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Geochemistry and assessment of hydrogeochemical processes in groundwater in the southern part of Bathinda district of Punjab, northwest India

Kuldip-Singh · H. S. Hundal · Dhanwinder-Singh

Abstract Hydrogeochemistry of groundwater is important for sustainable development and effective management of the groundwater resource. Fifty-six groundwater samples were collected from shallow tube wells of the intensively cultivated southern part of district Bathinda of Punjab, India, during pre- and post-monsoon seasons. Conventional graphical plots were used to define the geochemical evaluation of aquifer system based on the ionic constituents, water types, hydrochemical facies and factors controlling groundwater quality. Negative values of chloroalkaline indices suggest the prevalence of reverse ion exchange process irrespective of the seasons. A significant effect of monsoon is observed in terms chemical facies as a considerable amount of area with temporary hardness of Ca^{2+}–Mg^{2+}–HCO_3^{-} type in the pre-monsoon switched to Ca^{2+}–Mg^{2+}–Cl^{-} type (18%) followed by Na^{+}–HCO_3^{-} type (14%) in the post-monsoon. Evaporation is the major geochemical process controlling the chemistry of groundwater process in pre-monsoon; however, in post-monsoon ion exchange reaction dominates over evaporation. Carbonate weathering is the major hydrogeochemical process operating in this part of the district, irrespective of the season. The abundance of $Ca^{2+} + Mg^{2+}$ in groundwater of Bathinda can be attributed mainly to gypsum and carbonate weathering. Silicate weathering also occurs in a few samples in the post-monsoon in addition to the carbonate dissolution. Water chemistry is deteriorated by land-use activities, especially irrigation return flow and synthetic fertilisers (urea, gypsum, etc.) as indicted by concentrations of nitrate, sulphate and chlorides. Overall, results indicate that different natural hydrogeochemical processes such as simple dissolution, mixing, weathering of carbonate minerals locally known as ''kankar'' and silicate weathering are the key factors in both seasons.

Keywords Groundwater · Hydrogeochemistry · Punjab · Reverse ion exchange · Weathering

Introduction

Chemistry of groundwater is an important factor determining its use for domestic, irrigation and industrial purposes. Interaction of groundwater with aquifer minerals through which it flows greatly controls the groundwater chemistry. Hydrogeochemical processes that are responsible for altering the chemical composition of groundwater vary with respect to space and time. The hydrogeochemical processes of the groundwater system help to obtain an insight into the contributions of rock/soil–water interaction and anthropogenic influences on groundwater. These geochemical processes are responsible for the spatiotemporal variations in groundwater chemistry (Matthess 1982; Kumar et al. 2006). Groundwater chemistry, in turn, depends on a number of factors, such as general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water–rock interaction (Domenico 1972; Hem 1985; Schuh et al. 1997; Toth 1984). Such factors and their interactions result in a complex groundwater quality (Hussein 2004).

In the arid and semi-arid regions of India, due to uncertainty of monsoon and scarcity of surface water, dependence on groundwater resource has increased tremendously in recent years. India supports more than 16% of the world's population with only 4% of the world's fresh

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water resources (Singh 2003). The total area cultivated in India using groundwater has increased from 6.5 million hectare in 1951 to 35.38 million hectare in 1993 (GWREC 1997; Kumar et al. 2007). About 98% of the total sown area in Punjab is irrigated, out of which 73% is irrigated by tube wells and 27% by canals (Statistical abstract of Punjab, 2008). Although some studies have been reported on chemical quality and hydrogeochemical processes operated in other districts of Punjab, very little work has been done in the southern part of Bathinda district.

Groundwater is being continuously exploited in the Bathinda district of Punjab to meet the demand for water supply and irrigation, due to insufficiency of surface water as no river flows through the district, it is essential to know the hydrogeochemical processes that take place in the aquifer system. Therefore, the main objective of this study was to identify the major hydrogeochemical processes that are responsible for groundwater chemistry in the study region.

Study area

Bathinda district is in the southern part of Punjab State. It lies between 29°33′ and 30°36′ North latitude and 74°38′ and 75°46′ East longitude. It covers an area of 3,367 Sq. km. The Western Himalayas in the north and the Thar Desert in the south and southwest mainly determine the climatic conditions of Bathinda. The climate of Bathinda district can be classified as semi-arid and hot which is mainly dry except in rainy months and characterised by intensely hot summer and cold winter. Geologically the Bathinda district forms a part of Indo-Gangetic alluvium of Quaternary period (GSI 1976). The study area is underlain by an alluvial complex of fluviatile origin deposited by the ancestral tributaries of the Indus River system which include the ancient Satluj River (Wadia 1981). The alluvial complex consists of principally alternating beds of fine to medium sand, silt and clay. It is usually overlain by a thin layer of unstratified loam with lenses of organic matter. Concretions and nodules of calcium carbonate (kankar) are associated with fine-grained strata of the alluvium. The occurrence of kankar was observed beyond the depth of the water table as massive cover and nodular and granular beds. It has been found that there is no hard and fast rule regarding the association of kankar with a particular type of lithology (WRD 1982). Quaternary alluvial sediments consisting of fine to medium grained sand or sand and kankar with admixture of clay constitute the aquifer system of the area. In these soils, the basic cations are Ca^{2+} and Mg^{2+} and the distribution of calcium carbonate suggests different degrees of carbonate leaching (Sharma et al. 1998). Sand and silt fractions are dominated by primary quartz. Other minerals present in these fractions include muscovite, plagioclase and alkali feldspars, amphibole, biotite, anhydrite (gypsum) and chlorite. Illite, chlorite, and kaolinite have been identified in the clay fraction of these area soils (Sidhu and Gilkes 1977; Raj-Kumar et al. 2010). The aquifers in the area belong to the huge aquifer system of the lndo-Gangetic alluvial plain (Thomas et al. 1995).

Hydrogeology

The area is underlain by the Indus alluvium of the Quaternary age. The exploratory drilling in Indus basin also shows the presence of thick sandy aquifer zones with the intervening thin clay layers identifying it as one unified multi-aquifer system. Below the thick alluvial sediments, different types of basement rocks have been encountered. The area has both confined and unconfined aquifers (CGWB Report 2007; Gupta and Thakur 1989). All the aquifers were shallow and varied from 8 to 30 m. The mean annual rainfall in the district is 408 mm (2004–2008). Most of the rainfall occurs in four months of the southwest monsoon period from May to September (about 77.1%).

Materials and methods

Groundwater sampling campaigns were carried out during March 2007 (pre-monsoon) and October 2008 (post-monsoon). Twenty-eight water samples were collected during March 2007 (Fig. 1), and the same locations were again sampled in October 2008 to evaluate seasonal variations. Overall, 56 samples were collected for chemical analysis. Water samples were collected from different alluvial aquifers representing soil associations of Bathinda district (Sidhu et al. 1995). Southern parts of Bathinda district have 14 soil mapping units, and two water samples from each soil association were collected.

Duplicate water samples were collected in clean polyethylene bottles of 250 ml capacity. At the time of sampling, bottles were thoroughly washed 2–3 times with groundwater to be sampled. In the case of bore wells the water samples were collected after pumping for 10 min. This was done to remove groundwater stored in the well. One part of the water sample to be analysed for physical parameters and major anions was not acidified. The other part of the sample was acidified to make 1% in HNO_3, producing a pH around 1.5 sufficient to stabilise trace metals prior to analysis on ICAP-AES. The samples were placed in a cooled ice box during transportation and stored refrigerated until analysis (at 5°C). The non-acidified water samples were analysed for pH, EC, total dissolved solids, bicarbonate and chloride as per the standard procedures given in American Public Health Association (APHA 1998)
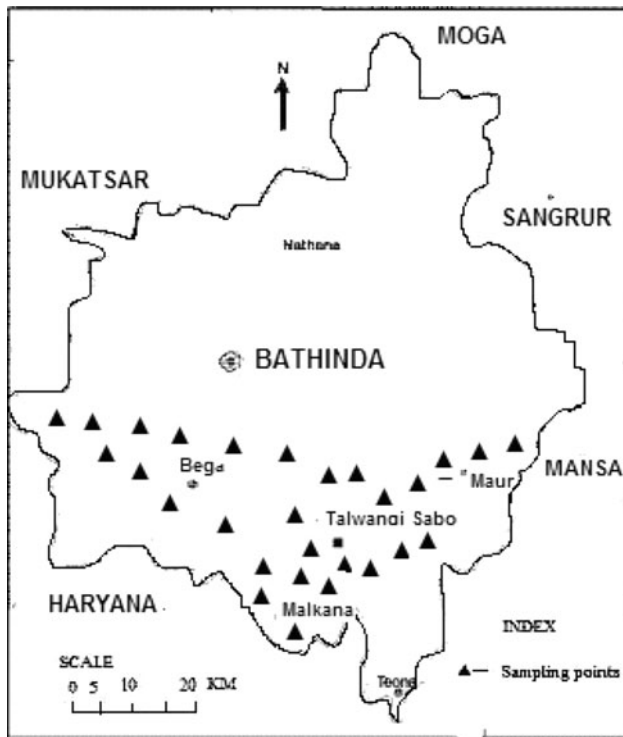
Fig. 1 Water sampling locations from shallow alluvial aquifers (8–30 M) of the southern part of Bathinda

Table 1 Statistical summary of hydrogeochemical parameters of groundwater of southern part of Bathinda district

Parameter	Pre-monsoon		Post-monsoon	
	Mean ± SD	Range	Mean ± SD	Range
Physical parameters				
pH	7.63 ± 0. 32	7.10–8.45	7.84 ± 0.39	7.35–8.67
EC	2120 ± 1230	220–4390	2270 ± 1190	672–4840
TDS	1251 ± 726	126–2590	1340 ± 702	396–2856
Major cations				
Na^+	239 ± 170	11–699	320 ± 270	13–842
Ca^{2+}	45 ± 31	2–247	37 ± 39	2–185
Mg^{2+}	38 ± 26	2–192	43 ± 31	5–223
K^+	36 ± 85	2–418	12 ± 10	3–59
Major anions				
HCO_3^-	534 ± 202	195–1025	739 ± 305	78–1372
SO_4^{2-}	273 ± 237	45–785	302 ± 254	39–887
Cl^-	61 ± 51	4–153	237 ± 180	28–696
F^-	5.5 ± 3.2	0–11.7	8.2 ± 2.7	0.9–14.0
NO_3^-	30 ± 23	BD–79	37 ± 25	BD–93
SiO_2	20.4 ± 10.1	6–54	18.3 ± 8.4	8–51
Trace elements				
Mn	0.018 ± 0.034	0–0.198	0.0071 ± 0.0204	0–0.1110
Zn	0.304 ± 1.114	0–6.081	0.552 ± 0.674	0.104–2.480
Fe	0.0085 ± 0.0168	0–0.0935	0.123 ± 0.130	0–0.829

All values are in mg l^{-1} except pH, EC (µS cm^{-1})

BD below detection limits

within 24 h of sampling. The reliability of pH analysis was checked after every five samples using standard buffer solutions of pH 7 and 9.2, whereas that of EC analysis was checked using standard EC solution provided by M/s Crison instruments SA having EC = 1413 µS cm^{-1}. These samples were also analysed for nitrate and silica using UV/visible spectrophotometer; and fluoride by potentiometer method, using the F1052F solid-state membrane electrode in conjunction with K401 calomel electrode.

Laboratory analysis of major and minor cations such as Ca, Mg, Na, K, Mn, Zn and Fe were analysed on Thermo Electron Corporation's Emission Spectrometer, iCAP 6300. The iCAP 6300 Duo model allows for simultaneous analysis of all elements from sub ppb to % level. The detection limits for Na, K, Ca, Mg, S, Fe and Mn on the iCAP duo emission spectrometer are 1.80, 0.60, 0.003, 0.010, 2.22, 0.25, and 0.07 ppb at 589, 766, 393, 279, 181, 260 and 258 nm, respectively. Overall, measurement reproducibility and precision for each analysis was less than 2%.

Results and discussion

Groundwater geochemistry

The chemical indices derived from hydrogeochemical parameters of pre- and post-monsoon groundwater samples

of Bathinda district of Punjab and their computed values have been presented along with their standard deviation in Table 1. Groundwater was found to be alkaline in nature with an average pH value of 7.63 and 7.84 in the pre- and post-monsoon, respectively. A slight increase in pH was noticed in the post-monsoon season in comparison to pre-monsoon. Increase in pH in the post-monsoon season suggests that dissolution has been enhanced due to high interaction between soil and rainwater (Subramanian and Saxena 1983). The electrical conductivity (EC) ranged from 220 to 4,390 µS cm^{-1} with a mean of 2,120 µS cm^{-1} and from 672 to 4,840 µS cm^{-1} with a mean of 2,270 µS cm^{-1} for pre- and post-monsoon water samples, respectively. The total dissolved solids (TDS) ranged from 126 to 2,590 mg l^{-1} with a mean of 1,251 mg l^{-1} and from 396 to 2,856 mg l^{-1} with a mean of 1,340 mg l^{-1} for pre- and post-monsoon water samples, respectively. The increase of EC and TDS in post-monsoon season is on the higher side than the pre-monsoon season. Salts, which held back in the interstice or pores in clay while groundwater is evaporated or water table falls, get leached back to the groundwater during the rainy period. Further, the groundwater level in the study area is rising in the last 30 years (CGWR 2007). Hence, the post-monsoon waters have higher TDS and EC values as compared to the pre-monsoon season. Very high

standard deviation in EC for both the pre- and post-monsoon seasons indicates the spatial variability of leaching and dilution with recharging rainfall water.

Dominant cations are in the order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in the Bathinda district of Punjab. Clear seasonal variations were observed both in minimum and maximum concentrations of these cations, but the difference in mean value is not significant except for K^+. Despite the greater resistance of potassium silicate to weathering, ions are released during weathering but they seem to be used up in the formation of secondary minerals. The concentration of potassium at a few places is unusually very high, which may be due to salt patches present geogenically and fertiliser leaching or return flow.

Dominant anions are in the order of $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$. Alkalinity is a measure of the ability of groundwater to neutralise acids to the equivalence point of carbonate or bicarbonate. Bicarbonate represents the major sources of alkalinity in these waters. Bicarbonates are higher in post-monsoon sampling periods indicating the contribution from carbonate weathering process. There is a slight variation observed in seasonal and spatial distribution of HCO_3^- but very significant at certain locations, which may be due to mixing of geogenically present salt patches in the soil profile and due to rise in the water table (Raj-Kumar et al. 2010). Chloride and sulphate show large variation between minimum and maximum value and also express high standard deviation. This inference not only suggests that the water chemistry in the study region is heterogeneous but also reveals the influences of complex contamination sources and geochemical process. Table 1 also shows a variation in the mean values of chemical parameters between pre- and post-monsoon data. The mean values of EC and major ions are higher in post-monsoon data compared to the pre-monsoon data, which apparently suggest the enhancement of solute load in the aquifer.

Characterisation of hydrogeochemical data

Hydrochemical diagrams are aimed at facilitating interpretation of evolutionary trends, particularly in groundwater systems, when they are interpreted in conjunction with distribution maps and hydrochemical sections. An overall characterisation of hydrogeochemical data can be possible by knowing the hydrochemical facies of water, generally known as water type, using various plots such as Durov diagram (1948), tri-linear diagram (Piper 1944), Schoeller diagram (1965), Stiff diagram and Radial plot. Chadha (1999) has proposed a new diagram for geochemical classification of natural waters and interpretation of chemical data which is used in this paper. The proposed diagram is a modification of the Hill Piper diagram with a
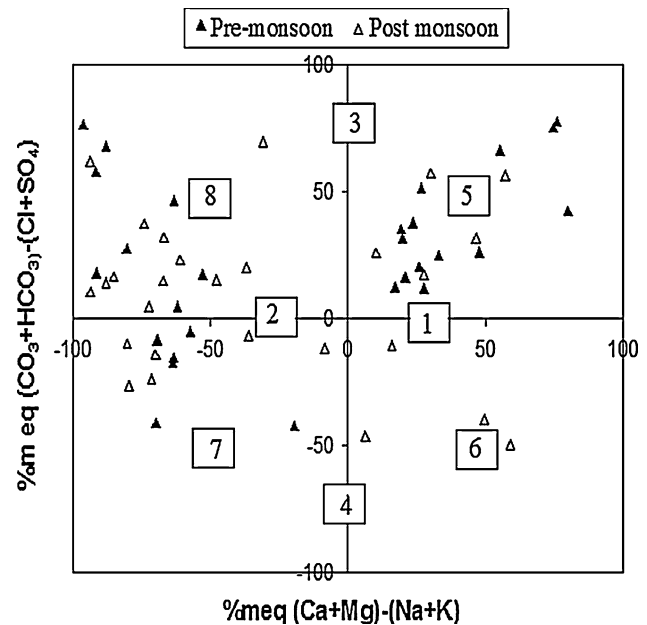
Fig. 2 Diagram showing geochemical classification and hydrochemical parameters of ground water

view to extend its applicability in representing water analysis in the simplest possible way. In the proposed diagram (Fig. 2), the difference in mill equivalent percentage between alkaline earths ($Ca^{2+} + Mg^{2+}$) and alkali metals ($Na^+ + K^+$), expressed as percentage reacting values, is plotted on the x-axis, and the difference in mill equivalent percentage between weak acidic anions ($CO_3^{2-} + HCO_3^-$) and strong acidic anions ($Cl^- + SO_4^{2-}$) is plotted on the y-axis. The mill equivalent percentage differences between alkaline earths and alkali metals and between weak acidic anions and strong acidic anions would plot in one of the four possible sub-fields of the rectangle diagram. The rectangular field describes the overall character of the water. To define the primary character of water, the rectangular field is divided into eight sub-fields, each of which represents a water type: (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 positions of data points in this domain represent Ca^{2+}–Mg^{2+}–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 sodium carbonate in irrigation use. The positions of data points in this domain represent Ca^{2+}–Mg^{2+}–Cl^- type, Ca^{2+}–Mg^{2+} dominant Cl^--type, or Cl^- dominant Ca^{2+}–Mg^{2+} type waters. (7) Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions.

Table 2 Classification of ground water samples (percent) on the basis of Chadha rectangular diagram

Domain	Pre-monsoon	Post-monsoon
5 (Ca^{2+}–Mg^{2+}–HCO_3^--type)	50	18
6 (Ca^{2+}–Mg^{2+}–Cl^--type)	–	18
7 (Na^+–Cl^--type)	21	21
8 (Na^+–HCO_3^--type)	29	43

The positions of data points in this domain represent Na^+–Cl^--type and Na^+–SO_4^{2-}-type Na^+-dominant Cl^- type, or Cl^- dominant Na^+-type waters. (8) Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions. The positions of data points in this region represent Na^+–HCO_3^--type waters. Results of analyses are plotted on the Chadha diagram (Fig. 2) to test its applicability for geochemical classification of groundwater (Table 2) and to study hydrochemical processes of pre- and post-monsoon seasons. From Table 2, it is evident that there is significant increase (18%) in the permanent hardness, i.e., domain 6 (Ca^{2+}–Mg^{2+}–Cl^- type) followed by 14% in domain 8 (Na^+–HCO_3^--type) in the post-monsoon as compared to the pre-monsoon samples where 50% samples fall in domain 5 of temporary hardness group. Sodium-bicarbonate type waters deposit residual sodium carbonate in irrigation use and causes foaming problems. Twenty-one percent samples of both the seasons fall under the category of Na^+–Cl^- type; such water creates salinity problems both in irrigation and drinking purposes. These observations suggest that monsoons have strong effect on the quality of water which further deteriorates after the monsoon season.

Identification of hydrogeochemical process

Reactions between groundwater and aquifer minerals have a significant role on water quality, which are also useful to understand the genesis of groundwater (Cederstorm 1946). The hydrogeochemical data are subjected to various conventional graphical plots to identify the hydrogeochemical processes operating in aquifer region of study area. Some of the possible identified processes are explained below.

Ion exchange

Knowledge of the changes brought about in the chemical composition of the groundwater during its travel underground is essential (Sastri 1994). Control on the dissolution of undesirable constituents in waters is impossible during the subsurface runoff, but it is essential to know the various changes undergone by waters during the travel (Pojasek 1977; Johnson 1979). The ion exchange between the

groundwater and its host environment during residence or travel can be understood by studying the chloroalkaline indices (CAI) (Schoeller 1965, 1967):

$$CAI\text{-}1 = [Cl^- - (Na^+ + K^+)]/Cl^- \quad \text{and}$$

$$CAI\text{-}2 = [Cl^- - (Na^+ + K^+)]/(SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-).$$

All values are expressed in meq l^{-1}. When there is an exchange between Na^+ or K^+ with Mg^{2+} or Ca^{2+} in the groundwater, both the above indices will be positive and if there is a reverse ion exchange prevalent then both these indices will be negative (Schoeller 1965, 1967, 1977). The groundwater samples of the study area (Fig. 3) indicates that the reverse ion exchange process is dominant in both the seasons as 96% samples in pre-monsoon and 67% samples in the post-monsoon season have negative ratios of CA 1 and CA 2. Only 33% samples in the post-monsoon have positive ratios and exhibit the ion exchange process. Fisher and Mulican (1997) have explained that when reverse ion exchange is a significant geochemical process for controlling the composition of groundwater, the relationship between Na^+–Cl^- and Ca^{2+} + Mg^{2+}–HCO_3^-–SO_4^{2-} should be linear with a slope of −1.0. Figure 4 apparently shows that most of the groundwater samples of the Bathinda followed a straight line ($R^2 = 0.96$ in pre-monsoon to 0.93 in post-monsoon) with a slope of −1.04, which indicates the occurrence of reverse ion exchange.

The plot of (Ca^{2+} + Mg^{2+}) versus (SO_4^{2-} + HCO_3^-) will be close to the 1:1 line if the dissolutions of calcite, dolomite and gypsum are the dominant reactions in a system. Ion exchange tends to shift the points to right due to an excess of SO_4^{2-} + HCO_3^- (Cerling et al. 1989; Datta and Tyagi 1996; Fisher and Mulican 1997). If reverse ion exchange is the process, it will shift the points to the left due to a large excess of Ca^{2+} + Mg^{2+} over SO_4^{2-} + HCO_3^-. The plot of Ca^{2+} + Mg^{2+} versus SO_4^{2-} + HCO_3^- (Fig. 5) shows that all the groundwater samples of the southern part of Bathinda district falls left to the 1:1 line irrespective of the seasons which indicate that reverse ion exchange tends to dominant over ion exchange process in the study area.

The plot of m(Ca^{2+} + Mg^{2+}) versus m(Cl^-) (Fig. 6a) indicates that Ca^{2+} and Mg^{2+} do not increase with increasing salinity which further proved that the reverse ion exchange is the main process in the clay/weathered layer except in a few samples of the pre-monsoon season.
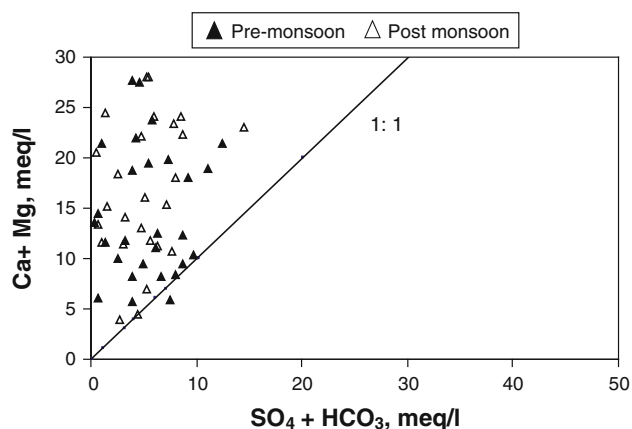
Carbonate weathering and dissolution

Calcium and magnesium are the dominant cations present in groundwater next to sodium in this region. Similarly,

Fig. 3 Chloro-alkaline indices 1 and 2 (CAI 1 and CAI 2) indicating ion exchange for pre- and post-monsoon season
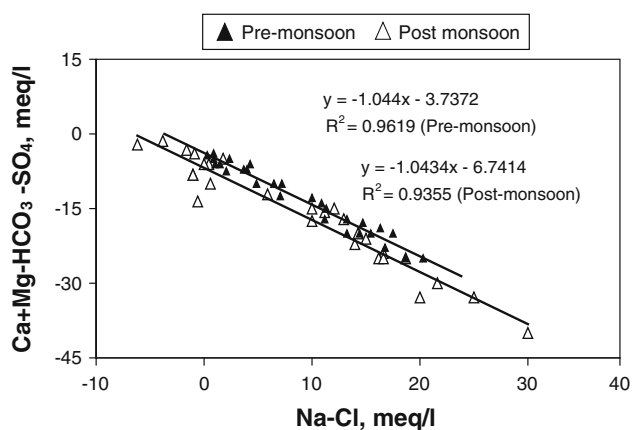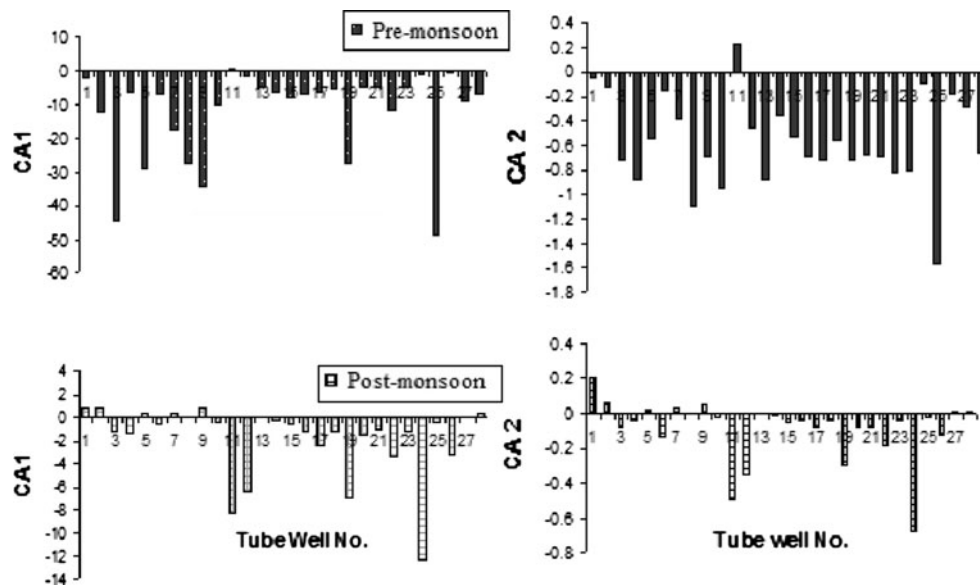
**Fig. 4** Na^+–Cl^- versus $Ca^{2+} + Mg^{2+}$–HCO_3^-–SO_4^{2-} scatter diagram illustrates reverse ion exchange

Fig. 5 Relationship between $(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-} + HCO_3^-)$

bicarbonate is also present in considerable amounts. The crystalline limestone, dolomitic limestone and kankar (the lime rich weathered mantle overlies carbonate rocks) are the major sources for carbonate in the area. The carbonates from these sources might have been dissolved and added to the groundwater system with recharging water during irrigation, rainfall or leaching and mixing processes. In $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$ scatter diagram (Fig. 5), the points falling along the equiline ($Ca^{2+} + Mg^{2+} = SO_4^{2-} + HCO_3^-$) suggest that these ions have resulted from weathering of carbonates and silicates (Datta and Tyagi 1996; Datta et al. 1996; Rajmohan and Elango 2004). Most of the points in this study fall in the $Ca^{2+} + Mg^{2+}$ side, suggesting that carbonate weathering is the major hydrogeochemical process operating in this part of Bathinda district, irrespective of the season. Also, it indicates that excess of calcium and magnesium may be derived from other processes such as reverse ion exchange reactions.

If the ratio Ca/Mg = 1, dissolution of dolomite should occur, whereas a higher ratio is indicative of greater calcite contribution (Maya and Loucks 1995). Molar ratio of Ca/Mg > 2 indicates the dissolution of silicate minerals, which contribute calcium and magnesium to groundwater (Katz et al. 1998). The plot of Ca/Mg ratio of the groundwater samples of the study area reveals that the dominant process is the dissolution of calcite and dolomite that present in the alluvium material of the Bathinda (Fig. 6b). The points closer to the line (Ca/Mg = 1) indicate the dissolution of dolomite. In the present study, most of the groundwater samples found to be below 1 ratio indicate the calcite weathering as the most prominent process. However, 16% in the pre- and 10% samples in

Fig. 6 Major ion relationship: **a** $Ca^{2+} + Mg^{2+}$ vs. Cl^-, **b** Scatter diagram of Ca^{2+}/Mg^{2+} molar ratio, **c** Ca^{2+} versus HCO_3^-, **d** Ca^{2+} versus SO_4^{2-} **e** $Ca^{2+} + Mg^{2+}$/HCO_3^- versus Cl^-, **f** $Na^+ + K^+$ versus total cations (TZ^+) for groundwater in the study area
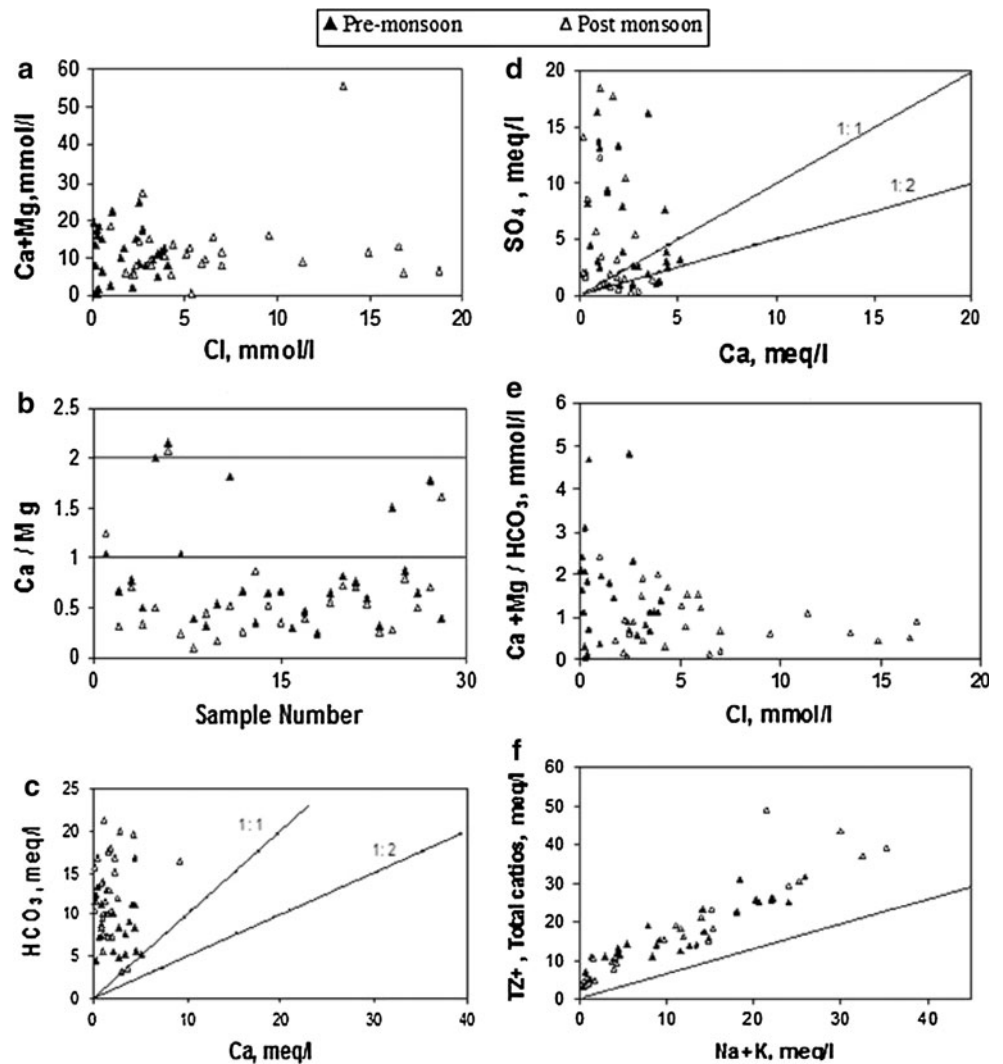
post-monsoon lie near the 1 ratio line revealing dolomite dissolutions. Only 6% samples in pre- and 3% in the post-monsoon lie above the ratio line 2 indicating the effect of silicate minerals. Presence of ''kankar'' carbonates in the alluvial sediments and occurrence of metamorphosed dolomite limestones could favour the weathering process. However, a possibility of calcite weathering by sulphuric acid is also there as indicated by Ca^{2+} and SO_4^{2-} ratio. Sulphuric acid may be produced by SOx emission dissolved in rain from industrial sources (Bathinda district has a thermal plant for electricity generation).

In silicate terrain, if the calcium and bicarbonate in groundwater are solely originated from calcite, the equivalent ratio of dissolved Ca^{2+} and HCO_3^- in the groundwater is 1:2, whereas from dolomite weathering, it is 1:4 (Garrels and Mackenzie 1971; Holland 1978). Similarly, if the calcium and sulphate in groundwater derived from dissolution of gypsum or anhydrite, then the Ca^{2+}/SO_4^{2-} ratio is almost 1:1 (Das and Kaur 2001). In Ca^{2+} versus

HCO_3^- scatter diagram (Fig. 6c), only three groundwater samples fall on the 1:1 line and most of them lie above the 1:1 equiline, indicating the contribution of calcite weathering on groundwater chemistry. Moreover, in Ca^{2+} versus SO_4^{2-} scatter diagram (Fig. 6d), there are almost 50:50 distributions of the samples above and below the 1:2 eqiline. This also shows the dominance of calcite weathering rather than dolomite (Garrels and Mackenzie 1971). Furthermore, it indicates the presence of dissolution of gypsum in the Bathinda district.

The sources of Ca^{2+} and Mg^{2+} in groundwater can be estimated from the m $(Ca^{2+} + Mg^{2+})$/$mHCO_3^-$ ratio. As this ratio does not increase with salinity (Fig. 6e), Ca and Mg are added to solution at a lesser rate than HCO_3^- which is evident as the majority of the samples of pre- and post-monsoon fall below one ratio. If Ca^{2+} and Mg^{2+} originate mainly from the dissolution of carbonates in the aquifer materials and from the weathering of accessory pyroxenes and amphibole minerals, this ratio would be about 0.5

(Sami [1992]). Therefore, the abundance of $Ca^{2+} + Mg^{2+}$ in groundwater of Bathinda can be attributed mainly to gypsum and carbonate weathering (Sharma et al. [1998]; Kumar et al. [2007]).

Silicate weathering

Silicate weathering may play a vital role in controlling the major ions chemistry of the groundwater, especially in hard rock aquifers (Mackenzie and Garrells [1965]; Rajmohan and Elango [2004]). Silicate weathering can be understood by estimating the ratio between $Na^+ + K^+$ and total cations (TZ+). The relationship between $Na^+ + K^+$ and total cations (TZ+) of the area revealed that most of the samples are plotted near the $Na^+ + K^+ = 0.5TZ+$ line (Fig. [6]f). This observation indicates the involvement of silicate weathering in the geochemical processes, which contributes mainly sodium and potassium ions to the groundwater (Stallard and Edmond [1983]; Sarin et al. [1989]).

Moreover, weathering of soda feldspar (albite) and potash feldspars (orthoclase and microcline) is greatly responsible for the contribution of Na^+ and K^+ ions to groundwater. Feldspars are more susceptible for weathering and alteration than quartz in silicate rocks. The $(Ca^{2+} + Mg^{2+})/HCO_3^-$ ratio of more than 3 (Fig. [6]e) of a few samples in the post-monsoon suggests that silicate weathering occurs in this region in addition to the carbonate dissolution.

Evaporation

The study region experiences dry and semiarid climatic condition, evaporation may also contribute in water chemistry. Gibbs ([1970]) suggested that a simple plot of TDS versus the weight ratio of $Na^+/(Na^+ + Ca^{2+})$ could provide information on the relative importance of the major natural mechanisms controlling groundwater chemistry. Hence, Gibbs' plot is employed in this study to understand and differentiate the influences of rock–water interaction, evaporation and precipitation on water chemistry. From the Gibbs plot (Fig. [7]), the dominant process determining the water composition is evaporation. Evaporation of surface water and moisture in the unsaturated zone is the main process in the evolvement of groundwater chemical composition. Evaporation concentrates the remaining water and led to precipitation and deposition of evaporates that are eventually leached into the saturated zone. This is expected, as evaporation greatly increases the concentration of ions formed by chemical weathering, leading to high salinity and TDS. This is clearly reflected in the Gibbs plot, which indicates a trend towards evaporations in the pre-monsoon and rock/soil-dominated dissolution in the post-monsoon season.
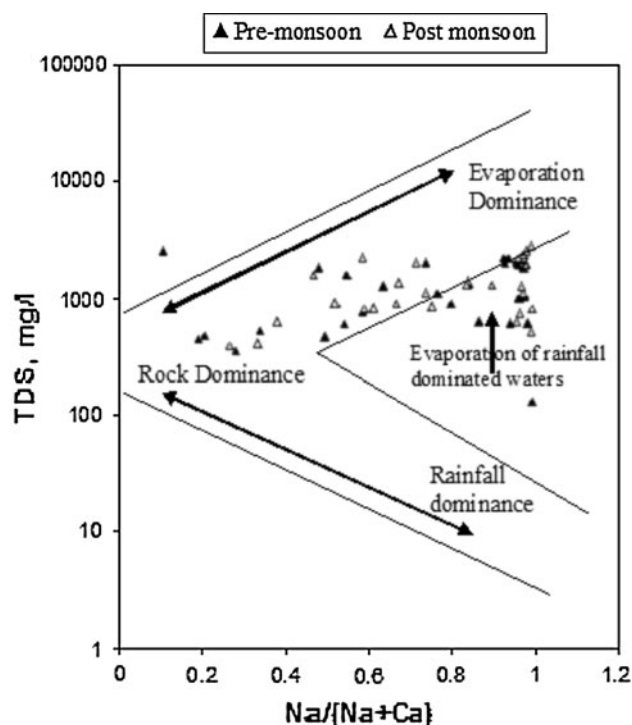

Fig. 7 Gibbs plot indicating the mechanisms that determine the major ion composition of groundwater in southern part of Bathinda district of Punjab

Furthermore, sodium versus chloride ratio can be used to identify the evaporation process in groundwater. Evaporation will increase the concentration of total dissolved solids in groundwater; and the Na/Cl ratio remains the same, and it is one of the good indicative factors of evaporation. If evaporation is the dominant process, Na/Cl ratio should be constant when EC rises (Jankowski and Acworth [1997]). Hence, the plot of Na^+/Cl^- versus EC would give a horizontal line, which would then be an effective indicator of concentration by evaporation and evapotranspiration. The EC versus Na/Cl scatter diagram of the groundwater samples (Fig. [8]a) shows that the trend line is horizontal for pre-monsoon indicating that evaporation is the major process for this season's samples. For post-monsoon samples trend line is inclined revealing that evaporation may not be the major geochemical process controlling the chemistry of groundwater or ion exchange reaction dominating over evaporation in the post-monsoon season.

Effect of land use on groundwater chemistry

The porous soils of the study area are characterised by high infiltration, low moisture retention and poor fertility due to limitation of organic matter. Groundwater is the main source for domestic and agricultural activities. Most of the study area is covered by agricultural lands and residents. Hence, groundwater contamination by irrigation return
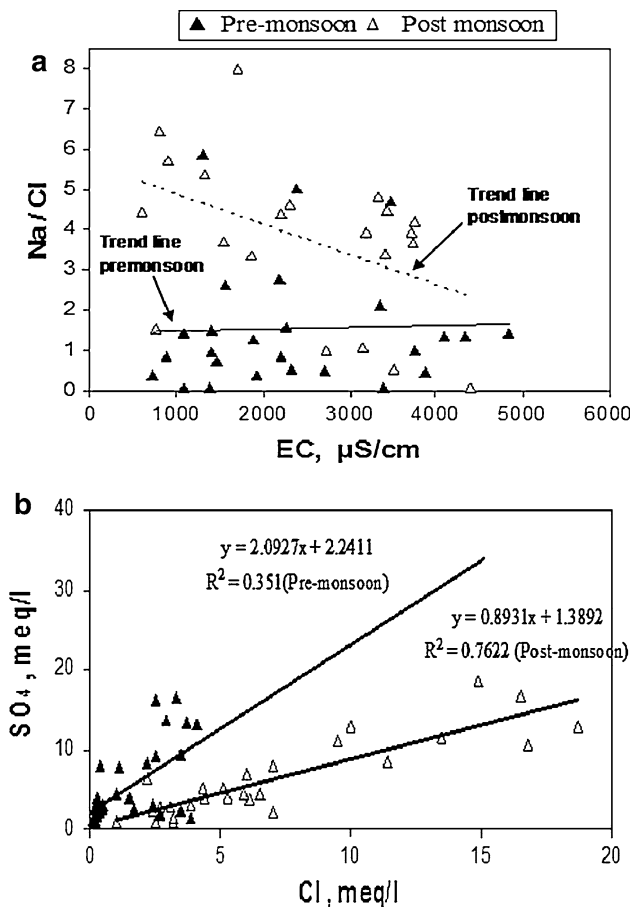
Fig. 8 Scatter diagram of **a** EC versus Na^+/Cl^-, **b** Cl^- versus SO_4^{2-}

flow, fertiliser and farm manure application, leaching of soil mineralised nitrogen, domestic sewage, runoff and leached rainfall water, etc., is also an important issue on groundwater contamination in the study area. The concentrations of nitrate and chloride in the groundwater justify the effect of anthropogenic source of contamination (Table 1). The nitrate concentration varies from below detection limit (BDL) to 79 mg l^{-1} with a mean value of 30 mg l^{-1} in pre-monsoon and from BDL to 93 mg l^{-1} with a mean value of 37 mg l^{-1}. However, six samples in pre-monsoon and 10 samples in post-monsoon exceed 50 mg l^{-1} permissible limit (WHO 1996) and are not fit for drinking, which may cause blue baby disease/methaemoglobinaemia in children and gastric carcinomas (Comly 1987; Johnson et al. 1987; Gilly et al. 1984; Kross et al. 1993). Also, as most of the study area is intensively irrigated and the nitrogen use efficiency is only 30–40%, therefore, higher concentration of nitrate in groundwater can be expected from the agricultural activities (Aulakh and Bijay-Singh 1997; Cassman et al. 2002). Similarly, chloride ranges from 4 to 153 mg l^{-1} in pre-monsoon

with a mean value 61 mg l^{-1} and 28 to 696 mg l^{-1} in post-monsoon with a mean value of 237 mg l^{-1}. Chloride content in pre-monsoon is well within the permissible limit (600 mg l^{-1}) set by WHO for drinking water and only 4% samples in post-monsoon exceeds the permissible limit. High chloride concentration in groundwater may indicate pollutions by sewage, industrial wastes or saline water intrusions (Bertram and Balance 1998). Sulphate varies from 45 to 785 mg l^{-1} with a mean value of 273 mg l^{-1} in pre-monsoon and 39 to 887 mg l^{-1} with a mean value of 302 mg l^{-1} in post-monsoon. Sulphate maximum permissible limit is 400 mg l^{-1} and causes a laxative effect on humans, together with excess magnesium in groundwater. Twenty-five and 29% samples in pre- and post- monsoon samples exceed the MPL. This may result in gastrointestinal irritation in the human system.

Sulphate and chloride show strong correlation in postmonsoon sampling data only [Fig. 8b (Post-monsoon) $R^2 = 0.76$] and implies the effect of surface contamination, especially irrigation return flow since gypsum application is very common in the paddy field to improve the physical conditions of the soils.

Conclusions

The results suggest that dissolution, mixing, weathering of carbonate (locally known as ''kankar'') and of silicate minerals and reverse ion exchange are the hydrogeochemical processes which occurred during pre- and postmonsoon seasons. There is a significant effect of monsoon observed in terms of hardness and the significant amount of area with temporary hardness in the pre-monsoon switched to permanent hardness domain by the post-monsoon. There is 14% increase in the Na^+–HCO_3^- type water in the postmonsoon. Elevated sodium content in water usually deteriorates the physical conditions of the soil. Therefore, there is a need to shift the cropping pattern from paddy (high water requirement crop)–wheat to cotton (less water requirement)–wheat rotation. Nitrate, sulphate and chloride concentrations reveal that water chemistry is impaired by land-use activities, especially irrigation return flow, synthetic fertilisers (urea, gypsum, ammonium sulphate, etc.) and farm manures. Therefore, there is a need to monitor these types of changes on the long-term basis over a period of time.

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