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Identification and evaluation of hydrogeochemical processes in the groundwater environment of Delhi, India

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Abstract A study of the hydrogeochemical processes in the national capital territory of India was carried out with the objective of identifying the geochemical processes and their relation with groundwater quality as well as to get an insight into the hydrochemical evalution of groundwater. Salinity and nitrate contamination are the two major problems in the area, which is alarming considering the use of this water for drinking. Various graphical plots and statistical analyses have been carried out using chemical data to deduce a hydrochemical evaluation of the aquifer system based on the ionic constituents, water types, hydrochemical facies and factors controlling groundwater quality. The prevailing hydrochemical processes operating here are simple dissolution, mixing, weathering of carbonate minerals, locally known as 'kankar', and of silicate, ion exchange, and surface water interaction. Limited reverse ion exchange has been noticed in a few parts of the study area especially in post-monsoon periods. Periodic seasonal switch-over has been clearly noticed in these hydrogeochemical processes that control groundwater quality of the area. The number of factors that control the overall mineralization and water quality of Delhi vary from season to season. In pre-monsoon, there are four factors while in post-monsoon it increases to five. The study highlights the descriptive capabilities of conventional and multivariate techniques as effective tools in groundwater evaluation.

Keywords Groundwater ·
Delhi · Water quality ·
Hydrogeochemical · Factor analysis

Introduction

The hydrogeochemical processes reveal the zones and quality of water that are suitable for drinking, agricultural and industrial purposes. Further, they help to understand the changes in water quality due to rock–water interaction as well as anthropogenic influences. The geochemical properties of groundwater also depend on the chemistry of water in the recharge area as well as the different geochemical processes that are occurring in the subsurface. These geochemical processes are responsible for the seasonal and spatial variations in groundwater chemistry (Matthess 1982). Groundwater chemically evolves by interacting with aquifer minerals or internal mixing among different groundwater along-flow paths in the subsurface (Domenico 1972; Wallick and Toth 1976; Toth 1984). Therefore, spatial distribution of chemical species gives some idea about the direction of groundwater movement. Schuh et al. (1997) indicated that increases in solute concentrations in the groundwater were caused by spatially variable recharge, governed by microtopographic controls. Generally, groundwater at the discharge zones tend to have higher mineral concentration compared to that at the recharge zones due to the longer residence time and prolonged contact with the aquifer matrix (Freeze and Cherry 1979). Further, the weathering of primary and

secondary minerals also contributes cations and silica in the system (Jacks 1973; Bartarya 1993).

Several conventional methods of data analysis are available for the simple interpretation and presentation of results (Back 1961; Matthess 1982; Hem 1989), e.g. histograms, trilinear analysis and semi-logarithimic diagrams (Lloyd and Heathcote 1985). Multivariate analysis, such as factor analysis, is used simply as a numerical method of discovering variables that are more important than other data for representing parameter variation or demonstrating hydrochemical processes. It relies on a set of assumptions about the nature of the present population from which samples are drawn. These assumptions provide the rationale for the operations that are performed, and the manner in which the results are interpreted (Dawdy and Feth 1967; Klovan 1975; Ashley and Llyod 1978).

In many parts of India, especially in the arid- and semi-arid regions, due to vagaries of monsoon and scarcity of surface water, dependence on groundwater resource has increased tremendously in recent years. Viewed in the international perspective of ' < 1,700 m^3/person/year' as water stressed and ' < 1,000 m^3/person/year' as water scarce, India is water stressed today and is likely to be water scarce by 2050 (Gupta and Deshpande 2004). Delhi being a rapidly growing city in Asia is facing both groundwater quality and quantity problems. The city is forced to meet 50% of its water requirement from groundwater. Except some reports on fluorosis, no documented (published) information is available on the extent of population that is exposed to contaminated groundwater in different parts of Delhi. Previous studies indicated groundwater recharge zones distributed in small patches in the study region (Das Brijraj et al. 1988; Datta and Tyagi 1996; Datta et al. 1996). Open unlined drains and the pollution dumping sites in the recharge areas act as source of pollution to the groundwater. Among these two, the unlined sewage channels are more hazardous in polluting the groundwater due to their perennial nature, but not much attention is paid to evaluate their impact on the groundwater quality.

In the present study, a detailed investigation was carried out with the objectives of identify hydrogeochemical processes and their relation with the groundwater quality, prominent water quality parameters controlling the hydrochemical evolution of the aquifer system through factor analysis and the seasonal variation in groundwater quality in the study area.

Study area

The National Capital Territory of Delhi has an area of 1,483 km^2. The area lies between 28°24′17″–28°53′00″N and 76°50′24″–77°20′37″E (Fig. 1). The Delhi region is a part of Indo Gangetic Alluvial Plains, at an elevation ranging from 198 to 220 m above mean sea level. Lithologically, the area is transected by a quartzite rocky ridge, a prolongation of Aravalli Hills extending along the southern border of Delhi and ending to the north on the west bank of the Yamuna river. The Ridge acts as a water divide between the eastern and western parts.

The climate is of semi-arid nature due to marked diurnal differences of the temperature, high saturation deficit and low–moderate rainfall. The climate is markedly periodic and is characterized by a dry and gradually increasing hot season between March and June, a dry and cold winter from October to February and the warm, monsoon period from July to September. The average rainfall (1954–2004) is 721 mm and the annual evaporation is about 2,565 mm. The mean minimum and maximum temperatures are 18.7 and 30.5°C, respectively, with daily maximum temperatures during the hottest months commonly exceeding 42.2°C.

Physiographically, the region shows four major variations. These are:

(a) The Delhi Ridge: A prolongation of the Aravalli hills consisting of quartzite rocks and extending from the southern part of the territory to the western bank of Yamuna for about 35 km. The alluvial formations overlying the quartzitic bed rock have different natures on either side of the ridge.
(b) The nearly closed Chattarpur alluvial basin covering an area about 48 km^2 that is occupied by the alluvium derived from the adjacent quartzite ridge.
(c) Alluvial plains on the eastern and western sides of the ridge.
(d) Yamuna flood plain deposits. These are of recent origin, also termed as Newer alluvium.

The Newer alluvium is characterized by the absence of permanent vegetation due to periodic flooding and lack of kankar. The thickness of alluvium overlying the bedrock increases in the direction away from ridge and reaches 300 m in the western parts of Nazafgarh, Kanjhawla block and in the northern part of Alipur block. The thickness of alluvium in the region of river Yamuna in the east of the ridge is about 165 m (CGWB 2003; CPCB 2001).

Land utilization in Delhi has changed significantly over the years due to conversion of agricultural land for urban needs. A large part of the area has alkaline and saline soils with abundant calcrete depositions at places (Wadia 1981). The alkaline soils contain sodium bicarbonate and carbonate among the soluble salts while the saline soils are impregnative with sodium chloride and sulphate as the main soluble salts. The distribution of these soils divides the study region into four geographical sub-regions. The north-west region is covered by calcareous, silty clay loam, the north-east soils are cal-

Fig. 1 Location and general geological map of NCT-Delhi, India
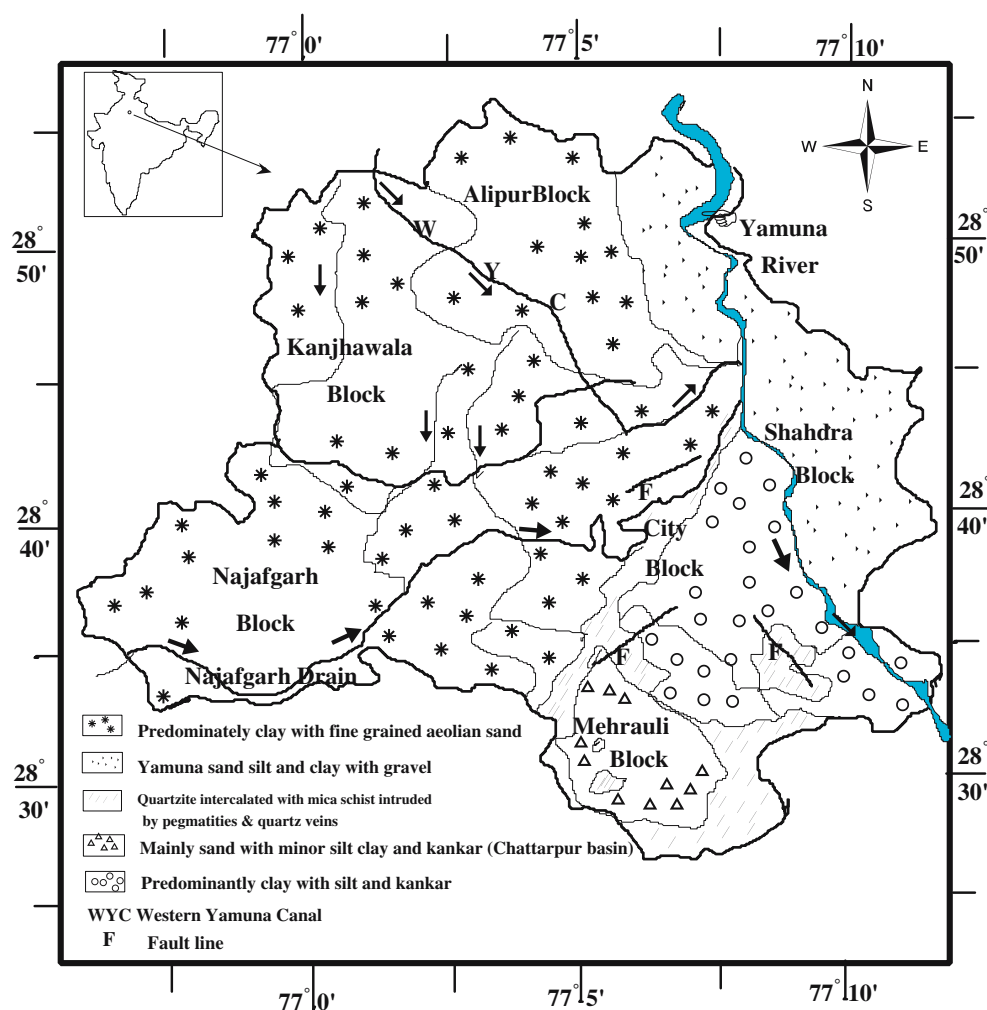
careous, silty, clay, and sandy-loam type, the southern region is occupied by the rocky Aravali ridge with dissected land spreads and the south-west zone is covered by sandy-loam (Fig. 2).

The general slope of the area is from north to south in accordance with the flow of the Yamuna river (Fig. 3). This general slope is altered in the southern side due to the presence of the Delhi Ridge and a prominent topographic depression in the south-west margins locally known as Nazafgarh Jheel. The drainage east of the ridge discharges into the Yamuna, whereas drains west of the ridge discharge into the Nazafgarh Jheel. The Nazafgarh drain contributes about 60% of the total waste-water that gets discharged from Delhi into the Yamuna. The northern part of the area, from the west to east, has a hydraulic gradient of about 0.79 m/km (Sett 1964). The southwestern part, from west to northwest, has a hydraulic gradient of about 0.75 m/km while the southeastern part has about 0.19 m/km. The total groundwater available in NCT Delhi is around 291.54 mcm/year from which the total withdrawal exceeds 86%. The spatial variation in groundwater availability as a result of variation in physiography and hydrogeology is reflected in several parts of the study region as a rapid decline in the groundwater table. The groundwater gradient in the plains runs parallel to the slope of the land surface and the water in the alluvium is under regional water table condition (Seth and Khanna 1969).

Materials and methods

Initially, to understand the general variation in groundwater chemistry over the study area, a well inventory survey was carried out during March 2003 and electrical conductivity (EC) and pH were measured. A Garmin global positioning system was used for location and elevation reading with the elevation accuracy of 0.5 m. This was supported by topographic sheets made available from Geological Survey of India. No significant difference was observed in elevation readings in two

Fig. 2 A generalized geological column for the study area
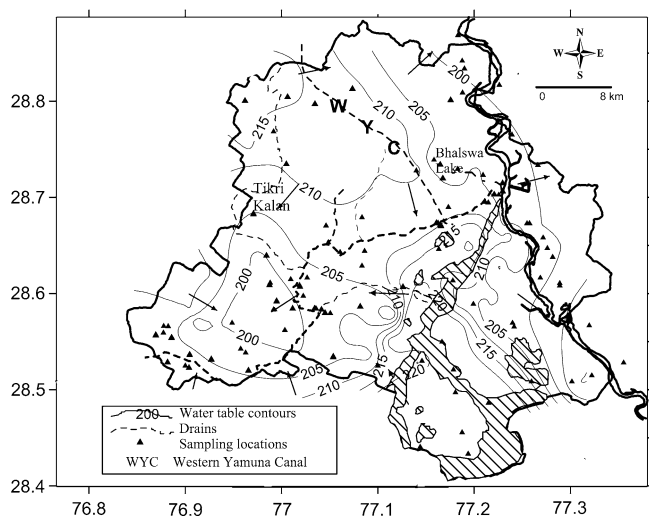
	Age Group	Lithology		Hydrological Condition	Groundwater potential
Unconsolidated Formation	Newer Alluvium (Quarternary)	Yamuna sand, slit and clay with gravel		30-40 m thick unconfined to semiconfined aqifers	Very large field 100-280 m³/hr
	Older Alluvium (Tertiary)	Predominantly clay associated with fined grained aeolian deposits		Fairly thick regional extensive, semi-confined aquifers	Large field prospects 30-100 m³/hr
		Predominantly clay with slit and kankar		Local, limited thick semi-confined aquifers	Moderate field prospects 23-100 m³/hr
Consolidated Formation	Delhi super group (PreCambrian)	Mainly sand with minor silt, clay & kankar (chattarpur basin)		Fairly thick regionally extensive aquifers	Low field prospects 10-30 m³/hr
		Quartzite interclated with mica schist, intruded by pegmatites & quartz veins		Weathered fractured quarzite, highly jointed	Limited field prospects 0-10 m³/hr

close locations. These data were used to select the representative wells and hand pumps for groundwater sampling. Sampling wells were selected in such a way that they represent different geological formations as well as land-use pattern at varying topography of this area. Eighty-four groundwater samples, 12 samples from different drains and canals and two river water samples (Fig. 3) were collected during pre-monsoon season (May 2003) and post-monsoon season (November 2003).

Water samples were collected in clean polyethylene bottles. At the time of sampling, sampling bottles were thoroughly rinsed 2–3 times using the groundwater to be sampled. In the case of bore wells and hand pumps, the water samples were collected after pumping the water for 10 min. In the case of open wells, water samples were collected 30 cm below the water level using a depth sampler. This was done to remove groundwater stored in the well itself and to obtain representative samples. In situ measurements included EC, pH, DO, oxidation–reduction potential (ORP), temperature and bicarbonate which were measured using a portable field kit and by titration.

Samples collected were brought to the laboratory and were filtered using 0.45 μm Millipore filter paper and acidified with nitric acid (Ultrapure Merck) for cation analyses and HBO_3 acid was used as preservative for nitrate analysis (M. Kumar, unpublished data). For anion analyses, these samples were stored below 4°C. Major cations like Ca^{2+}, Mg^{2+}, Na^+, K^+ and Li^+ were analyzed on flame photometer and heavy metals were analyzed using Schimadzu AAS. The chemical analysis was carried out as per standard procedure given in APHA (1995). To analyze fluoride, Thermo-Orion Benchtop Ion Selective Electrodes were used. Nitrate analysis was performed by using Brucine Method. The analytical precision for the measurement of ions was determined by calculating the ionic balance error. Apart from the collection and analysis of water samples, other data were collected from the Central Ground Water Board and Central Pollution Control Board, New Delhi. Surfer software was used to make contours and Aqua-chem was used for plotting the Piper, Scholler, Durov and radial diagrams.

Results

Data validation

The analytical precision for the measurement of ions was determined by calculating the Normalized Inorganic Charge Balance (Huh et al. 1998) which is defined as $\{\sum_{cation} - \sum_{anion} / \sum^+ + \sum^-\}$ and represents the fractional difference between the total cations and total anions (Edmond et al. 1995). As exemplified by

Fig. 3 Water table elevation, flow direction and sampling locations in the study area

Huh et al. (1998) the measured major ions (Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, NO_3^-, HCO_3) are generally enough to give a charge balance. More than 98% of the groundwater samples showed a charge imbalance mainly in favour of positive charge excess, but some inversely with a negative charge deficit. Maximum charge imbalance that was calculated was 14.23%. Positive charge excess higher than 5% agrees with the database of the dissolved load in Yamuna river and Nazafgarh drain, where the greater imbalance appeared during the low-flow periods (Sharma et al. 2004). This imbalance of negative charges could be related to the fact that no analysis was made of organic matter (Berner-Kay and Berner 1987; Edmond et al. 1995; Huh et al. 1998) which is mainly produced by biological activities during spring and summer.

Water chemistry with its spatial and temporal variations

The average, minimum and maximum values for each water quality parameter analyzed for both the pre-monsoon and post-monsoon seasons is given in Table 1 with the percentage of samples exceeding permissible limit for the drinking water given by WHO (1984). Almost all parameters other than ORP, DO, PO_4^{2-} and heavy metals show a wide fluctuation in both the seasons. The pH values for groundwater from different lithologies indicate alkalinity and their low values in the post-monsoon indicate dilution due to influx of rain-water of lower alkalinity. In general, EC is found to be high all along the western border of the study area (Fig. 4). Along the west, on moving from north to south, EC increases from 3,000 µs/cm and reaches a maximum value of 37,500 µs/cm at Tikri Kalan village near the western border of Delhi with Haryana and thereafter it gets diluted on moving south towards the Nazafgarh depression zone where it reaches 4,000 µs/cm, indicating a salinity mound close to the middle of the western region near the Tikri Kalan. The concentrations of SO_4^{2-} and Cl^- measured at this site were 6,866.67 and 4,400 mg/l, respectively, which are also the highest among all the measured sites. In addition to this general trend, local points of high salinity like Bhalswa are also seen in the study area. The highest salinity in the location close to the river Yamuna is observed at the site near Bhalswa Lake. It is a low-lying area located ~5 km west of the river Yamuna in north Delhi and the EC measured at this site was 11,400 µs/cm. Such a high salinity at the proximity of a perennial river raises suspicion about the source of this salinity. Throughout the area, groundwater is saline while in the western parts of the region, even the shallow groundwater is saline (Seth and Khanna 1969; Das Brijraj et al. 1988). One of the dominant fresh water recharging sources in north Delhi

Table 1 Summary statistics for concentrations of chemical constituents in pre-monsoon and post-monsoon samples

Pre-monsoon					Post-monsoon			
Constituents	Average	Minimum	Maximum	Percentage of samples[a]	Average	Minimum	Maximum	Percentage of samples[a]
Temperature (°C)	26.4	25.9	34	NA	24.5	23	32.2	NA
Oxidation–reduction potential (eV)	145.34	116	173	NA	277.3	123	670	NA
DO (mg/l)	7.6	4.5	14.5	NA	8.2	5.5	16.3	NA
pH	7.32	6.5	9.91	0	7.26	6.87	8.58	0
TDS (mg/l)	2,977	121.1	26,264	53	1,807	35.5	7,000	44
Electrical conductivity (µS/cm)	3,074.9	453	37,500	64	2,982	392	10,000	59
Na^+ (mg/l)	108.1	0.59	490.58	12	189	1	1,374	41
K^+ (mg/l)	11.71	B.D	107.07	28	9.44	0.39	258.98	7
Ca^{2+} (mg/l)	77.12	1.33	122.22	0	250	43	1,049	21
Mg^{2+} (mg/l)	18.62	1.76	20.76	0	45.96	15.4	59.16	0
HCO_3^- (mg/l)	88.57	28	220	0	362.44	120	1,050	0
Cl^- (mg/l)	177	5.67	4,400	11.7	699.36	14	3,935	28
SO_4^{2-} (mg/l)	441.16	1.28	6,867	2	111.6	2	319	0
SiO_2 (mg/l)	23.18	2.31	35.22	0	27.29	2.98	37.58	0
PO_4^{3-} (mg/l)	0.48	0.03	3.34	6	0.31	0.10	0.93	4
NO_3^- (mg/l)	43.56	9.29	109	41	37.73	4.06	300	23
F^- (mg/l)	0.47	0.12	4.13	5	0.48	0.02	4.04	13
Fe (mg/l)	1.73	0.11	23.08	6	0.21	B.D	0.86	0
Zn (mg/l)	0.54	B.D	2.12	0	0.23	B.D	2.06	0
Mn (mg/l)	0.18	0.01	1.96	0	0.11	B.D	2.13	5
Cu (mg/l)	0.14	B.D	0.17	0	0.56	0.012	0.16	0

[a] Percentage of samples beyond the permissible limits as prescribed by WHO (1984)

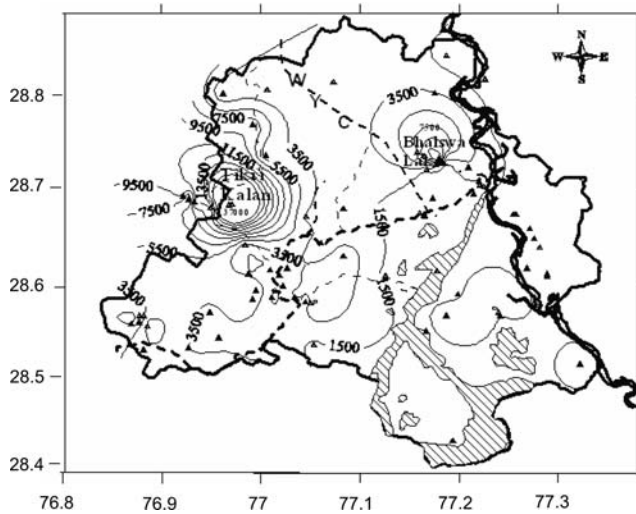**Fig. 4** Distribution map of electrical conductivity (µS/cm)

is the Western Yamuna canal. Water samples collected all along the canal up to the Nazafgarh drain were found to be fresh (EC is ∼500 in 100 ft depth, ∼800 at 50 ft depth) indicating the canal to be the predominant recharge source for north Delhi along its stretch. In general, a correlation appears between the potentiometric surface and groundwater salinity. Groundwater in high land areas of ridge and canal appears fresh, and in the low-lying area towards the west and south-west the salinity increases.

The average value of chloride in the post-monsoon is much more than that in pre-monsoon, which is perhaps due to the rising water table in the post-monsoon periods which dissolves more salts from the soils (Ramesam 1982; Ballukraya and Ravi 1999). The chloride concentrations were found higher in the area covered with sand dunes, especially the western and northern parts of the study area (Fig. 5). High chloride weathering of ridge material also contributed to the salinity problem in the area. Previous studies also reported chloride levels as high as 1,680 ppm (Paliwal and Yadav 1976). In the sand dunes, rainwater may react with the evaporate deposits to enhance the topsoil with Cl^-, HCO_3^- and Na (Subramanian and Saxena 1983). Besides these, anthropogenic sources such as domestic waste-water and industrial discharge also have an impact on groundwater quality. The large lateral variations of chloride concentration indicate recharge and discharge zones of lateral flow regime. Local recharge to the unconfined aquifer is more dominant than recharge from lateral flow (Datta and Tyagi 1996). The chloride ion is also considered to be conservative in groundwater of the Delhi Area (Datta et al. 1996). Groundwater is under-saturated with respect to NaCl. Therefore, physical processes such as mixing with another aquifer of different Cl^- concentra-

tion and change in evaporation rate during recharge either spatially or temporally may cause the changes in the chloride content of groundwater.

Dissolution of carbonates and reaction of silicates with carbonic acid accounts for the addition of HCO_3^- to the groundwater. In post-monsoon, HCO_3^- dominates over SO_4^{2-} and at many places over Cl^-. Silica occurs as silicic acid (H_4SiO_4) in natural water at pH < 9. The average value of dissolved silica is found to be higher than the prescribed value for groundwater, i.e. 17 mg/l (Davis 1986), which is due to the silicate weathering in the study area. Sulphate concentration is variable in quartzite (75–750 ppm), alluvium (200–831 ppm) and sand dunes (665–2,531 ppm). The variation indicates the constituents of leaching and dissolved solids from sand dunes/alluvium. The concentration of phosphate was relatively higher in drains and river water near Okhala barrage (M. Kumar, unpublished data). The high concentration is attributed to input from the domestic and industrial waste-water. A few groundwater samples from the northern and eastern parts of the study area exhibited very high phosphate concentration. This may be due to local factors such as discharge of agriculture runoff or due to mixing of sewage with the shallow groundwater table and leachates from the landfill sites.

The common sources of nitrate in water are the leachates from the landfill sites, local agricultural fields, domestic sewage etc. However, because of laminar flow condition and due to difference in specific gravity and viscosity between nitrate slugs and the natural freshwater, some diffusion is bound to occur. But no such nat-
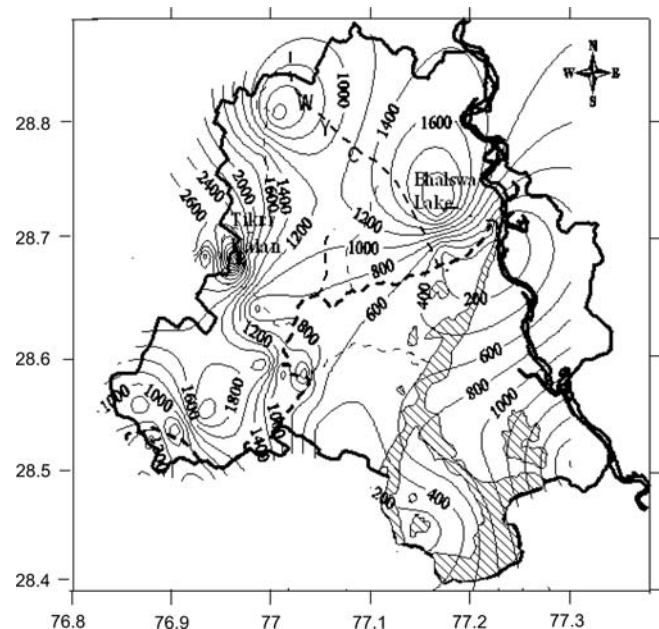

Fig. 5 Distribution map of chloride (mg/l)

ural sources are reported to exist in the area for NO_3^- (Handa 1988). Even then, the average value of NO_3^- is close to the permissible limit for drinking water, which is an alarming situation and shows the anthropogenic impact on the groundwater quality (Fig. 6). In order to investigate fertilizer input as a probable common source of potassium and nitrate to the groundwater as was thought in the earlier studies (Datta et al. 1997), a cross plot between NO_3^- and K^+ was examined, instead of relying on their weak correlation coefficient (Fig. 7). The plot indicates that an excess nitrate above a median value is normally associated with a low potassium content (< 20 ppm). This indicates a different source for the nitrate and not a common source as it was thought earlier. The soils of Delhi and the alluvium have significant amounts of illite, which may fix K from water. Hence, certain groundwaters in Delhi have very low K^+ values (Subramanian and Saxena 1983).

Sodium ion shows higher concentrations because it behaves like a conservative element as it is not used up in biological process, and also as a non-conservative element as it gets fixed in clay mineral formation by ion exchange (Subramanian and Saxena 1983). Ca^{++} and Mg^{++} show good correlation among themselves and also with Na, indicating a same source.

The concentration of Mn for all sampling seasons is higher in the eastern part of the study area which may be attributed to anthropogenic activities such as waste discharge from industrial units. The lower concentration of Ni and Cu in surface water as compared to groundwater favours the point that there could be a decrease in trace element concentration in the river (Durum and Haffty 1963). The Cu concentration in groundwater is higher in the western part of study area, but it is well within the WHO standards for drinking water. The
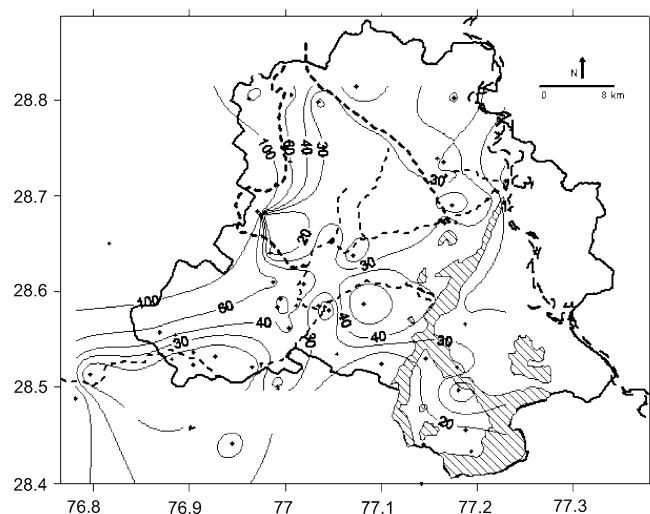
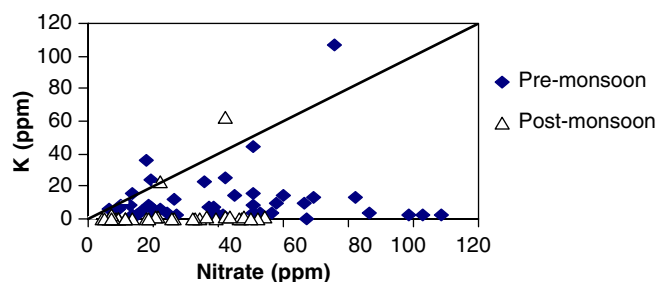**Fig. 7** Scatter diagram of NO_3^- versus K^+ in groundwater of Delhi

groundwater samples show relatively higher concentration of Zn especially in the the southern and western parts, which may be attributed to agricultural field runoff.

Drinking water suitability

To foresee the suitability of groundwater for drinking purpose, each sample was compared with the WHO guidelines (1984) for drinking water and percentages were deduced for the samples having values higher than the permissible limit for that particular parameter (Table 1). It is found that saline water is the major problem existing in the study area as evident from the EC, Na and Cl concentrations for which 64, 12 and 21% (pre-monsoon) and 59, 41 and 28% (post-monsoon) of samples are showing values higher than their permissible limits, respectively. It is also evident from the classification of water type on the basis of their TDS values (Catroll 1962; Freeze and Cherry 1979), which are presented in Table 2. More than 50% of samples of both seasons fall under brackish type of water. Nearly the same percentage of samples has salinity beyond the maximum permissible limit for drinking water as per the WHO standard, i.e. 1,500 mg/l.

The second problem with using the groundwater for drinking is nitrate contamination which is mainly caused due by the landfill leachate, a subject of future research, as fertilizer is not the main source. Around 41% of the samples of pre-monsoon and 23% of post-monsoon have nitrate concentrations more than permissible.

Fig. 6 Distribution map of Nitrate (mg/l)

Table 2 Classification of water by salinity (adapted from Davis and Dewiest 1967)

Name	Concentration of TDS (mg/l)	Percentage of sample (pre-monsoon)	Percentage of sample (post-monsoon)
Fresh	0–1,000	36	45
Brackish	1,001–10,000	62	55
Salty	10,001–100,000	2	0
Brine	> 100,000	0	0

Other than Fe, the rest of the heavy metals are either in between desirable and permissible limits or below desirable limits.

Graphical representation of hydrochemical data

In the present study, water quality data is analyzed through statistical distribution diagrams such as Scho-eller diagram, Piper diagram and Durov plot (Durov 1948) to gain better insight into the hydrochemical processes operating in the groundwater flow system that resulted in the observed spatial and temporal variation in the groundwater quality.

Water quality data for the post-monsoon season when mapped using Schoeller scheme (Schoeller 1965) (Fig. 8a, b) fingerprints two distinct water types on the basis of Na concentration. One type has low Na content in the range 0.08–0.3 meq/l and the other high Na concentration in the range 10–80 meq/l. In general, water type with high Na content also has high Cl concentration. The high Na water is of two types, one with Ca in the range 25–35 meq/l, designated as Na–Ca–Cl–CO_3 and other in which Ca is in the 6–9 meq/l, designated as Na–Ca–Cl type. The low Na water is of Ca–Cl–HCO_3 and Ca–Mg–Cl types, indicating its close proximity to the recharge area. This indicates enrichment of salinity in the groundwater of types Ca–Cl–HCO_3 and Ca–Mg–Cl in the pre-monsoon period due to mixing of fresh and saline waters. The scenario indicates cyclic freshening/salinization phenomenon operating in the groundwater system of the study area.

Furthermore, the major cations and anions for the analyzed water were plotted on a Piper diagram. Hydrochemical diversity among the samples is revealed by the Piper diagram (Fig. 9a, b). Pre-monsoon samples show intermediate character followed by permanent hardness domain with a Ca–Mg–SO_4 water type. Na–Ca–Cl–HCO_3 water type suggesting very shallow sources has little water–rock interaction; Ca–Na and Cl–SO_4 are the major cations and anions, respectively. The post-monsoon plot shows a number of Ca–Mg, Na–Mg and Cl–HCO_3 types reflecting ion exchange and dissolution process occurring due to recharge in monsoon. In deep aquifer, Na–Ca–Cl–SO_4 is predominant while in shallow water, Na–Ca–Cl–HCO_3 is dominant. In the pre-monsoon season, facies changes and SO_4 comes into the role. Durov plot (Fig. 10a, b) indicates that most of the samples show no dominant cation or anion in pre-monsoon, while some samples show Na as a dominant cation and Cl and SO_4 as dominant anions. In the post-monsoon season, HCO_3 is dominating with Cl and Na is replaced by Ca and Mg indicating some reverse ion exchange and recharge.

The Radial (Fig. 10c) and Stiff methods are not practical to produce a great number of samples. These methods are considered by some researchers to be more or less subjective (Guler et al. 2002). Therefore, using graphical methods for group samples is not efficient and can produce biased results. These methods are generally only useful to present maps showing hydrochemical facies.

Statistical analysis
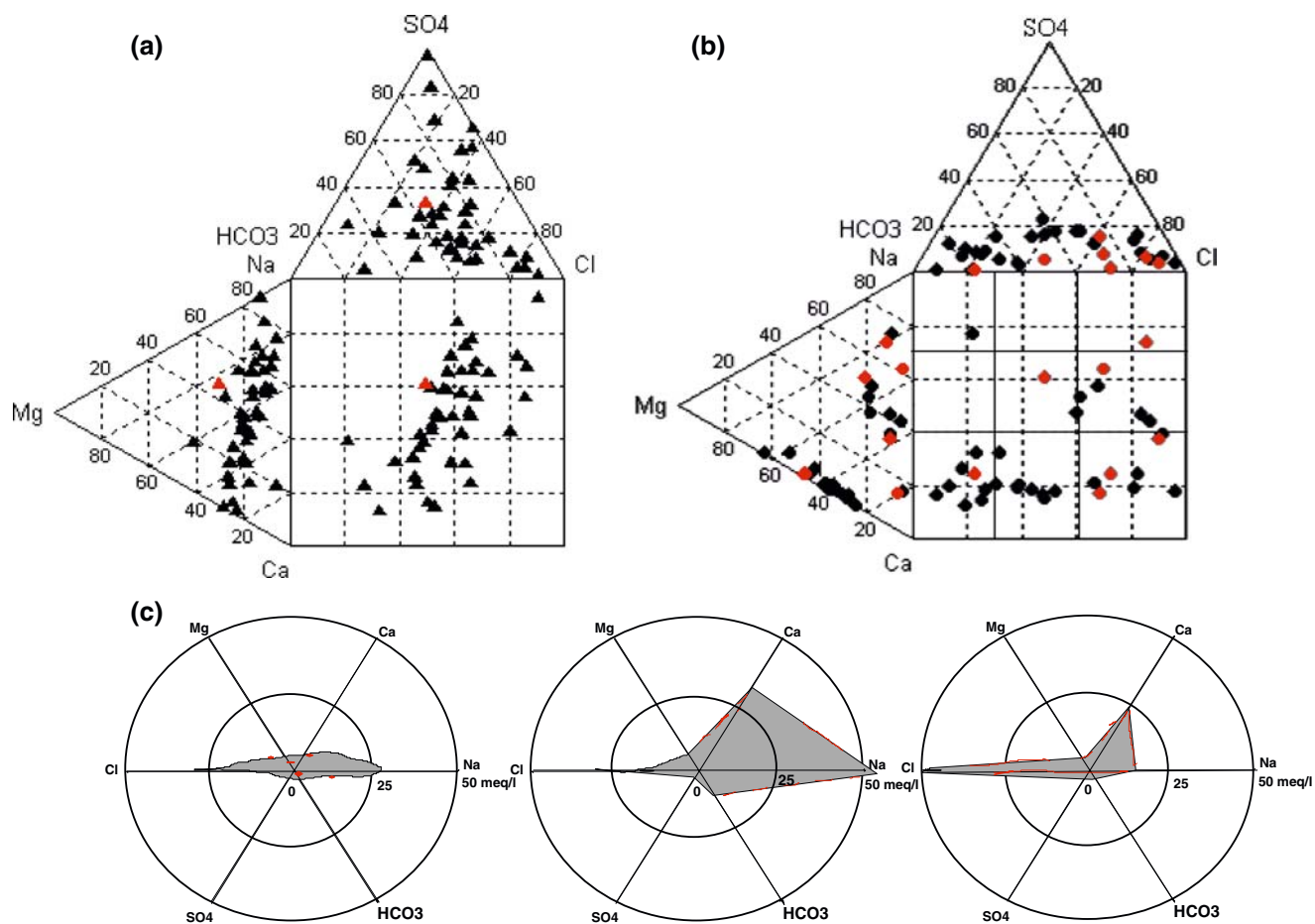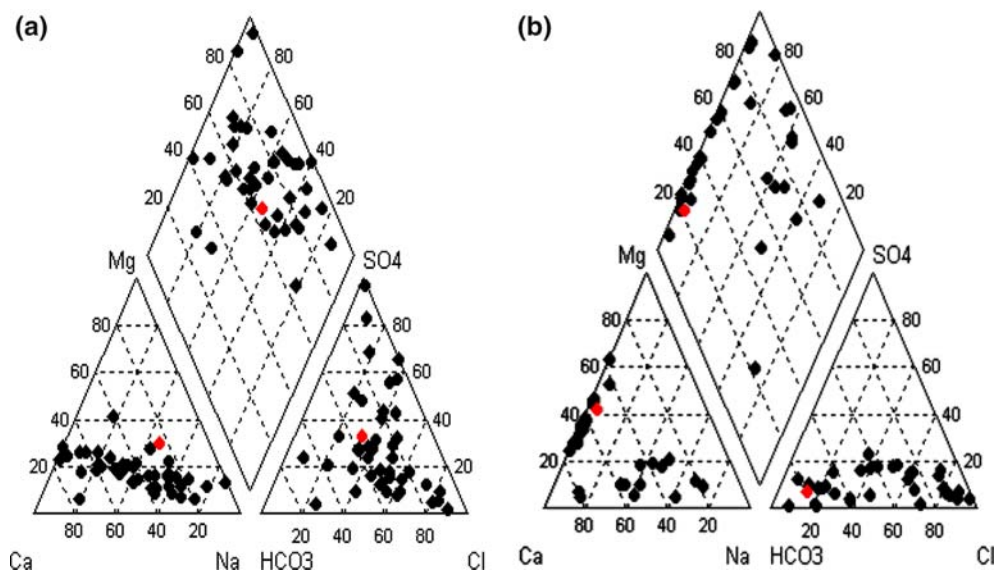
Correlation analysis

A correlation analysis is a bivariate method applied to describe the degree of relation between two hydrochemical parameters. The result of the correlation analysis is considered in the subsequent interpretation.

Fig. 8 Scholler plot for **a** pre-monsoon and **b** post-monsoon
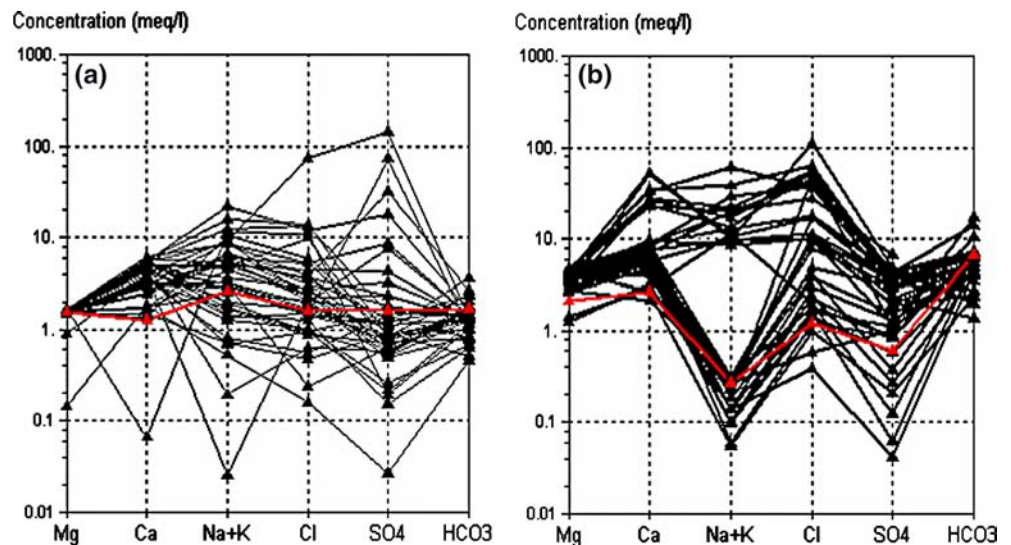
Fig. 9 Piper plots for **a** pre-monsoon and **b** post-monsoon

Fig. 10 Graphical representation of groundwater samples **a** Dhurov plots for premonsoon, **b** Dhurov plots for post-monsoon, **c** Radial plots for sample numbers 32, 34, 36

A high correlation coefficient (near 1 or −1) means a good relationship between two variables and its value around zero means no relationship between them at a significant level of $p < 0.05$. More precisely, it can be said that parameters showing $r > 0.7$ are considered to be strongly correlated whereas r between 0.5 and 0.7 shows moderate correlation.

In this study, the relationship between various elements has been studied using Spearman rank coefficient which is based on the ranking of the data and not their absolute values (Table 3). The resultant matrix shows up the negative correlation of pH with most of the variables. It likewise reveals strong correlation of EC with Cl^-, SO_4, Li and Na in both the seasons. For both the post-monsoon and pre-monsoon seasons, some pairs of species show moderate to strong correlation ($r > 0.6$), e.g. Cl–Br, Cl–SO_4, Mg–SO_4 and Na–SO_4. The major exchangeable ions Na–Ca and Na–Mg correlate positively and correlation coefficient is found to be more for the post-monsoon samples (Table 4). It can therefore be postulated that the concurrent increase/decrease in the cations is the result mainly of dissolution/precipitation reaction and concentration effects.

Factor analysis

In the present study, the factor analysis was used as an alternative tool for corroboration of the concept obtained from molar concentrations. Factor analyses serve for basic, independent dimensions of variables. With the help of linear combinations, an originally large number of variables are reduced to a few factors. These factors can be interpreted in terms of new variables. Factor analysis aims to explain observed relation between numerous variables in term of simpler relations. It is also a way of classifying manifestation of variables (Cattel 1965).

Factor analysis is used here as a numerical method of discovering variables that are more important than others for representing parameter variation and identifying hydrochemical processes. The factor model used is expressed as:

$$X_j = \sum_{r=1}^{p} a_{jr} f_r \varepsilon_j$$

where f_r are the rth common factors, p is the specified number of factors, 'j' is the random variation unique to the original variable X_j, a_{ji} is the loading of the jth variate on the rth factor. It corresponds to the loading or weights on principal components.

The principal component approach starts by extracting Eigenvalues and Eigenvectors of the correlation matrix and then discarding the less important of these (Davis 1986). Eigenvectors are then transformed to the factors of the data set. The number of variables retained in the factors or communalities is obtained by squaring the elements in the factor matrix and summing the total within each variable. The magnitude of communalities is dependent upon the number of factors retained. This type of analysis is called R-mode factor analysis. Varimax rotation was then adopted. The results of the factor analysis are summarized in Table. 5 and 6. For the water chemistry of the Delhi region, during pre-monsoon season, four factors are identified which control groundwater quality. Factor 1 accounts for 21.88% variance in the data. The variables

Table 3 Correlation matrix for pre-monsoon

	pH	Electrical conductivity	TDS	K	Na	Ca	Mg	Cl	HCO$_3$	SO$_4$	PO$_4$	NO$_3$	SIO$_2$	Mn	Cu	Ni	Zn	Fe
pH	1																	
Electrical conductivity	−0.24	1																
TDS	0.15	0.81	1															
K	0.007	0.18	0.66	1														
Na	−0.23	0.46	0.87	−0.05	1													
Ca	−0.31	0.11	0.52	0.07	0.41	1												
Mg	−0.38	0.14	0.71	0.15	0.51	0.36	1											
Cl	−0.19	0.96	0.91	0.21	0.47	0.57	0.11	1										
HCO$_3$	−0.48	−0.47	0.56	−0.36	0.69	−0.06	−0.51	0.78	1									
SO$_4$	−0.1	0.8	0.72	0.36	0.13	0.14	0.07	0.83	−0.36	1								
PO$_4$	0.43	−0.14	0.32	0.05	−0.14	−0.24	0.05	−0.13	0.26	−0.13	1							
NO$_3$	−0.12	−0.92	0.44	0.12	0.01	0.37	0.01	−0.12	0.51	−0.18	−0.16	1						
SiO$_2$	−0.18	−0.22	0.23	0.08	−0.12	0.18	0.04	−0.19	−0.63	−0.22	0.08	0.4	1					
Mn	0.03	0.45	0.11	0.1	0.11	0.16	0.09	0.46	−0.64	0.64	0.05	0.18	0.32	1				
Cu	0.07	−0.14	0.21	−0.06	−0.22	−0.06	−0.003	0.1	0.52	−0.08	0.03	−0.2	0.19	−0.11	1			
Ni	0.04	−0.05	0.18	0.1	−0.05	0.04	0.01	−0.05	−0.54	−0.04	−0.06	−0.07	−0.3	−0.07	0.21	1		
Zn	−0.23	−0.31	0.13	0.03	0.06	0.09	0.21	0.04	0.66	0.13	0.89	0.15	−0.04	−0.16	−0.22	0.15	1	
Fe	0.02	−0.07	0.16	0.03	−0.01	−0.09	0.02	0.03	0.06	−0.07	0.013	0.01	−0.14	−0.06	−0.04	−0.05	0.34	1

Table 4 Correlation matrix for post-monsoon

	pH	Electrical conductivity	TDS	K	Na	Ca	Mg	Cl	HCO$_3$	SO$_4$	PO$_4$	NO$_3$	Sio$_2$	Mn	Cu	Ni	Zn	Fe
pH	1																	
Electrical conductivity	0.06	1																
TDS	0.05	0.68	1															
K	0.09	0.37	0.56	1														
Na	−0.08	0.56	0.77	0.32	1													
Ca	−0.31	0.29	0.42	0.41	0.52	1												
Mg	0.15	0.42	0.61	0.16	0.55	0.51	1											
Cl	−0.15	0.56	0.82	0.28	0.64	0.73	0.33	1										
HCO$_3$	−0.98	0.49	0.73	−0.73	0.81	−0.39	0.96	−0.17	1									
SO$_4$	−0.07	0.38	0.62	0.21	0.58	0.58	0.57	0.61	−0.16	1								
PO$_4$	−0.97	0.25	0.42	0.85	0.99	−0.16	0.99	−0.23	−0.26	−0.22	1							
NO$_3$	0.01	0.47	0.34	0.01	0.46	0.11	0.37	0.37	−0.46	0.31	0.72	1						
SiO$_2$	−0.18	−0.22	0.33	0.28	0.62	0.53	−0.29	0.56	−0.32	0.28	0.36	1						
Mn	0.28	0.03	0.01	0.85	0.34	0.21	0.21	0.26	−0.25	0.32	0.32	0.03	0.28	1				
Cu	−0.17	−0.16	0.11	−0.16	0.22	−0.03	−0.12	−0.17	−0.15	−0.16	0.23	0.33	0.16	−0.27	1			
Ni	0.14	−0.04	0.08	0.35	0.04	−0.07	−0.14	−0.16	−0.47	−0.28	0.15	0.22	0.05	0.34	0.04	1		
Zn	−0.32	−0.13	0.03	0.01	0.03	0.07	0.01	0.04	0.71	0.13	0.86	0.11	0.09	−0.04	−0.13	−0.12	1	
Fe	−0.23	0.21	0.06	−0.06	0.15	0.24	0.09	0.27	0.96	0.29	0.96	0.34	0.26	−0.16	−0.08	−0.12	0.18	1

present in this factor are Na, K, Ca and Mg. This factor indicates ion exchange and the contribution of weathering process in the study area. Factor 2 accounts for 17.35% of total variance. The variables are EC, Cl and SO$_4$. This factor is attributed to the contribution from precipitation and deposition from dust material. Factor

Table 5 Multivariate analysis for pre-monsoon

Variable	Communality	Factor	Eigenvalue	Percentage of variable	Cumulative percentage
Final statistics					
EC	0.896	1	3.88	21.88	21.88
Na$^+$ + K$^+$	0.878	2	1.79	17.35	39.23
Cl$^-$	0.845	3	1.42	11.77	51.0
Ca^{2+}	0.803	4	1.11	8.66	59.66
Mg^{2+}	0.740				
NO$_3^-$	0.671				
PO$_4^{3-}$	0.651				
HCO$_3^-$	0.642				
F$^-$	0.603				
pH	0.562				
SO$_4^{2-}$	0.562				

Table 6 Multivariate analysis for post-monsoon

Variable	Communality	Factor	Eigenvalue	Percentage of variable	Cumulative percentage
Final statistics					
Ca^{2+}	0.850	1	3.42	21.703	21.703
EC	0.818	2	1.84	16.461	38.164
Mg^{2+}	0.814	3	1.32	9.862	48.026
Na$^+$ + K$^+$	0.784	4	1.15	9.662	57.688
PO$_4^{3-}$	0.755	5	1.07	8.317	66.005
HCO$_3^-$	0.754				
SO$_4^{2-}$	0.735				
F$^-$	0.720				
Cl$^-$	0.701				
pH	0.669				
NO$_3^-$	0.584				

3 accounts for 11.77% variance in the data. The variables are pH, F, HCO$_3$ and NO$_3$. This factor may be attributed to leaching from soils in the study area. Factor 4 accounts for 8.66% variance in the data. This factor shows positive loading only for PO$_4$, which may be attributed to anthropogenic activity such as domestic and industrial waste discharge, runoff from agriculture field, etc. In the post-monsoon season, five factors were found to be responsible for the variation in groundwater quality. Factors 1 and 2 include the same variables as in pre-monsoon with a slight change in their percentage of the total variance. In Factor 3 the variables are pH and SiO$_2$ instead of HCO$_3$ and NO$_3$. Thus this factor can be attributed to the fresh silicate weathering from the surface soils due to high alkalinity. Factor 4 includes the variables like F, HCO$_3$ and PO$_4$ accounting for 9.66% variance in the data. This factor may be attributed to leaching from soils. Factor 5 accounts for 8.32% variance in data and shows positive loading for NO$_3$. It indicates the anthropogenic influences.

Five factors accounted for 66.005% of the variance in the data set. The first factor is interpreted as relating mainly to salinization of groundwater due to dissolution processes. The main contributors Ca, Mg, Fe and HCO$_3$ correlate positively indicating the influence of geological matrix. Associations between Ca, Mg, Fe and HCO$_3$ suggest dissolution of calcite, dolomite and siderite. The factor 2 is the next predominant force and occupies the northeastern part of the study area. The leaching from the soils along with weathering process seems to be a major factor.

Hydrogeochemical evaluation

The results from the chemical analyses were used to identify the geochemical processes and mechanisms in the aquifer region. All the identified processes are explained in detail.

Weathering of silicate rocks in the region is one of the important processes responsible for the higher concentration of Na in groundwater of this area. In general, it is expected that the evaporation process would cause an increase in concentrations of all species in water. If the evaporation process is dominant, assuming that no mineral species are precipitated, the Na/Cl ratio would be unchanged (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 evapo-transpiration. If halite dissolution is responsible for sodium, the Na/Cl molar ratio should be approximately equal to 1, whereas a ratio greater than 1 is typically interpreted as Na released from a silicate weathering reaction (Meybeck 1987). In the present study, the molar ratio of Na/Cl for groundwater samples of the study area generally ranges
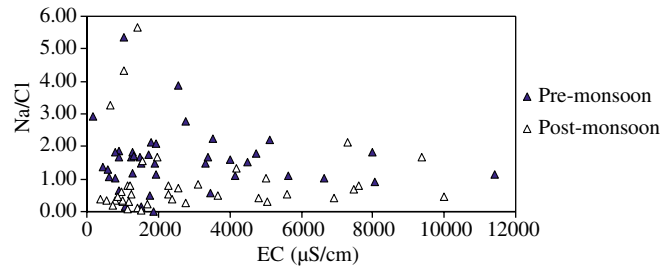

Fig. 11 Plot of Na/Cl ratio versus EC

from 0.03 to 5.73 (Fig. 11). As most of the samples have Na/Cl molar ratio around or above 1 pre-monsoon and less than 1 post-monsoon, it indicates that ion exchange is the major process which is prevalent in the study area in the post-monsoon season, which is replaced by silicate weathering in the pre-monsoon season. The sodium versus chloride (Fig. 12) plot indicates that most of the pre-monsoon samples lie slightly above the equiline. The excess of Na is attributed from silicate weathering (Stallard and Edmond 1983). Post-monsoon samples lie below the equiline, indicating that evaporation may be the cause of addition of Cl in post-monsoon due to water level rise which causes more salt dissolution from the soil. Na concentration is also being reduced by ion
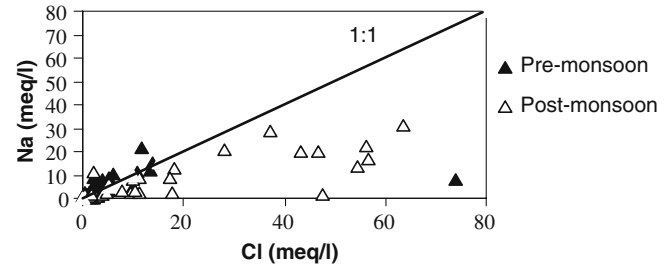

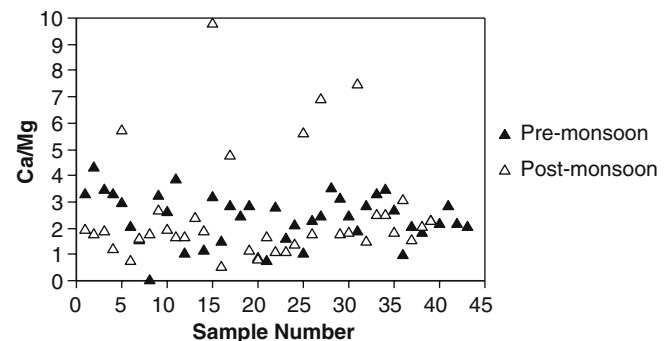**Fig. 12** Sodium and chloride plot for pre-monsoon and post-monsoon

Fig. 13 Plot of Ca/Mg molar ratio

exchange. Hence, Na and Cl do not increase simultaneously.

The study of the Ca/Mg ratio of groundwater from this area suggests the dissolution of calcite and dolomite present in the alluvium (Fig. 13). That is, 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). Higher Ca/Mg molar ratio (> 2) indicates the dissolution of silicate minerals, which contribute calcium and magnesium to groundwater. The points closer to the line (Ca/Mg = 1) indicate the dissolution of dolomite. Those with values greater than 2 indicate the effect of silicate minerals. Most of the post-monsoon samples have a ratio between 1 and 2 indicating the dissolution of calcite, while most of the pre-monsoon samples lie between 2 and 3 which indicates the effect of silicate minerals. By and large, the chemical composition of the groundwater in the study area has resulted from the dolomite weathering by carbonic acid. Presence of 'kankar' carbonates in the alluvial sediments and occurrence of metamorphosed dolomite limestones in Delhi Aravalli rocks could favor the weathering process. However, a possibility of calcite weathering by sulfuric acid is also there as indicated by Ca and SO_4 ratio. Sulfuric acid may be produced by SO_x emission dissolved in rain from automobile and industrial sources.

The plot of Ca + Mg versus SO_4 + 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 + HCO_3 (Cerling et al. 1989; 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 + Mg over SO_4 + HCO_3. The plot of Ca + Mg versus SO_4 + HCO_3 (Fig. 14) for both pre- and post-monsoon shows that most of the groundwater samples are clustered around and below the 1:1 line except for a few samples from post-monsoon. Exceptional points do indicate reverse ion exchange but extent is very less. The plot of m(Ca + Mg) versus m(Cl) (Fig. 15) indicates the
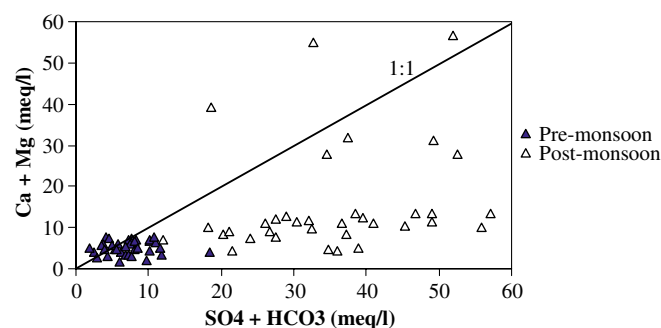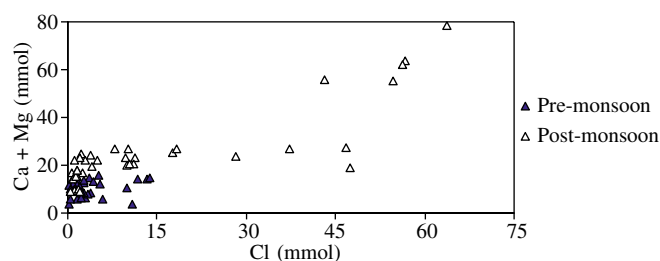

Fig. 15 Relation between Ca + Mg and Cl

same as Ca and Mg do not increase with increasing salinity which could be the indication of reverse ion exchange in the clay/weathered layer except again for a few samples of post-monsoon. The sources of Ca and Mg in groundwater can be deduced from the m(Mg + Ca)/$m$$HCO_3$ ratio. As this ratio also does not increase with salinity (Fig. 16), Mg and Ca are added to solution at a lesser rate than HCO_3 ratio which is evident from the samples of post-monsoon which show this ratio below 1 and around 0.5. If Ca and Mg originate solely 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 + Mg in groundwater in Delhi can be attributed to mainly carbonate weathering (Datta and Tyagi 1996). The carbonate alkalinity in the few samples can be balanced by alkalies Na + K through either silicate weathering or dissolution of alkaline soil salts.

Conclusions

The groundwater quality of the study area has a primary problem of salinity followed by nitrate contamination which needs special attention. The prevailing hydrochemical processes in pre-monsoon and post-monsoon seasons are entirely different, namely silicate weathering and simple dissolution, and evaporation and weathering of carbonate minerals including kankar. Other than this
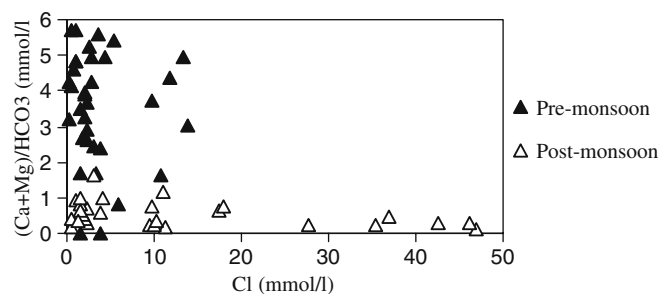

Fig. 14 Relation between Ca + Mg and SO_4 + HCO_3

Fig. 16 Relation between (Ca + Mg)/HCO_3 and Cl (mmol/l)

ion exchange, surface water interaction and limited reverse ion exchange has been also noticed in a few parts of the study area especially in post-monsoon. Local recharge is associated with low salinity of Ca–Mg–HCO$_3$ type which is through rainfall and the surface water body, especially west Yamuna canal and Yamuna river. Large lateral variation of conservative elements shows that recharge through lateral flow is not dominant in the area. Highly saline and brackish groundwater in the discharge zones like northwestern and southwestern parts of the area seem to be associated with a long history of evaporation and oxidation of sulfur gases in low-lying areas. The number of factors that control the overall mineralization and water quality of Delhi varies for the different seasons. In pre-monsoon there are four factors while in post-monsoon it increases to five. The major exchangeable ions Na–Ca and Na–Mg correlate positively and correlation coefficient is found to be more for the post-monsoon samples. It can therefore be postulated that the concurrent increase/decrease in the cations is the result mainly due to ion exchange, dissolution/precipitation reaction and concentration effects.

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