 3 ( $Ca^{2+} + Mg^{2+}$  vs.  $HCO_3^-$   
283  $+CO_3^{2-}$ ) indicates the  $Ca^{2+}$  and  $Mg^{2+}$  are in excess and the alkalinity of the water  
284 (hardness) is balanced by the alkaline earth metals in aquifer of Sirsa city. Figure 3 also  
285 indicates that the majority of the charge is balanced by  $SO_4^{2-}$  and  $Cl^-$ . This is further  
286 supported by the middle graph of Figure 3 ( $Ca^{2+}+Mg^{2+}$  vs  $HCO_3^-+SO_4^{2-}$ ); where most of  
287 the point falls near the equiline. The lower graph of  $Na^+K^+$  vs.  $Tz^+$  shows all the points  
288 fall below the equiline indicating the lesser contribution towards the charge balance  
289 (Figure 2 and 3). This indicated that despite the dominance of  
290 evaporation/crystallization processes occurring in the groundwater of Sirsa city, the ion  
291 chemistry is mostly controlled by alkaline earth metals rather than alkali metals. This is  
292 also supported by the Gibb's plot (Figure 4), which shows the majority of the samples  
293 fall in the rock dominance and result from the weathering of calcite, dolomite or  
294 gypsum rocks. Even though  $Na^+$  being the most dominant cations, the ground water  
295 chemistry is governed by alkaline earth metal namely  $Ca^{2+}$  and  $Mg^{2+}$ .

296

297 The groundwater quality of Sirsa was evaluated through a diagram (Figure 5) as  
298 proposed by Chadha (1999). The rectangular field of the plot described the primary  
299 character of the water and is divided into eight sub-fields, each of which represents a  
300 water type and hardness domain (Figure 4) as follows: (1) Alkaline earths exceed alkali  
301 metals. (2) Alkali metals exceed alkaline earths. (3) Weak acidic anions exceed strong  
302 acidic anions. (4) Strong acidic anions exceed weak acidic anions. (5) Alkaline earths  
303 and weak acidic anions exceed both alkali metals and strong acidic anions, respectively.  
304 Such water has temporary hardness. The position of data points in this domain  
305 represents Ca-Mg- $HCO_3$  water type. (6) Alkaline earths exceed alkali metals and strong  
306 acidic anions exceed weak acidic anions. Such water has permanent hardness and does  
307 not deposit residual Na- $CO_3$  in irrigation use. The position of data points in this domain  
308 represents Ca-Mg-Cl type of waters. (7) Alkali metals exceed alkaline earths and  
strong acidic anions exceed weak acidic anions. Such water generally creates salinity

309 problems both in irrigation and drinking uses. The position of data points in this domain  
310 represents Na-Cl type and Na-SO<sub>4</sub> type of waters. (8) Alkali metals exceed alkaline  
311 earths and weak acidic anions exceed strong acidic anions. The graph shows the  
312 dominance of alkali metal over alkaline earths and strong acidic anions exceed weak  
313 acidic anions. The hydro geochemistry of the aquifer of Sirsa city shows dominance of  
314 both alkali metal and alkaline earth metal. However, the temporary hardness was also  
315 observed at some sampling locations.

316

#### 317 **4.2 Correlation Matrix**

318 The correlation matrix describes the interrelationship among various variables  
319 and results are shown in Table 5. pH was found to be negatively correlated with Ca<sup>2+</sup> (r  
320 = -0.60\*\*), Mg<sup>2+</sup> (r = -0.30), TH (r = -0.43\*), K<sup>+</sup> (r = -0.29), Cl<sup>-</sup> (r = -0.15) and F<sup>-</sup>  
321 (r = -0.01). It showed a high degree of positive correlation with CO<sub>3</sub><sup>2-</sup> (r = 0.77\*\*) and  
322 correlation is significant at 0.01 level. EC or TDS are mainly contributed by salts of  
323 Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>. Table 5 also shows a moderate degree of correlation of Na<sup>+</sup>, with  
324 CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and TA. Furthermore, TA is highly correlated with HCO<sub>3</sub><sup>-</sup> (r = 0.99).  
325 This suggest that the Salts of Na-CO<sub>3</sub><sup>2-</sup> and Na-HCO<sub>3</sub><sup>-</sup> contribute significantly towards  
326 total alkalinity Cl<sup>-</sup> was found to be significantly correlated with Ca<sup>2+</sup> and Mg<sup>2+</sup>  
327 indicating the presence of chloride salts of Ca<sup>2+</sup> and Mg<sup>2+</sup>. SO<sub>4</sub><sup>2-</sup> was significantly  
328 correlated with Na<sup>+</sup>, indicating the presence of Na-SO<sub>4</sub><sup>2-</sup> salt. TH also showed a high  
329 degree of positive correlation with Mg<sup>2+</sup> (r = 0.943). Cursory examination of the data  
330 reveals that the majority of the groundwater samples in this region are dominated by  
331 Mg<sup>2+</sup> hardness as compared to Ca<sup>2+</sup> hardness.

332

#### 333 **4.3 Factor analysis**

334 Factor analysis is a multivariate technique designed to analyze the  
335 interrelationship within a set of variables or objects. As a result, a small number of  
336 factors will usually account for approximately the same amount of information as do the  
337 much larger set of original observations (Lambrakis et al., 2004; Singh et al., 2005; Mor  
338 et al., 2006; Chen et al., 2007). In the present study, the interpretation was based on  
339 rotated factors, rotated loadings and rotated eigen values. All the analyzed parameters  
340 including cations, anions, EC and pH were considered and the results of factor analysis  
341 are shown in Table 6. The factor loading correlates the variables and they represent the  
342 most important information on which interpretations of the factors are based.

343 Factors having Eigen value more than 1 were retained, which reveals 11 factors.  
344 The first factor is generally more closely correlated with the variables than the second  
345 factors because of the fact that these factors are extracted successively, each one  
346 accounting for as much of the remaining variables as possible. The first 4 factors cover  
347 around 80% of total variance and hence are discussed here. Factor 1, illustrates strong  
348 positive loading of TA,  $\text{HCO}_3^-$ , and moderate loading of  $\text{CO}_3^{2-}$ . These factors indicate  
349 that in the study area the TA may be mainly due to the  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  salts of  $\text{Na}^+$  in  
350 the aquifer. Factor 2, was found to be associated with strong loading of EC, TDS and  
351 moderate loading of  $\text{Na}^+$ . This factor revealed that EC and TDS are mainly due to  $\text{Na}^+$ -  
352 salts in this study area. Factor 3, shows high loading for  $\text{Mg}^{2+}$ , TH with low loadings of  
353  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ . This factor can be associated with the permanent hardness of water.  
354 Hardness is mainly contributed by Mg-salts as compared to Ca-salts. Factor 4, is  
355 characterized by a strong loading of pH,  $\text{CO}_3^{2-}$  and low loading of  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . All  
356 these ions show their contribution towards hardness and salinity. The remaining factors  
357 were characterized by the dominance of only one variable and low loading of other  
358 variables; hence they can be considered as irrelevant for describing the factor model of  
359 groundwater chemistry of Sirsa city.

360

## 361 **5. Conclusions**

362 Groundwater quality of Sirsa city wells were evaluated for their best ecological  
363 uses. Generally the groundwater falls in hard to very hard category and only 15% of  
364 samples are within permissible limit of TDS. The rest of the groundwater samples have  
365 a TDS value of more than 500-1500 mg/l. Na-salts of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  were identified as a  
366 major contributor to TDS or EC. With the exception of one sample, all the samples have  
367 a TH value within the maximum limits of (600 mg/l).  $\text{Na}^+$  content was beyond  
368 permissible limit (50 mg/l) for 65% of water samples. An increase in the concentration  
369 of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and other ions is the main cause of the salinization in Sirsa  
370 district. The problem seems mainly enhanced by the rainfall and irrigation with poor  
371 quality water/groundwater, which enhance salt leaching.

372 However,  $\text{F}^-$  content in most of the samples falls within maximum limit but it  
373 poses the risks of dental caries in the populace of Sirsa city. Factor analysis of  
374 groundwater generated 11 factors. The first 4 factors were able to explain 80% of total  
375 variance of data and were considered as representative of factor model. A high degree of  
376 positive correlation of total hardness with  $\text{Mg}^{2+}$  indicates that hardness was mainly

377 contributed by salts of  $Mg^{2+}$ . This analysis also strengthens the finding of correlation  
378 matrix and confirmed that TH was mainly contributed by Mg-salts as compared to Ca-  
379 salts. Further, high loading of TA,  $HCO_3^-$  and  $CO_3^{2-}$  in the first factor indicated that TA  
380 was mainly due to  $CO_3^{2-}$  and  $HCO_3^-$  of  $Na^+$ . The study also highlights the need to  
381 estimate SAR of any aquifer before its utilization in irrigation to protect sensitive crops  
382 from  $Na^+$  phytotoxicity and to limit the salinization.

383

#### 384 **Acknowledgements**

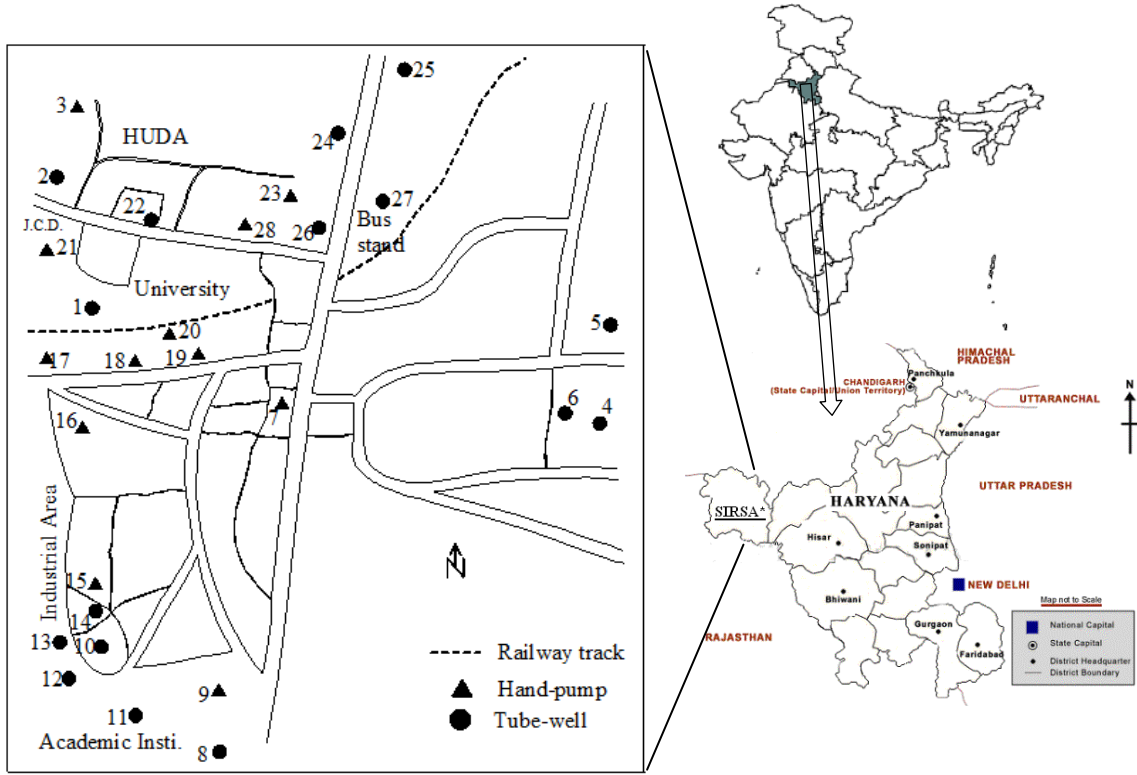
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387

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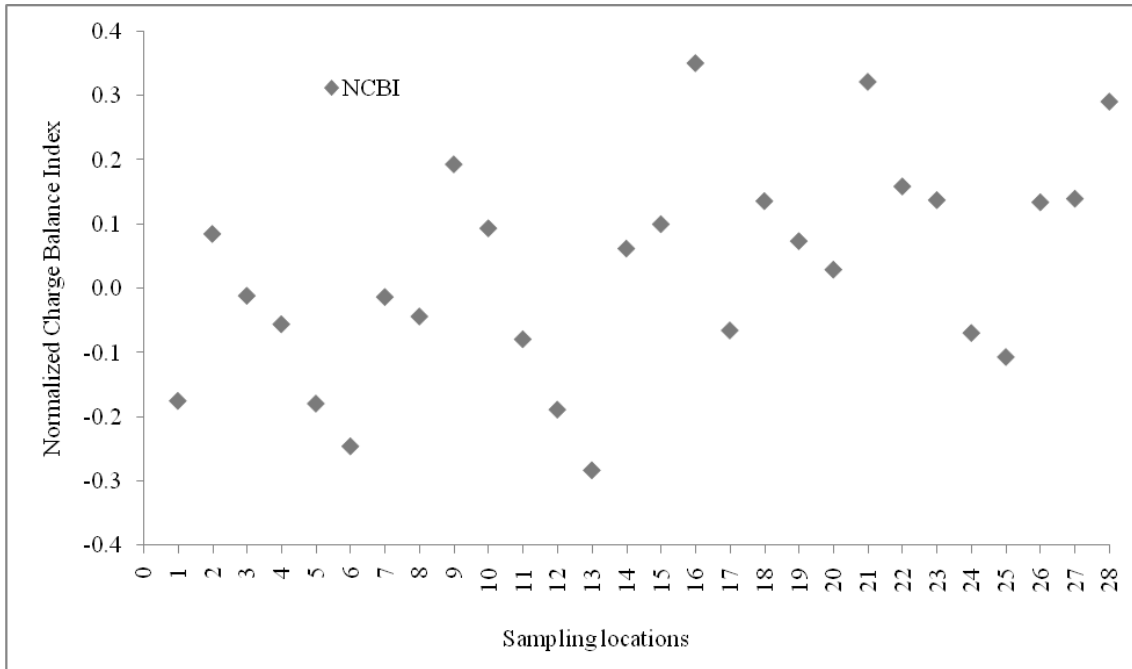
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**Figure 1: Location of Sirsa district in India and details of sampling locations.**

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466 **Figure 2: Normalized charge balance index (NCBI) of the samples collected from**

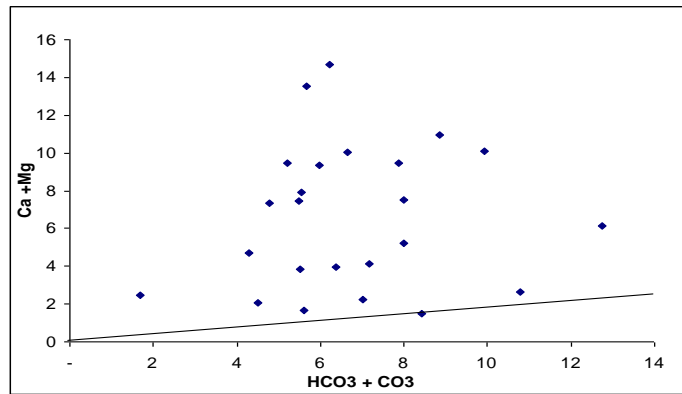
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**Sirsa**

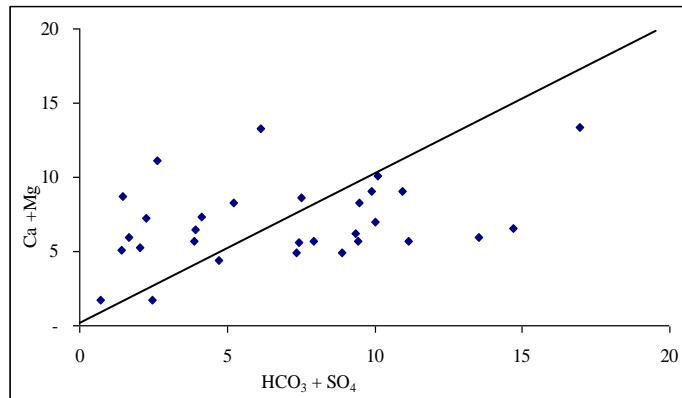
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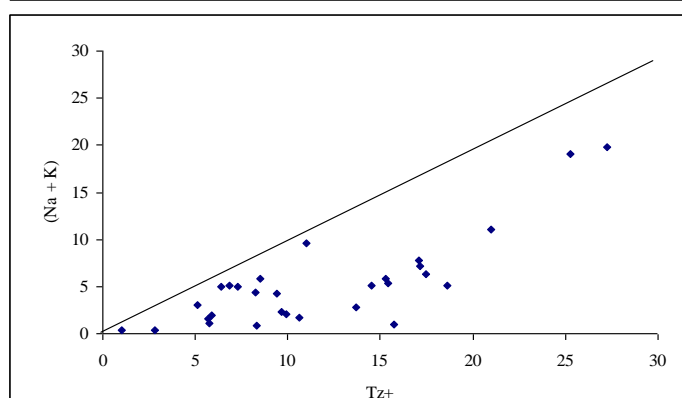
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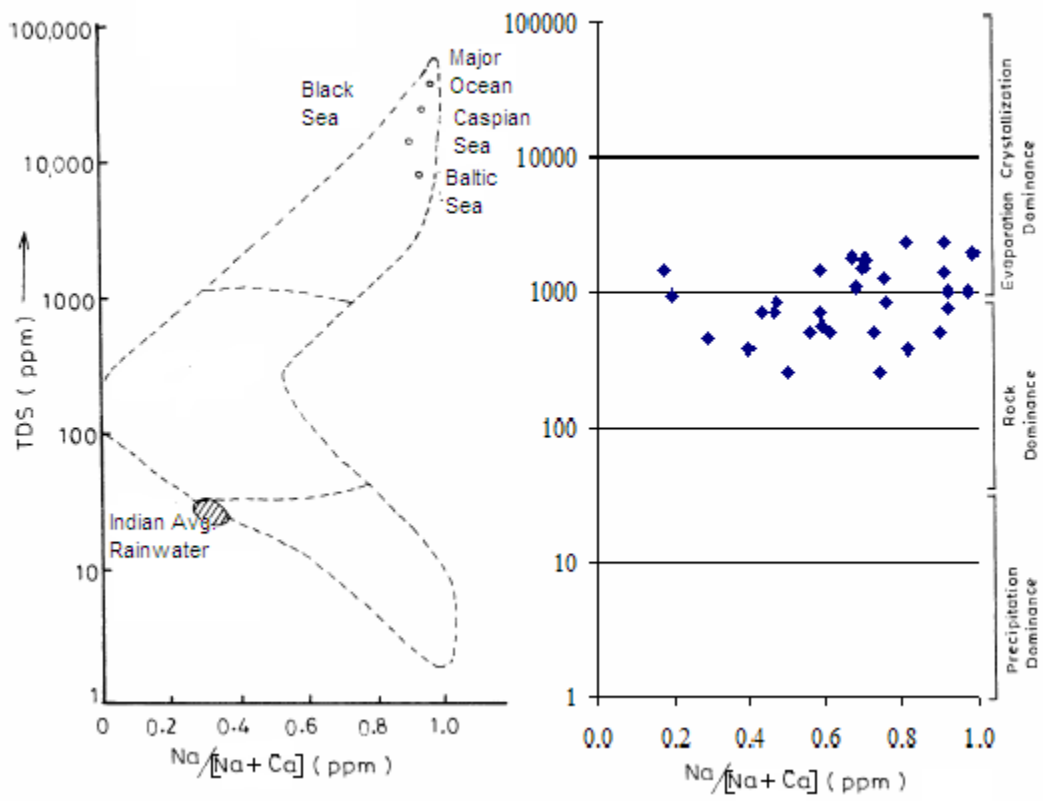


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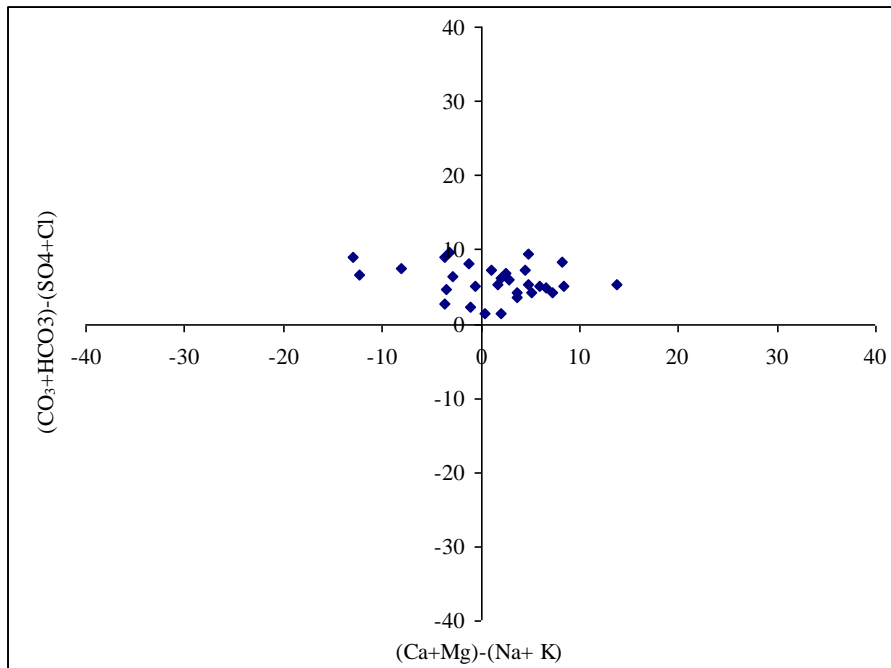
**Figure 3: Graphs of (Ca + Mg) vs. Alkalinity, (Ca + Mg) vs. acidic anion (HCO<sub>3</sub> + SO<sub>4</sub>), and Alkali metals (Na + K) vs. total cations. [Values are expressed in equivalents per million (epm). The trend line represents an ideal situation where the charge balance is 100% or the error percentage in the calculation is nil]**



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**Figure 4: Gibb's plot showing hydrogeochemical processes in groundwater in Sirsa**

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**Figure 5: Hydrogeochemical evaluation of groundwater in Sirsa.**

**Table 1: Sampling locations of Sirsa city, Haryana**

Sample no.	Sampling locations	HP/TW*	Approx. depth (meter)	Age (Year)
1.	University Campus	T.W.	87	5
2.	District Jail	T.W.	117	7
3.	Dhani Valecha, Govt. School.	H.P.	N.A.	N.A.
4.	Dera Sacha Sauda	T.W.	N.A.	5
5.	VITA Milk Plant	T.W.	167	N.A.
6.	Shri Jagdambe Paper Mill	T.W.	90	2.5
7.	Rori Bazar	H.P.	93	65
8.	Tara Baba Kutia	T.W.	67	0.5
9.	Govt. Polytech. For Women	H.P.	N.A.	2
10.	C-Block	H.P.	N.A.	N.A.
11.	Lord Shiva College of Pharmacy	T.W.	N.A.	N.A.
12.	Ganga Cotton Mills	T.W.	25	15
13.	Gurudatta Cotton Mills	T.W.	N.A.	N.A.
14.	HUDA Park, C-Block	T.W.	N.A.	3
15.	Ashok Ice Factory	H.P.	67	25
16.	Hanuman Mandir, Dabwali Road	H.P.	23	3
17.	Khairkan Village, Sirsa	H.P.	27	25
18.	Airforce Residence, Sirsa	H.P.	33	0.1
19.	Sarraff Filling Station, Dabwali Road	H.P.	13	30
20.	Old Truck Union, Dabwali Road	H.P.	27	15
21.	Housing Board	H.P.	23	1
22.	Police Line Stadium	T.W.	N.A.	1
23.	D.C. Colony	H.P.	42	22
24.	Sharda Palace, Hisar Road	T.W.	83	5
25.	Rajendra College of Pharmacy	T.W.	N.A.	N.A.
26.	National College, Sirsa	T.W.	60	3
27.	Bus Stand, Sirsa	T.W.	N.A.	15
28.	Barnala Road, Sirsa	H.P.	N.A.	N.A.

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\* TW =Tube-Well, HP =Hand-Pump , \*\*Distance from University Campus (Central point)

**Table 2: Comparison of groundwater quality parameters of Sirsa city with drinking water quality standards (Indian & WHO)**

Parameters	Samples range	BIS Standards		WHO Limit
		Acceptable limit	Maximum limit	
pH	6.8 – 8.7	7.0-8.5	6.5-9.2	6.5-9.2
EC	0.40 – 3.7	-	-	-
TDS	256 – 2368	300	1500	500
TA	112 – 964	200	600	-
TH	60 – 728	300	600	300
Na <sup>+</sup>	6 – 448	50	-	200
K <sup>+</sup>	2 – 48	-	-	200
Ca <sup>+2</sup>	6 – 106	75	200	105
Mg <sup>+2</sup>	5 – 140	30	100	50
CO <sub>3</sub> <sup>2-</sup>	10 – 187	75	200	75
HCO <sub>3</sub> <sup>-</sup>	102 – 777	30	-	150
Cl <sup>-</sup>	28 – 388	250	1000	250
F <sup>-</sup>	0.1 – 1.9	1.0	1.5	0.5
SO <sub>4</sub> <sup>2-</sup>	2 – 29	250	400	200

\* Units of all the parameter are in mg/l except EC (mS) and pH

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**Table 3: Suitability of groundwater for drinking purpose based on several classifications**

	<b>Water Class</b>	<b>Number of water samples</b>
<b>Based on TDS (mg/l)</b>		
<300	Excellent	1
300-600	Good	8
600-900	Fair	6
900-1200	Poor	4
%>1200	Unacceptable	9
<b>Based on Total hardness as CaCO<sub>3</sub> (mg/l) after Sawyer and McCarty (1967)</b>		
<75	Soft	4
75-150	Moderately hard	4
150-300	Hard	4
>300	Very hard	16
<b>Based on Total hardness as CaCO<sub>3</sub> (mg/l) after Durfor and Beckor (1964)</b>		
0-60	Soft	1
61-120	Moderate	6
121-180	Hard	1
>181	Very hard	20

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**Table 4a: Suitability of groundwater with different constituents for irrigation**

Parameters	Class of water					
	I		II		III	
	Range	<i>n</i>	Range	<i>n</i>	Range	<i>n</i>
TDS	0-700	9	700-2000	18	> 2000	1
SO <sub>4</sub> <sup>2-</sup>	0-192	28	192-480	0	> 480	0
Cl <sup>-</sup>	0-142	21	142-355	7	> 355	0
EC	0-0.75	5	0.75-2.25	17	>2.25	6
<b>Suitability for irrigation</b>	<i>Excellent to good for irrigation</i>		<i>Good to injurious suitable soil</i>		<i>Unfit for irrigation</i>	

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[*n* = Number of groundwater samples in the respective range; the ranges of all the parameter are in mg/l except for EC (mS)]

**Table 4b: Suitability of groundwater for irrigation with different value of SAR**

SAR range	<i>n</i>	Suitability for irrigation
<b>1-10</b>	<b>10</b>	Suitable for all types of crops and soil except for those crops sensitive to sodium
<b>11-18</b>	<b>8</b>	Suitable for coarsed textured or organic soil with permeability
<b>19-26</b>	<b>2</b>	Harmful for almost all soil
<b>&gt; 27</b>	<b>8</b>	Unsuitable for irrigation

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(*n* = Number of groundwater samples in the respective range)

**Table 5: Correlation matrix of analyzed groundwater quality parameters**

	pH	EC	TDS	Ca <sup>2+</sup>	Mg <sup>2+</sup>	TH	Na <sup>+</sup>	K <sup>+</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TA	Cl <sup>-</sup>	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	
<b>pH</b>	1.000														
<b>EC</b>	.181	1.00													
<b>TDS</b>	.181	1.00**	1.00												
<b>Ca<sup>2+</sup></b>	-.603**	.189	.189	1.00											
<b>Mg<sup>2+</sup></b>	-.302	.183	.183	.462*	1.00										
<b>TH</b>	-.429*	.241	.241	.680**	.942**	1.000									
<b>Na<sup>+</sup></b>	.423*	.693**	.693**	-.039	.053	.039	1.00								
<b>K<sup>+</sup></b>	-.289	.170	.170	.112	.181	.117	-.026	1.00							
<b>CO<sub>3</sub><sup>2-</sup></b>	.768**	.346	.346	-.325	-.006	-.120	.650**	-.136	1.000						
<b>HCO<sub>3</sub><sup>-</sup></b>	.089	.409*	.409*	-.046	.151	.080	.602**	.193	.553**	1.000					
<b>TA</b>	.230	.426*	.426*	-.103	.135	.050	.654**	.141	.686**	.986**	1.00				
<b>Cl<sup>-</sup></b>	-.148	.398*	.398*	.476*	.401*	.499**	.201	.222	-.067	-.010	-.023	1.00			
<b>F<sup>-</sup></b>	-.005	.208	.208	-.279	-.122	-.158	.141	.264	-.043	.224	.187	.247	1.00		
<b>SO<sub>4</sub><sup>2-</sup></b>	.353	.408*	.408*	-.181	.065	-.010	.554**	.110	.395*	.322	.361	.277	.571**	1.00	

\*\* Correlation is significant at the 0.01 level (2-tailed)

\* Correlation is significant at the 0.05 level (2-tailed)



**Table 6: Factor loading matrix and total variance explained**

Variable	Factors			
	1	2	3	4
pH	0.037	0.132	-0.254	0.897
EC	0.205	0.949	0.103	0.093
TDS	0.205	0.949	0.103	0.093
Ca <sup>2+</sup>	-0.043	0.152	0.395	-0.388
Mg <sup>2+</sup>	0.087	0.0543	0.979	-0.057
TH	0.022	0.137	0.924	-0.176
Na <sup>+</sup>	0.468	0.542	-0.010	0.293
K <sup>+</sup>	0.093	0.082	0.075	-0.144
CO <sub>3</sub> <sup>2-</sup>	0.511	0.176	-0.012	0.790
HCO <sub>3</sub> <sup>-</sup>	0.966	0.197	0.059	0.040
TA	0.948	0.206	0.054	0.195
Cl <sup>-</sup>	-0.076	0.257	0.302	-0.045
F <sup>-</sup>	0.11	0.094	-0.131	-0.073
SO <sub>4</sub> <sup>2-</sup>	0.18	0.236	0.026	0.230
<b>Eigen value</b>	<b>4.6</b>	<b>3.4</b>	<b>1.6</b>	<b>1.4</b>
<b>Variance (%)</b>	<b>33.2</b>	<b>24.2</b>	<b>11.7</b>	<b>9.7</b>
<b>Cumulative (%)</b>	<b>33.2</b>	<b>57.4</b>	<b>69.1</b>	<b>78.8</b>