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

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Abstract

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

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

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1. Introduction

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

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

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

In the present study, the groundwater quality of Sirsa city was evaluated from various tube-well (deep aquifers) and hand-pumps (shallow aquifers) to understand the geochemistry of the aquifer with special attention to F^- and salinity. Furthermore, its suitability for domestic, drinking and irrigation purposes was also evaluated. The applications of various multivariate techniques (correlation, factor analysis, geochemical diagrams) were used to understand the interdependence of various ions and their groundwater chemistry. The geochemical evaluation of groundwater was performed using ‘charge balance index’ and ‘Gibb’s plot’, whereas the ‘sodium absorption ratio (SAR)’ was applied to assess the ecological best use of groundwater.

2. Material and methods

2.1 Sampling site

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

2.2 Collection of groundwater samples

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

2.3 Analytical methodology

The groundwater samples were analyzed using APHA (1995) procedure and suggested precautions were taken to avoid contamination. The various parameters determined were pH, EC, total dissolved salts (TDS), total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), total alkalinity (TA), carbonate (CO_3^{2-}), bicarbonate (HCO_3^{-}), chloride (Cl^{-}), sulphate (SO_4^{2-}) , F^{-}, sodium (Na^{+}) and potassium (K^{+}). pH and EC were determined on the spot using µ-pH system-361 (Systronic, India) and conductivity meter Mode-306 (Systronic, India), respectively, including temperature. The values of TDS were calculated from EC by multiplying a factor that varies with the type of water (United States Salinity Laboratory, 1954). TH, Ca^{2+}, Mg^{2+}, TA, CO_3^{2-}, HCO_3^{-}, Cl^{-} were estimated by titrimetry, whereas Na^{+} and K^{+} by flame photometry (Systronic-128). F^{-} was estimated by SPADNS method and SO_4^{2-} was estimated using Perkin-Elmer UV/VIS lambda-2 spectrophotometer. Observed data was statistically analyzed using SPSS-11.0 software. All the experiments were carried out in triplicate and the results were found reproducible within ± 3% error limit.

3. Results and Discussion

3.1 Physico-chemical parameters and health risks

The physiochemical characteristic of groundwater in Sirsa City has been shown in Table 2. The groundwater of the study area is slightly alkaline in nature. Four samples were found to deviate from the acceptable limit with pH values in samples varying from 6.8 – 8.7. The highest value for pH was observed at location number 18. The hand pump of this location is the newest of all the sampling locations. In general groundwater pH is slightly alkaline due to the influx of HCO_3^{-} ions in the groundwater aquifer, which is due to percolation of rain water through soil (Mor et al., 2006; Kumar et al., 2007). The EC is an indicator of salinity and also signifies the amount of TDS. EC of collected water samples ranges from 0.4 – 3.7 mS/cm. TDS indicates the inorganic pollution load. TDS values ranged from 256 mg/l to 2792 mg/l and only one water sample lies within BIS permissible limit for TDS.

Hardness is mainly due to HCO_3^{-}, CO_3^{2-}, SO_4^{2-} and Cl^{-} of Ca^{2+} and Mg^{2+} in groundwater (BIS 1991). The higher incidence rate of gallbladder disease, urinary stones, arthritis and arthropathies has been reported in area supplied with drinking water harder than 500 mg/l $CaCO_3$. Depending on the interaction with other factors such as pH and alkalinity, water with hardness above 200 mg/l may cause scale deposition in distribution systems. On the other hand, soft water with hardness less than 100 mg/l has a greater tendency to cause corrosion of pipe resulting from the presence of heavy metals such as Pb, Zn, Cu and Cd in drinking water. Durfor and Beckor (1964) have classified water as soft, moderate, hard and very hard. As per this classification, 20 samples come under the very hard category. Only seven samples fall in category of soft to moderate as presented in Table 2. The TA in the water samples ranged from 60–728 mg/l. The Ca^{2+} and Mg^{2+} are the most abundant elements in the groundwater Ca^{2+}may dissolve readily from carbonate rocks and lime stones or be leached from soils. However, the dissolved Mg^{2+} concentration is lower than Ca^{2+} in the groundwater. Ca^{2+} is an essential nutritional element for humans and helps in maintaining the structure of plant cells and soils. Mg^{2+} is a constituent of bones and is essential for normal metabolism of Ca^{2+}. Its deficiency may lead to protein energy malnutrition. The optimum concentration of Ca^{2+} is required in drinking water to prevent cardiac disorder and for proper functioning of metabolic processes. The estimated Ca^{2+} contents in water samples range from 6–106 mg/l, while Mg^{2+} concentration varied from 5–140 mg/l. Only 3 water samples of Sirsa city have Ca^{2+} content above the permissible limit. Mg^{2+} content in two water samples is beyond the maximum permissible limit and only 8 samples lie within desirable limit.

Alkalinity of water is mainly due to the presence of CO_3^{2-} and HCO_3^{-}. It is a measure of the ability of water to neutralize acids. The alkalinity in natural water system may be contributed by $H_3BO_3^{2-}$, HPO_4^{2-}, and HS^{-}. These compounds results from dissolution of mineral substances in soil. TA of samples ranged from 112-964 mg/l. CO_3^{2-} and HCO_3^{-} in water are present mainly in association with Ca^{2+} and Mg^{2+}. HCO_3^{-} ranged from 102–777 mg/l, while CO_3^{2-} ranged from 10-187 mg/l. High alkalinity does not pose a health risk but can cause problems such as alkali taste to water. Alkalinity is a big problem for industries; if alkaline water is used in boiler for steam generation then it may leads to the formation of scale and embrittlement and the lowered efficiency of electric water heater.

Cl^{-} occurs naturally in some sedimentary bed rock layer, particularly shales. Cl^{-} is soluble in water and moves freely with water through soil and rocks. Cl^{-} is more persistent in nature than nitrate as it is not readily consumed by microorganisms. High content of Cl^{-} may give a salty taste to groundwater and can corrode pipes, pumps and plumbing fixtures. People who are not accustomed to high chlorine in drinking water are subjected to laxative effects. Cl^- concentration in the study area varied from 28-388 mg/l. SO_4^{2-} is a naturally occurring ion in almost all kinds of water bodies and is a major contributor to total hardness. SO_4^{2-} content more than 200 mg/l is objectionable for domestic purposes, beyond this limit SO_4^{2-} causes gastro-intestinal irritation. All the water samples of Sirsa city had SO_4^{2-} content within permissible limits, ranging from 2 – 29 mg/l.

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

3.2 Hydrogeology and salinity in Sirsa

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

3.3 Fluoride and fluorosis

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

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

3.4 Ecological best use

Evaluation of groundwater based on various physico-chemical analyses indicated that 9 (out of 28 samples) are unsuitable for drinking purpose (Table 2 and 3). Furthermore, more than 50% of the samples fall in the hard to very hard category. The non availability of the groundwater for daily chorus was found to be related with the presence of excess CO_3^{2-} and HCO_3^- and TDS. Suitability of groundwater for irrigation purposes was also assessed using the criteria shown in Table 4a and 4b. A comparison of EC or TDS values with irrigation standards shows that only 35% of samples can be considered in class I, whereas 65% are in class II. In the absence of other water sources they are suitable with permeable soil (Kumar et al., 2007). Chloride content of 79% of the samples showed that the groundwater is excellent for irrigation, while it may be injurious to crops for rest of samples. SO_4^{2-} content of all the water samples indicates that these water samples are of class II (Table 4a).

In addition to the EC, TDS, Cl^- and SO_4^{2-}; Na^+ is also an important parameter. Excess quantities of Na^+ can cause the soil quality to deteriorate and may cause damage to the sensitive crops because of sodium phyto-toxicity. Na^+ in water can be denoted by Na^+ absorption ratio (SAR) and it was calculated by using following formula

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

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

4. Multivariate analysis and Groundwater chemistry

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

4.1 Geochemical evaluation

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

$$NCBI = \frac{\sum Tz^{-} - \sum Tz^{+}}{\sum Tz^{-} + \sum Tz^{+}} \qquad \text{--- (2)}$$

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

The groundwater quality of Sirsa was evaluated through a diagram (Figure 5) as proposed by Chadha (1999). The rectangular field of the plot described the primary character of the water and is divided into eight sub-fields, each of which represents a water type and hardness domain (Figure 4) as follows: (1) Alkaline earths exceed alkali metals. (2) Alkali metals exceed alkaline earths. (3) Weak acidic anions exceed strong acidic anions. (4) Strong acidic anions exceed weak acidic anions. (5) Alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions, respectively. Such water has temporary hardness. The position of data points in this domain represents Ca-Mg-HCO_3 water type**.** (6) Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions. Such water has permanent hardness and does not deposit residual Na-CO_3 in irrigation use. The position of data points in this domain 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 problems both in irrigation and drinking uses. The position of data points in this domain represents Na–Cl type and Na-SO_4 type of waters. (8) Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions. The graph shows the dominance of alkali metal over alkaline earths and strong acidic anions exceed weak acidic anions. The hydro geochemistry of the aquifer of Sirsa city shows dominance of both alkali metal and alkaline earth metal. However, the temporary hardness was also observed at some sampling locations.

4.2 Correlation Matrix

The correlation matrix describes the interrelationship among various variables and results are shown in Table 5. pH was found to be negatively correlated with Ca^{2+} (r = –0.60**), Mg^{2+} (r = –0.30), TH (r = –0.43*), K^+ (r = –0.29), Cl^- (r = –0.15) and F^- (r = –0.01). It showed a high degree of positive correlation with CO_3^{2-} (r = 0.77**) and correlation is significant at 0.01 level. EC or TDS are mainly contributed by salts of Na^+, SO_4^{2-} and Cl^-. Table 5 also shows a moderate degree of correlation of Na^+, with CO_3^{2-}, HCO_3^- and TA. Furthermore, TA is highly correlated with HCO_3^- (r = 0.99). This suggest thats the Salts of Na-CO_3^{2-} and Na-HCO_3^- contribute significantly towards total alkalinity Cl^- was found to be significantly correlated with Ca^{2+} and Mg^{2+} indicating the presence of chloride salts of Ca^{2+} and Mg^{2+}. SO_4^{2-} was significantly correlated with Na^+, indicating the presence of Na-SO_4^{2-} salt. TH also showed a high degree of positive correlation with Mg^{2+} (r = 0.943). Cursory examination of the data reveals that the majority of the groundwater samples in this region are dominated by Mg^{2+} hardness as compared to Ca^{2+} hardness.

4.3 Factor analysis

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

Factors having Eigen value more than 1 were retained, which reveals 11 factors. The first factor is generally more closely correlated with the variables than the second factors because of the fact that these factors are extracted successively, each one accounting for as much of the remaining variables as possible. The first 4 factors cover around 80% of total variance and hence are discussed here. Factor 1, illustrates strong positive loading of TA, HCO_3^{-}, and moderate loading of CO_3^{2-}. These factors indicate that in the study area the TA may be mainly due to the CO_3^{2-} and HCO_3^{-}salts of Na^+ in the aquifer. Factor 2, was found to be associated with strong loading of EC, TDS and moderate loading of Na^+. This factor revealed that EC and TDS are mainly due to Na^+-salts in this study area. Factor 3, shows high loading for Mg^{2+}, TH with low loadings of Ca^{2+} and Cl^-. This factor can be associated with the permanent hardness of water. Hardness is mainly contributed by Mg-salts as compared to Ca-salts. Factor 4, is characterized by a strong loading of pH, CO_3^{2-} and low loading of CO_3^{2-} and SO_4^{2-}. All these ions show their contribution towards hardness and salinity. The remaining factors were characterized by the dominance of only one variable and low loading of other variables; hence they can be considered as irrelevant for describing the factor model of groundwater chemistry of Sirsa city.

5. Conclusions

Groundwater quality of Sirsa city wells were evaluated for their best ecological uses. Generally the groundwater falls in hard to very hard category and only 15% of samples are within permissible limit of TDS. The rest of the groundwater samples have a TDS value of more than 500-1500 mg/l. Na-salts of SO_4^{2-} and Cl^- were identified as a major contributor to TDS or EC. With the exception of one sample, all the samples have a TH value within the maximum limits of (600 mg/l). Na^+ content was beyond permissible limit (50 mg/l) for 65% of water samples. An increase in the concentration of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and other ions is the main cause of the salinization in Sirsa district. The problem seems mainly enhanced by the rainfall and irrigation with poor quality water/groundwater, which enhance salt leaching.

However, F^- content in most of the samples falls within maximum limit but it poses the risks of dental caries in the populace of Sirsa city. Factor analysis of groundwater generated 11 factors. The first 4 factors were able to explain 80% of total variance of data and were considered as representative of factor model. A high degree of positive correlation of total hardness with Mg^{2+} indicates that hardness was mainly contributed by salts of Mg^{2+}. This analysis also strengthens the finding of correlation matrix and confirmed that TH was mainly contributed by Mg-salts as compared to Ca-salts. Further, high loading of TA, HCO_3^- and CO_3^{2-} in the first factor indicated that TA was mainly due to CO_3^{2-} and HCO_3^- of Na^+. The study also highlights the need to estimate SAR of any aquifer before its utilization in irrigation to protect sensitive crops from Na^+ phytotoxicity and to limit the salinization.

Acknowledgements

Authors would like to thank Mr. Pawan Kumar (CDL University, Sirsa, India) for his help during sampling.

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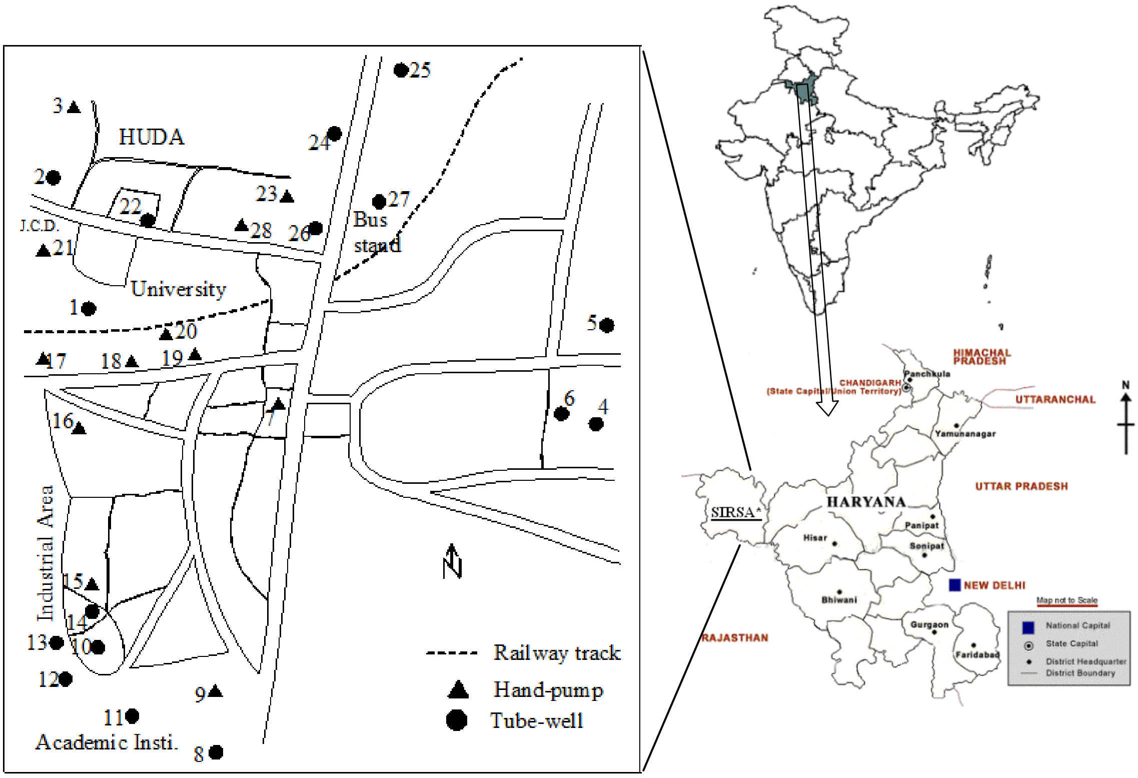

Figure 1: Location of Sirsa district in India and details of sampling locations.

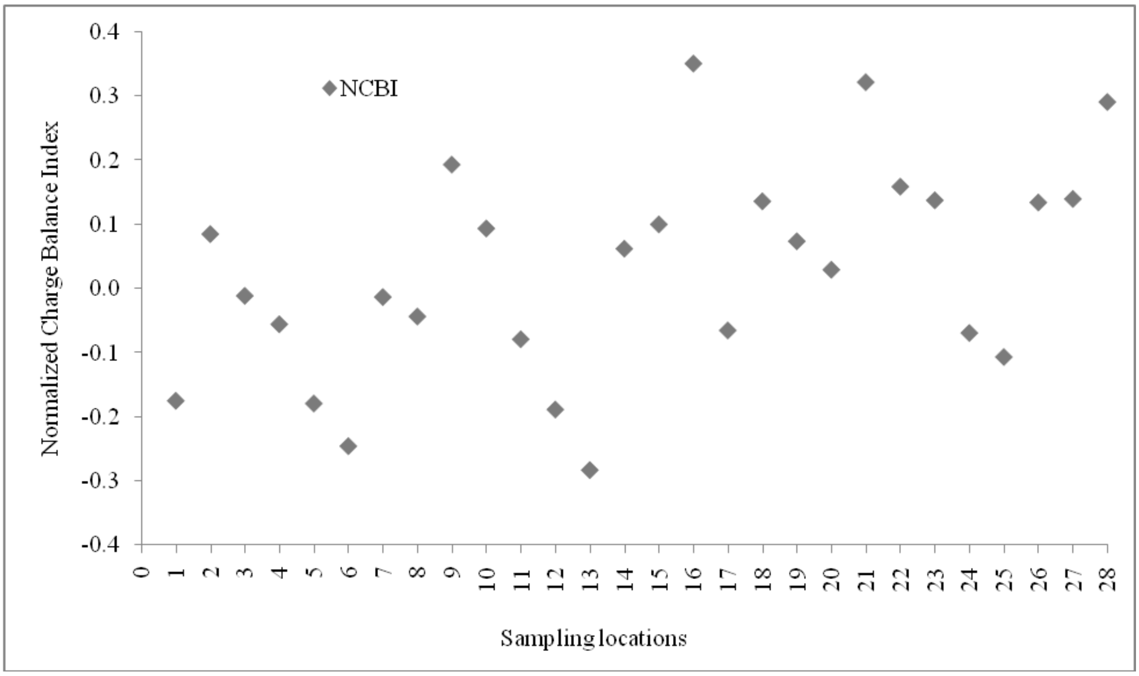

Figure 2: Normalized charge balance index (NCBI) of the samples collected from Sirsa

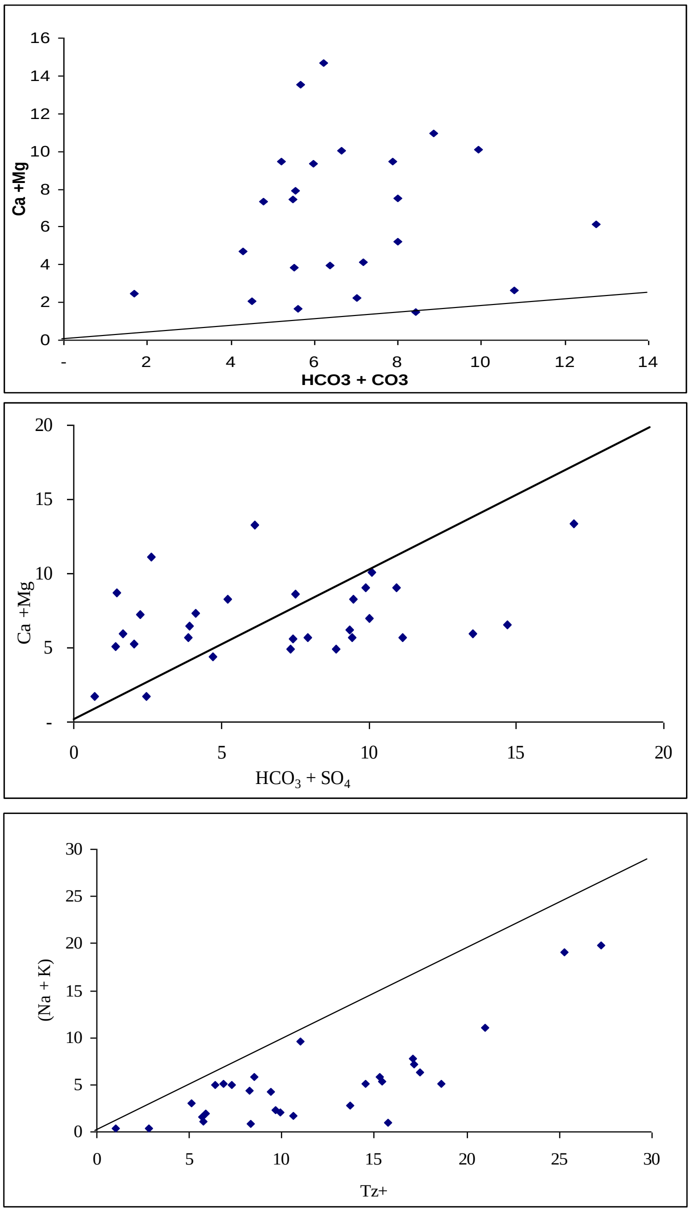

Figure 3: Graphs of (Ca + Mg) vs. Alkalinity, (Ca + Mg) vs. acidic anion (HCO_3 + SO_4), and Alkali metals (Na + K) vs. total cations. [Values are expressed in equivalents per million (epm). The trend line represents an ideal situation where the charge balance is 100% or the error percentage in the calculation is nil]

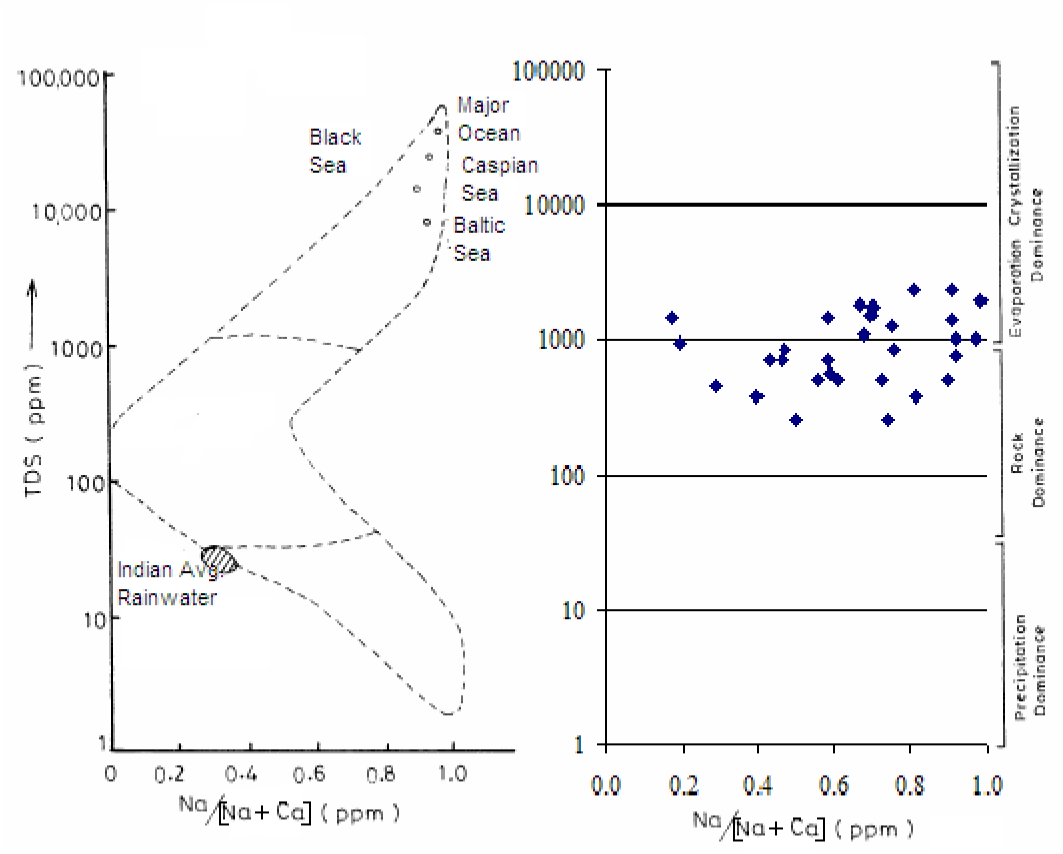

Figure 4: Gibb's plot showing hydrogeochemical processes in groundwater in Sirsa

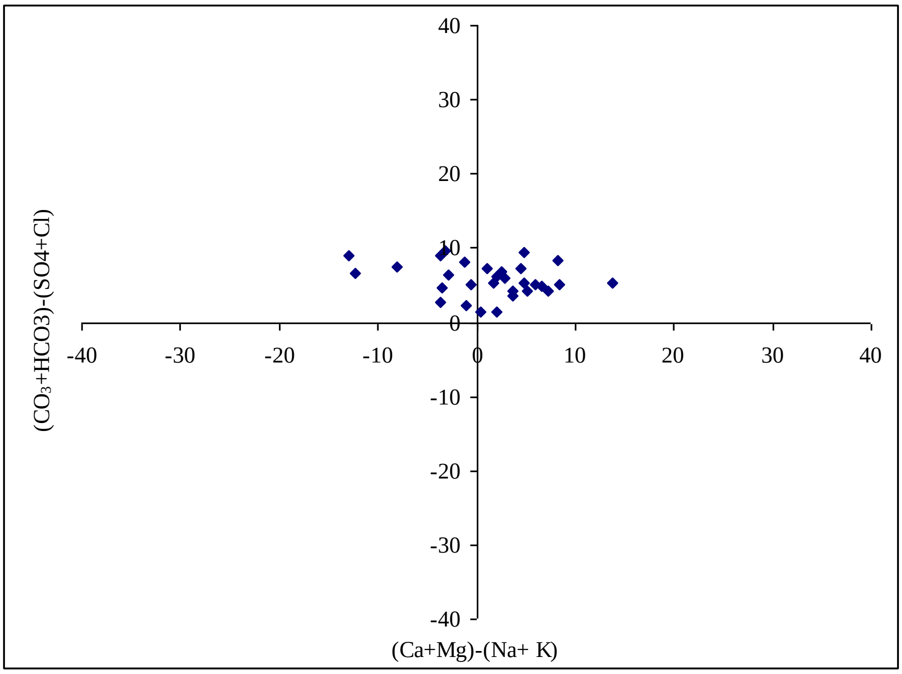

Figure 5: Hydrogeochemical evaluation of groundwater in Sirsa.

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.	Sarraf 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.

* 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^+	6 – 448	50	-	200
K^+	2 – 48	-	-	200
Ca^{+2}	6 – 106	75	200	105
Mg^{+2}	5 – 140	30	100	50
CO_3^{2-}	10 – 187	75	200	75
HCO_3^-	102 – 777	30	-	150
Cl^-	28 – 388	250	1000	250
F^-	0.1 – 1.9	1.0	1.5	0.5
SO_4^{2-}	2 – 29	250	400	200

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

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

	Water Class	Number of water samples
Based on TDS (mg/l)		
<300	Excellent	1
300-600	Good	8
600-900	Fair	6
900-1200	Poor	4
%>1200	Unacceptable	9
Based on Total hardness as $CaCO_3$ (mg/l) after Sawyer and McCartly (1967)		
<75	Soft	4
75-150	Moderately hard	4
150-300	Hard	4
>300	Very hard	16
Based on Total hardness as $CaCO_3$ (mg/l) after Durfor and Beckor (1964)		
0-60	Soft	1
61-120	Moderate	6
121-180	Hard	1
>181	Very hard	20

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

Parameters	**Class of water**					
	I		**II**		**III**	
	Range	***n***	**Range**	***n***	**Range**	***n***
TDS	0-700	9	700-2000	18	> 2000	1
SO_4^{2-}	0-192	28	192-480	0	> 480	0
Cl^-	0-142	21	142-355	7	> 355	0
EC	0-0.75	5	0.75-2.25	17	>2.25	6
Suitability for irrigation	***Excellent to good for irrigation***		***Good to injurious suitable soil***		***Unfit for irrigation***	

[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	***n***	**Suitability for irrigation**
1-10	**10**	Suitable for all types of crops and soil except for those crops sensitive to sodium
11-18	**8**	Suitable for coarsed textured or organic soil with permeability
19-26	**2**	Harmful for almost all soil
> 27	**8**	Unsuitable for irrigation

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

Table 5: Correlation matrix of analyzed groundwater quality parameters

	pH	**EC**	**TDS**	**Ca^{2+}**	**Mg^{2+}**	**TH**	**Na^{+}**	**K^{+}**	**CO_3^{2-}**	**HCO_3^{-}**	**TA**	**Cl^{-}**	**F^{-}**	**SO_4^{2-}**
pH	1.000													
EC	.181	1.00												
TDS	.181	1 .00**	1.00											
Ca^{2+}	-.603**	.189	.189	1.00										
Mg^{2+}	-.302	.183	.183	.462*	1.00									
TH	-.429*	.241	.241	.680**	.942**	1.000								
Na^{+}	.423*	.693**	.693**	-.039	.053	.039	1.00							
K^{+}	-.289	.170	.170	.112	.181	.117	-.026	1.00						
CO_3^{2-}	.768**	.346	.346	-.325	-.006	-.120	.650**	-.136	1.000					
HCO_3^{-}	.089	.409*	409*	-.046	.151	.080	.602**	.193	.553**	1.000				
TA	.230	.426*	.426*	-.103	.135	.050	.654**	.141	.686**	.986**	1.00			
Cl^{-}	-.148	.398*	.398*	.4 76*	.401 *	.499**	.201	.222	-.067	-.010	-.023	1.00		
F^{-}	-.005	.208	.208	-.279	-.122	-.158	.141	.264	-.043	.224	.187	.247	1.00	
SO_4^{2-}	.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^{2+}	-0.043	0.152	0.395	-0.388
Mg^{2+}	0.087	0.0543	0.979	-0.057
TH	0.022	0.137	0.924	-0.176
Na^{+}	0.468	0.542	-0.010	0.293
K^{+}	0.093	0.082	0.075	-0.144
CO_3^{2-}	0.511	0.176	-0.012	0.790
HCO_3^{-}	0.966	0.197	0.059	0.040
TA	0.948	0.206	0.054	0.195
Cl^{-}	-0.076	0.257	0.302	-0.045
F^{-}	0.11	0.094	-0.131	-0.073
SO_4^{2-}	0.18	0.236	0.026	0.230
Eigen value	**4.6**	**3.4**	**1.6**	**1.4**
Variance (%)	**33.2**	**24.2**	**11.7**	**9.7**
Cumulative (%)	**33.2**	**57.4**	**69.1**	**78.8**