



# Multivariate statistical analysis and geochemical modeling for geochemical assessment of groundwater of Delhi, India



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## ABSTRACT

Groundwater is the most important source of drinking waters supply in the National Capital Territory (NCT) of New Delhi, India. A diverse geological and topographical set up along with the fast growing population and anthropogenic activities has created a need of groundwater quality assurance for drinking and domestic water supply in the region. The major hydro-geochemical process and impacts of anthropogenic activities can be deciphered using multivariate statistical analysis, conventional graphical plots and saturation indices. Groundwater samples were collected from 170 locations spread over entire region and were analysed for a total of 12 water quality physico-chemical parameters. It is observed that the groundwater is neutral to alkaline in nature with electrical conductivity (EC) value ranging from 460 to 8980  $\mu\text{S}/\text{cm}$ . Chemometric analysis was performed along with geochemical modeling. The 3 clusters obtained through HCA were clearly differentiated based on their chemical characteristics i.e. concentration of major ions. High concentration of nitrate ( $\text{NO}_3^-$ ) and fluoride ( $\text{F}^-$ ) exceeding WHO standards was found in 29% and 27% of the water samples respectively. It is observed that semi-arid climatic conditions along with rock-water interaction, weathering and ion-exchange are the major factors controlling groundwater quality in the region. Oversaturation of fluorite and gypsum has resulted into high concentration of  $\text{F}^-$  in study area. It is found that the results from statistical and geochemical models compliment the findings using conventional plots and are able to decipher comprehensive geochemistry of groundwater in the region.

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## 1. Introduction

Groundwater is a major concern for the community as it is the most important and reliable source of freshwater supply on earth. Groundwater is a renewable and finite natural resource, vital for man's life, socio-economic development and a valuable component of the ecosystem, vulnerable to natural and human impacts (Singh et al., 2011a). In general groundwater is considered to be safe than surface water in terms of microbial contamination because of the unique filtration capacity of soil matrix above the aquifer, however it also induces geogenic contaminants at times. Groundwater quality in an area is a function of physico-chemical parameters that are greatly influenced by natural processes such as intermixing of water, water chemistry in recharge area, flowpath, rock-water interaction, climatic conditions along with geological formations and anthropogenic activities (Barbecot et al., 2000;

Belkhiri et al., 2010; L-Ruiz et al., 2015). Natural processes such as recharge and discharge, precipitation or dissolution of aquifer minerals, ion-exchange, oxidation-reduction, residence time and mixing of water has a great influence on groundwater quality (Reghunath et al., 2002). Anthropogenic activities such as over withdrawal of groundwater, leaching of fertilizers and accidental spillages also influences the quality of groundwater. The contamination in groundwater persists for longer duration due to low flow rate of groundwater in aquifer system. Chemical characteristics of groundwater determine the suitability of water for domestic, agricultural or industrial use (Mondal et al., 2010; Li et al., 2012; Roques et al., 2014; Kumar and Singh, 2015). Increased population, unplanned landuse practices and high water supply demands has deteriorated both the quality and quantity of groundwater (Hamilton and Helsel, 1995; Machiwal and Jha, 2015; Liu et al., 2016). In recent past, studies have been conducted using different methods including multivariate statistical analysis (Yidana and Yidana, 2010; Singh et al., 2011b; Machiwal and Jha, 2015), geochemical modeling (L-Ruiz et al., 2015; Suma et al., 2015; Singh et al., 2012; Yidana et al.,

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2008), stable isotopes (Barbieri et al., 2005; Carucci et al., 2012), redox indicator, structural equation modeling (Belkhiri and Narany, 2015) to investigate the geochemical evolution and hydrochemical processes controlling the chemical characteristics of groundwater. Statistical analysis do not necessarily establish cause and effect relationships, but collates the information in a compact format by removing data redundancy as the first step in the complete analysis and thus assist in generating hypothesis for the interpretation of various hydrochemical processes (Guler et al., 2002). Multivariate analysis of geochemical data operates on the concept that each aquifer zone has its own unique groundwater quality signature, based on the chemical characteristics of the sediments that surround it (Singh and Mukherjee, 2015). Inverse geochemical modeling involves a mass balance model which is used to quantify the reactions and thus the chemistry of groundwater in its flowpath and rock-water interaction (Barbieri et al., 2005; Carucci et al., 2012; Yidana et al., 2008; Appelo and Postma, 2005). Contaminants such as nitrate ( $\text{NO}_3^-$ ) and fluoride ( $\text{F}^-$ ) have an adverse impact on human health. High concentration of  $\text{NO}_3^-$  in groundwater may cause methemoglobinemia, pre-mature birth and blue baby syndrome, whereas high concentration of  $\text{F}^-$  may cause lack of enamel formation,

moulting of teeth, bone fragility and at the severe stage it may cause bilateral lameness and stiffness of gait (Edmunds and Smedley, 2005; Singh et al., 2011a; Singh et al., 2013a)

With the above background an attempt has been made to decipher the geochemistry of groundwater using statistical and geochemical models and to determine and understand the fate of contaminants such as  $\text{F}^-$  and  $\text{NO}_3^-$  as these are harmful from public health perspective.

## 2. Material and methods

### 2.1. Study area

The national capital city of India, New Delhi is situated between  $28^\circ 23' 17''\text{N}$ – $28^\circ 53' 00''\text{N}$  latitude and  $76^\circ 50' 24''\text{E}$ – $77^\circ 20' 37''\text{E}$  longitude (Fig. 1). The study region covers around  $1480\text{ km}^2$  of area and the altitude varies from 213 m to 305 m from mean sea level. The climate is of semi-arid nature and average rainfall of Delhi is 714 mm, most of the rainfall (81%) occurs in monsoon season. The study area is a part of Gangetic alluvial plain as River Yamuna passes through the eastern part of the city. Geologically the study area is composed of older

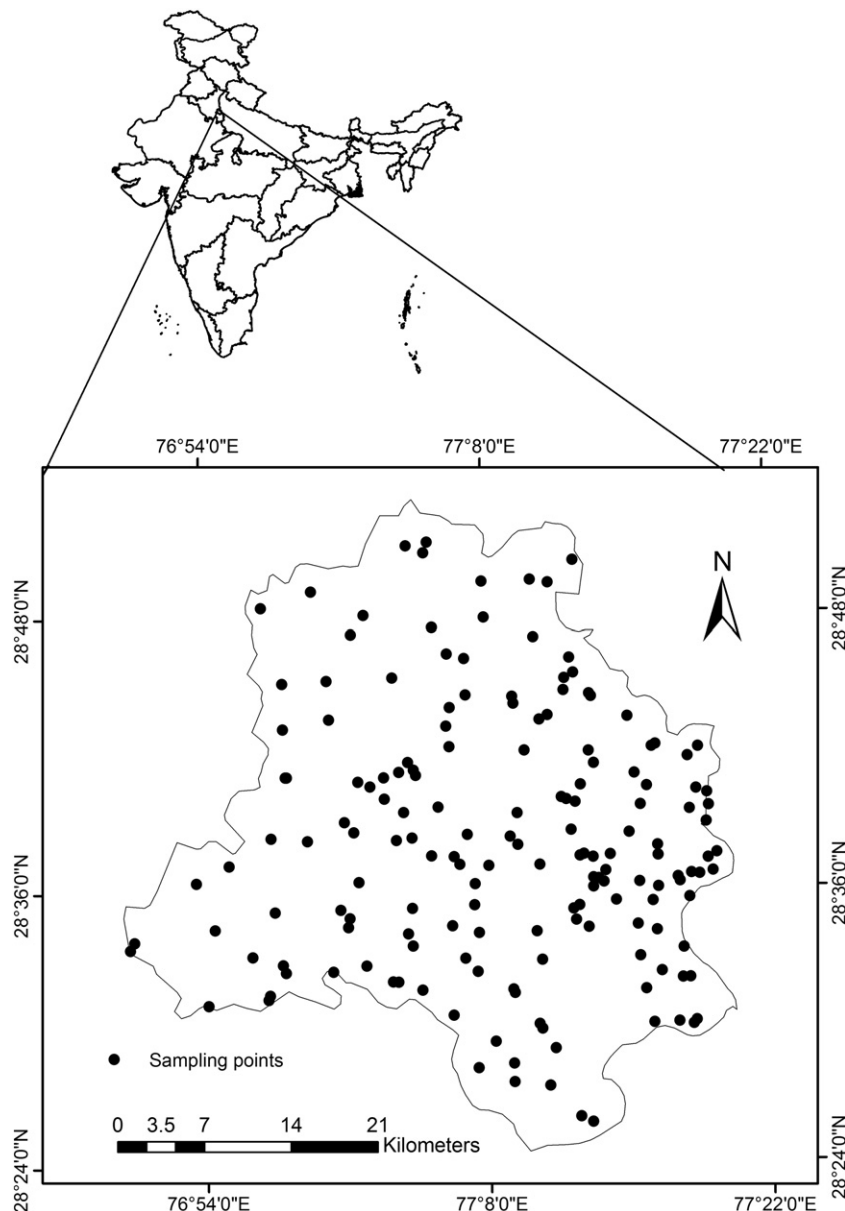


Fig. 1. Study area along with sampling locations.

alluvium, newer alluvium, channel alluvium, aeolian surface and quartzite with inter bedded schist (Mallick et al., 2015).

Newer alluviums are mostly sand mixed with silt clay and gravel and it is distributed in ridge region, floodplain of Yamuna and Chattarpur closed basin. The aquifer systems are mostly semi-confined (Datta et al., 1996). Absence of permanent vegetation makes a clear distinction between new and older alluvium. The older alluviums are consists of clay mixed with silt and Kankar's ( $\text{CaCO}_3$ ) which are calcareous in nature. The active floodplain near the Yamuna River is important for groundwater prospective as they are comparatively coarser i.e.; sand, pebbles and gravels and thus has high groundwater recharge potential. The bedrock is represented by the Delhi Ridge is precambian metamorphic rock composed of quartzite and mica schist belonging to Delhi super group of Lower Proterozoic age which consist Alwar group. Alluvial floodplain and quartzite hard rocks are the major hydrogeological features in the study area. The occurrence of groundwater is controlled by the four major physiographic unit's (Adriano, 1986) NNE-SSW trending quartzitic ridge (Alya et al., 2014) Alluvial plain on the eastern

and western part of the ridge (APHA (American Public Health Association), 1995) Yamuna flood plain deposits (Appelo and Postma, 1993) Isolated and nearly closed Chattarpur alluvial basin as shown in Fig. 2 (CGWB, 2003; Mallick et al., 2015).

Presence of groundwater is reported in all the geological formations in the study area (Sarkar et al. 2016). The western part which is adjoining to Delhi ridge is characterized by marginal alluvium where 0 to 30 m thick layer of alluvium overlain on weathered and fractured quartzite rocks are present. The alluvium consists of clay, silt and fine to medium sand. A substantial amount of Kankar ( $\text{CaCO}_3$ ) is also mixed with the clayey-silt below 20 m depth. The top soil zone predominantly consists of silty-clay material followed by thin partings of clayey-silt, sandy-silt and clay layers alternatively. Sandy-silt strata behave as favourable aquifer zone in order to get a substantial discharge. The western part of Delhi ridge tube wells are tapping water from prevailing formations, both the alluvium as well as hard rock whereas in the eastern part tube wells tapping water from alluvium has a yield of 200 to 500 (lpm). The extreme eastern part of New Delhi district is bounded by River Yamuna

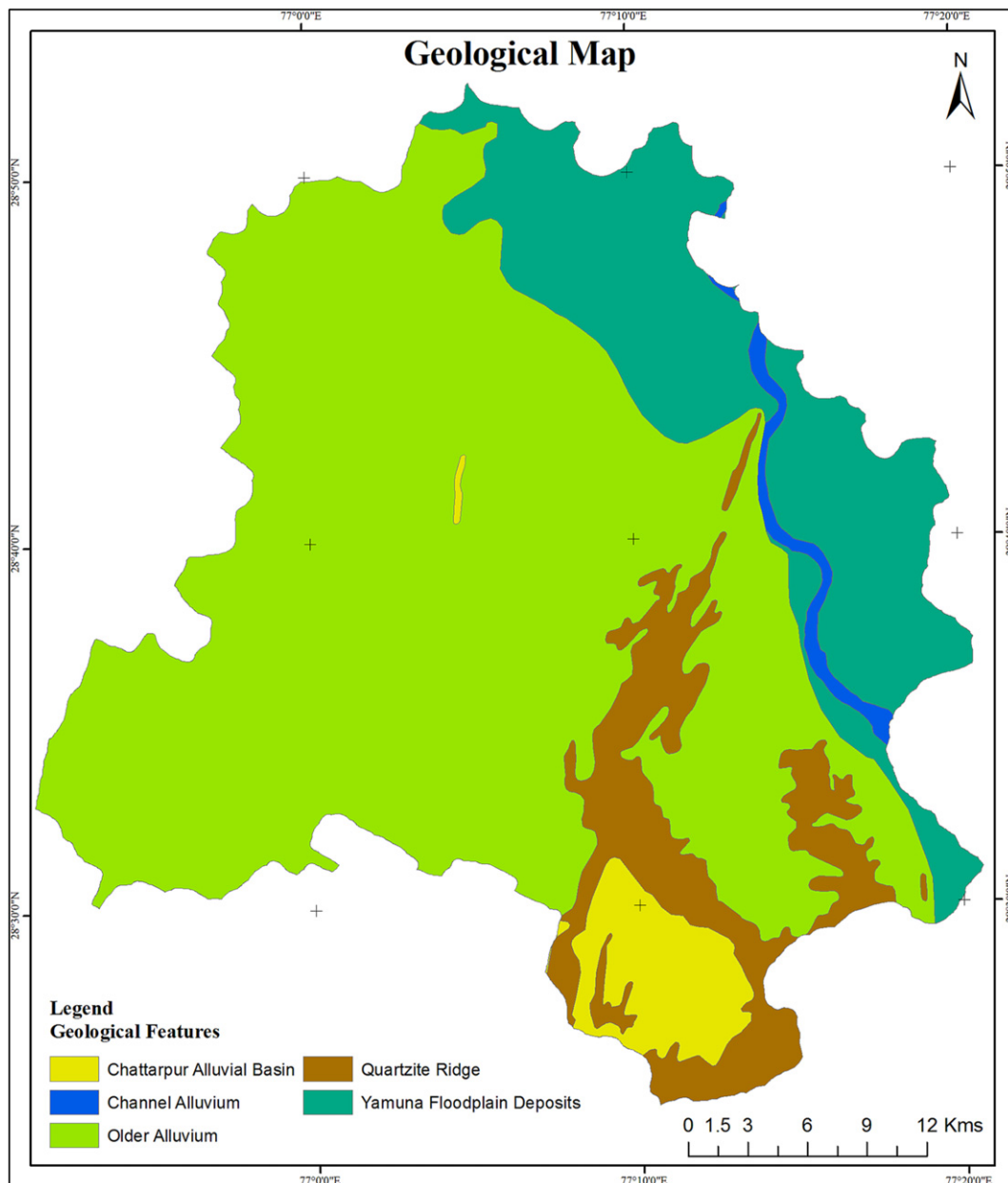


Fig. 2. Geology of the study area.

and represents a linear plain of Yamuna. Groundwater potential in this formation is relatively high i.e. ranging from 500 to 1600 lpm. The depth to water level ranges from 5 to 25 mbgl and the wide variation occurs due to wide range of topographic relief. These aquifer zones are generally encountered alternatively below the depth of 20 mbgl and onward up to the basement rock. On the NW part of the area beyond the depth of 50 m, silty–clay and clay (light yellow) beds with Kankars increases with depth. The semi-plastic and plastic clay beds are also common at deeper depth i.e. 80 to 250 mbgl. The granular zones (fine sand and silty–sand) at deeper depth are not as frequent as in the shallower depth. The Southern region shows mountainous undulating terrain exposed with Delhi quartzite. The district is also characterized by vast alluvium field in the central part of the district popularly known as Chattarpur Basin. The overburden is composed of unconsolidated clay, silt, sand and varying proportions of kankars. In the deep basin area, depth zone of 38 m to 55 m is characterized as prominent gravel zone mixed with silt and fine sand followed by clayey-silt and fine sand with occasional kankar nodules. Near to the depth zone of basement somewhat medium sand and angular gravel (ferruginous and gritty quartzites) are also encountered. At some places near to the basement rock, lenses of sticky yellowish clay is also encountered. The area across southern Delhi ridge is characterized with marginal alluvium deposits where depth of overburden ranges from 60 m to 94 m. Below this quartzitic basement rock occurs. The borehole constructed in quartzitic body reveals that moderately fractured zones are prevalent in the depth of 30 m to 90 m and the fractures gradually decreases as depth increases. The weathered zone is found at every place above hard rock but thickness of weathered zone varies spatially. The discharge of the aquifers in alluvial floodplain varies from 20 to 180 m<sup>3</sup>/h with the transmissivity 130–2000 m<sup>2</sup>/day while in quartzite hard rock aquifer the discharge varies from 2 to 10 m<sup>3</sup>/h with transmissivity 5–135 m<sup>2</sup>/day (CGWB, 2003).

Majority of the soil in the region is dominated by coarse loamy sand while fine loamy sand and clay are also significantly present (Mallick et al., 2015). 37.96% of the total area is built-up followed by agriculture and fallow land (32.61%) as is depicted by Land use and Land cover (LULC) map in Fig. 3. Central and southern part of the study area is mostly covered with dense built-up while agriculture and fallow land are most dominant in the northern and western part (Fig. 3). Sparse and dense vegetation contributes 9.2% and 6.2%. Delhi is situated at the Yamuna River bank and discharges from industries and municipal drains in river making it one of the most polluted rivers in India.

## 2.2. Samples collection and analysis

A random sampling plan was adopted to study the spatial distribution of groundwater quality parameters. A total of 170 groundwater samples uniformly spread over the study area were collected (Fig. 1). Samples were collected in almost all geological formations from handpumps in polypropylene plastic bottles after pumping 20–25 strokes to minimize the impacts of iron pipes and homogenize the sample, and location was geocoded using global positioning system (Garmin GPS).

The pH, total dissolved solid (TDS), and electrical conductivity (EC) of the water samples were measured onsite using portable pH, and EC electrodes (Oakton) and TDS meter (HANNA). The samples were acidified using nitric acid (50%) pH < 2 for cation analysis. The samples were stored in an icebox, carried to the laboratory and kept at 4 °C for further chemical analysis. Immediately after the water samples were transported to the laboratory, the major cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>) were analysed using an atomic absorption spectrometer (Thermo Fisher Scientific M series), and the major anions (F<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>) were analysed using an ion chromatograph (Dionex). Bicarbonate (HCO<sub>3</sub><sup>-</sup>) was determined by titrimetric method as described in APHA (1995). Normalized charged balance index,  $\{NCBI = (\sum T_{z-} - \sum T_{z+}) / (\sum T_{z-} + \sum T_{z+})\}$  where,  $\sum T_{z+}$  = total sum of cations (in epm)

and  $\sum T_{z-}$  = total sum of anions (in epm)} of the samples was calculated which ranged between +0.15 to -0.15.

## 2.3. Statistical and inverse geochemical modeling

### 2.3.1. Statistical modeling

Factor analysis is mostly used to identify the hidden dimension which may not be interpreted in direct analysis. Principal Component Analysis (PCA) is a method used to reduce the volume of large dataset with minimum loss of information. PCA was performed using Varimax rotation with Kaiser Normalization using XL-stat extension of Microsoft Excel. Bartlett's sphericity test of normalized data has been carried out which shows  $\chi^2$  (cal) = 2204.2 is greater than the  $\chi^2$  (crit) = 85.9 (at degree of freedom 66, significant level 0.05 and *p* value < 0.0001) these values indicates that PCA can successfully be used for dimension reduction. All variables were auto scaled using mean value to 0 and variance to 1 respectively. Principal components (PCs) with eigen values > 1 were only taken into consideration for interpretation of the dataset. Hierarchical cluster analysis (HCA) is used to group statistically distinct hydrochemical variables. It is an unsupervised pattern detection method in which clusters/groups of variables are formed on the basis of their similarities. Q-mode cluster analysis has been performed to find out the spatial association between the sampling locations based on their chemical characteristics. Wards linkage method with Euclidean distance was used for measurement of similarity between the water quality variables. The clusters (groups) obtained from the HCA was used to understand hydro-geochemical process occurring in the region.

### 2.3.2. Inverse geochemical modeling

Inverse geochemical modeling has been widely used to determine the geochemical process responsible for the evolution of groundwater (Belkhir et al., 2011, Singh and Mukherjee, 2015). It is a mass balance simulation which indicates the chemical reactions and change in chemical characteristics i.e.; dissolution/precipitation of minerals and gases in groundwater flowpath. The values of Saturation Indices (SI) indicate the tendency of minerals to dissolve or precipitate in groundwater aquifer system. The accuracy of the inverse modeling depends on the understanding and conceptualization of aquifer system based on assumptions. It has been assumed that the initial and final groundwater sampling points represents the same flowpath and the hydrochemistry of groundwater is not influenced by the diffusion and mineral phase taken into consideration as these are present in the aquifers under chemically steady state.

Results of saturation indices is useful to understand the different stages of hydro-geochemical evolution and it also helps in identifying geochemical process responsible for chemical characteristics of groundwater. Geochemical modeling was performed using Phreeqc version 3 and SI has been calculated using following equation:

$$SI = \log \left( \frac{IAP}{K_t} \right) \quad (1)$$

where, IAP is the ion activity product of the dissociated chemical species in solution and  $K_t$  = equilibrium solubility product of the mineral. The negative value of the SI for any mineral phase indicates that the water is undersaturated with respect to that mineral and therefore would dissolve until the equilibrium is reached whereas the positive value indicates oversaturation and the mineral will have tendency to precipitate.

### 2.3.3. Geospatial database

The geological map was collected from Geological Survey of India which was scanned, geocoded and then digitized using Arc GIS 10.1. Landsat 7ETM+ satellite dataset was used to generate LULC of the region. Supervised classification with maximum likelihood algorithm was used as classifier and the area was classified into 7 major classes (Fig. 2). Spatial distribution of water quality parameters was generated



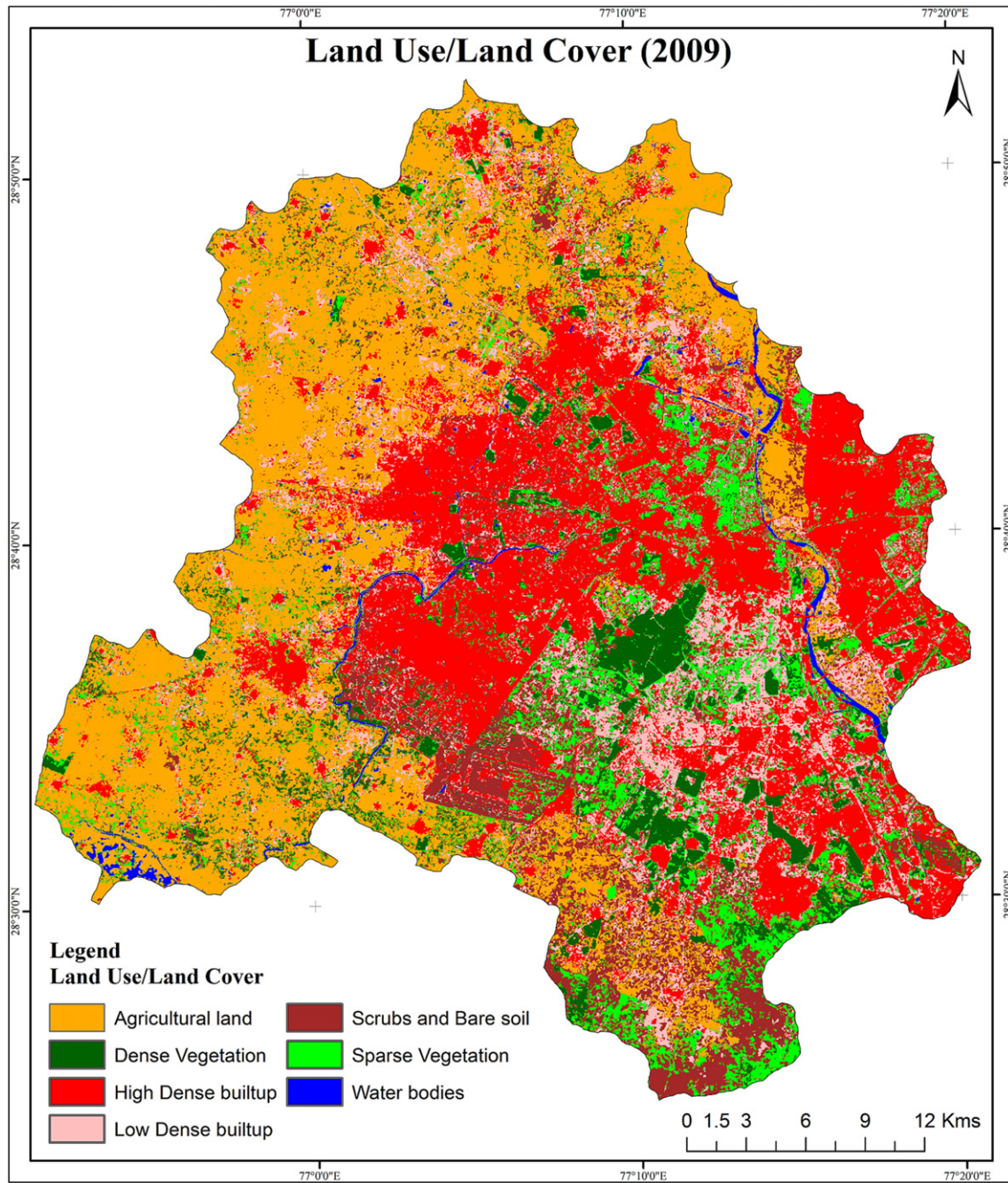


Fig. 3. LULC map of study area.

**Table 1**  
Descriptive statistics and comparison with WHO (2009) and BIS (1995) norms.

Variable	Detection Limit	Minimum	Maximum	Mean	Median	Std. deviation	WHO (2009)	BIS (1995)	Samples above WHO limits (%)
pH	>0.1	7	8.5	7.7	7.66	0.3	6.5–8	6.5–9.5	14.7%
EC	>1.0	460	8980	1969.2	1378	1466.6	1500	–	44.7%
TDS	>1.0	0.01	5875	1310.4	922.5	1039.1	1000	500	44.4%
HCO <sub>3</sub> <sup>-</sup> (mg/l)	–	93	2021	479.9	437	217.5	300	600	87.6%
Cl <sup>-</sup> (mg/l)	0.1	9.9	2610	339.8	150.5	465.5	250	1000	35.2%
SO <sub>4</sub> <sup>2+</sup> (mg/l)	0.1	BDL	1220	190.5	125.5	212.9	250	400	23%
NO <sub>3</sub> <sup>-</sup> (mg/l)	0.03	BDL	600	51	22.5	79.2	50	45	29.4%
F <sup>-</sup> (mg/l)	0.01	BDL	12.5	1.5	0.825	1.9	1.5	1.5	27%
Ca <sup>2+</sup> (mg/l)	0.04	1.8	907	104.2	84	94	200	200	6.4%
Mg <sup>2+</sup> (mg/l)	0.01	3.4	512	62.4	42	63.7	150	100	7%
Na <sup>+</sup> (mg/l)	0.04	BDL	1525	262.9	181	272.9	200	–	40%
K <sup>+</sup> (mg/l)	0.02	BDL	180	14.7	5.75	27.8	30	–	10.5%

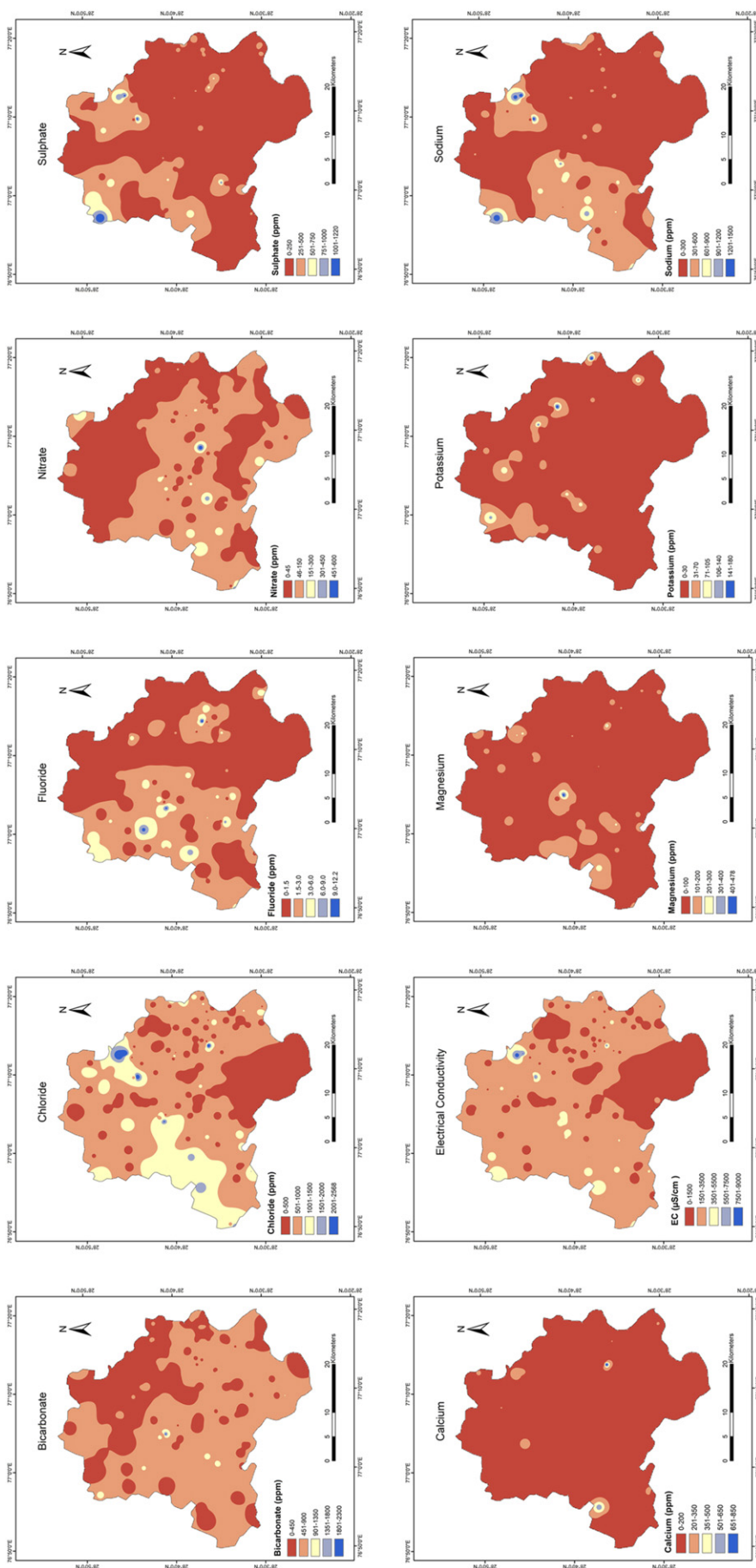
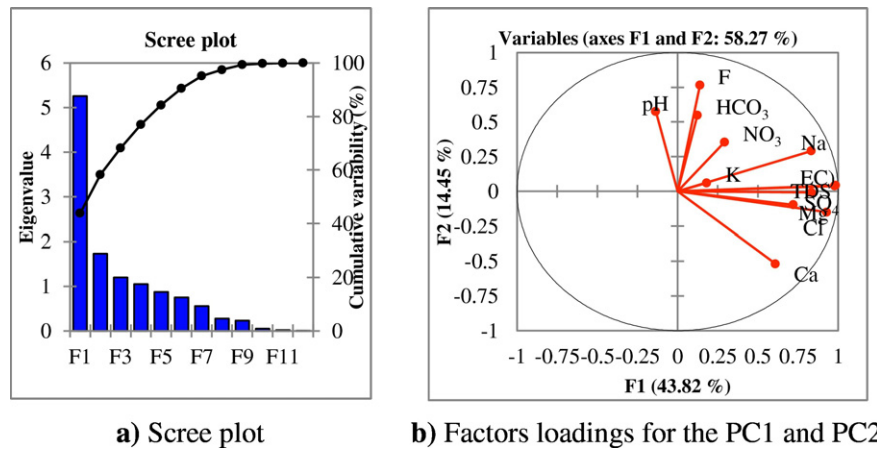


Fig. 4. Spatial distribution of water quality parameters.

**Table 2**  
Correlation matrix of physio-chemical parameters.

Variables	pH	EC	TDS	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>
pH												
EC	-0.075											
TDS	-0.079	<b>0.978</b>										
HCO <sub>3</sub> <sup>-</sup>	0.091	0.149	0.144									
Cl <sup>-</sup>	-0.080	<b>0.913</b>	<b>0.914</b>	-0.121								
SO <sub>4</sub> <sup>2-</sup>	-0.209	<b>0.791</b>	<b>0.819</b>	0.006	<b>0.696</b>							
NO <sub>3</sub> <sup>-</sup>	-0.054	0.270	0.264	0.240	0.162	0.097						
F <sup>-</sup>	0.323	0.139	0.151	0.208	0.043	0.178	0.178					
Ca <sup>2+</sup>	-0.260	<b>0.558</b>	<b>0.555</b>	-0.129	<b>0.637</b>	0.414	0.075	-0.183				
Mg <sup>2+</sup>	-0.058	<b>0.712</b>	<b>0.707</b>	0.315	<b>0.638</b>	0.439	0.196	-0.085	<b>0.534</b>		0.348	
Na <sup>+</sup>	-0.003	<b>0.824</b>	<b>0.837</b>	0.124	<b>0.794</b>	<b>0.776</b>	0.272	0.308	0.191	0.348		
K <sup>+</sup>	-0.064	0.176	0.164	0.037	0.106	0.180	0.093	0.032	0.033	0.060	0.102	



**Fig. 5.** a Scree plot b Factors loadings for the PC1 and PC2.

using the point data IDW algorithm was used to generate the surface for water quality variables using spatial analyst module of Arc GIS 10.1.

### 3. Results

#### 3.1. Distribution of major ions

Hydro-geochemistry is influenced by the rock-water interaction along with another chemical processes occurring in the region. The analysed water quality parameters with their basic statistics and prescribed limits of WHO (World Health Organization, 2009) and BIS (Bureau of Indian Standard, 1995) are summarized in Table 1. pH value ranges between 7.0 and 8.5 (mean value of 7.77) indicating neutral to alkaline nature of groundwater. High pH value suggests interaction between soil and rain water, thus imparting alkaline characteristics to the groundwater (Subramanian and Saxena, 1983). Large variation in EC was observed which ranges between 460 and 8980  $\mu\text{S}/\text{cm}$  with the mean value of 1969.2  $\mu\text{S}/\text{cm}$ . Results suggests that only 1 sample out of 170 has EC < 500  $\mu\text{S}/\text{cm}$  (fresh water) while around 54.7% (93 out of 170) of water samples are under marginal water (500–1500  $\mu\text{S}/\text{cm}$ ), 40% (68 out of 170) of samples have EC value between 1500 and 5000  $\mu\text{S}/\text{cm}$  and rest 4.7% of the sample have EC value > 5000  $\mu\text{S}/\text{cm}$  (Davis and Dewiest, 1967). Study area has semi-arid climate and thus high evaporation contributing to increase in salt concentration in groundwater. High EC (> 1500  $\mu\text{S}/\text{cm}$ ) is observed all over the study area other than southern part where it is < 1500  $\mu\text{S}/\text{cm}$ . Wide variation in groundwater parameters indicates that groundwater characteristics are influenced by the anthropogenic activities along with climatic factors and geogenic factors such as rock-water interaction. Na<sup>+</sup> is found as the most dominant cation followed by the Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> respectively. Concentration of

Na<sup>+</sup> varies from below detection limit (bdl) to 1525 mg/L with an average value of 262.9 mg/L. Na<sup>+</sup> is conservative in nature and it binds with clay minerals due to ion exchange (Subramanian and Saxena, 1983). High concentration of Na<sup>+</sup> is found in NE and western part of the region (Fig. 4). Concentration of Ca<sup>2+</sup> varies from 1.82 mg/L to 907 mg/L with the average value of 104.2 mg/L while the concentration of Mg<sup>2+</sup> and K<sup>+</sup> varies from 3.4 mg/L to 512 mg/L and bdl to 180 mg/L respectively. Ca<sup>2+</sup> and Mg<sup>2+</sup> along with HCO<sub>3</sub><sup>-</sup> determine the hardness of the groundwater. At soil zone precipitation of Ca<sup>2+</sup> and Mg<sup>2+</sup> occurs due to temporary hardness and these precipitated salts might get leached from the soil zone with rainwater or irrigation water and contributes high concentration of these ions in groundwater. Distribution of Ca<sup>2+</sup> is homogenous and it is found below WHO limits of 200 mg/L except

**Table 3**  
Factor loading plots for different principle components.

Water quality variables	PC 1	PC 2	PC 3	PC 4
pH	-0.068	<b>0.666</b>	0.034	-0.403
EC	<b>0.959</b>	-0.02	0.204	0.056
TDS	<b>0.967</b>	-0.008	0.191	0.057
HCO <sub>3</sub> <sup>-</sup>	-0.027	0.151	<b>0.865</b>	-0.078
Cl <sup>-</sup>	<b>0.958</b>	-0.093	-0.047	-0.018
SO <sub>4</sub> <sup>2-</sup>	<b>0.849</b>	0.049	-0.053	0.241
NO <sub>3</sub> <sup>-</sup>	0.157	0.051	<b>0.62</b>	0.273
F <sup>-</sup>	0.154	<b>0.798</b>	0.145	0.102
Ca <sup>2+</sup>	<b>0.611</b>	-0.54	-0.022	-0.149
Mg <sup>2+</sup>	<b>0.652</b>	-0.317	<b>0.467</b>	-0.247
Na <sup>+</sup>	<b>0.843</b>	0.326	0.072	0.182
K <sup>+</sup>	0.093	-0.036	0.093	<b>0.807</b>
Eigen value	<b>5.258</b>	<b>1.734</b>	<b>1.196</b>	<b>1.050</b>
% of variance explained	<b>43.818</b>	<b>14.448</b>	<b>9.968</b>	<b>8.753</b>
Cumulative %	<b>43.818</b>	<b>58.265</b>	<b>68.234</b>	<b>76.987</b>



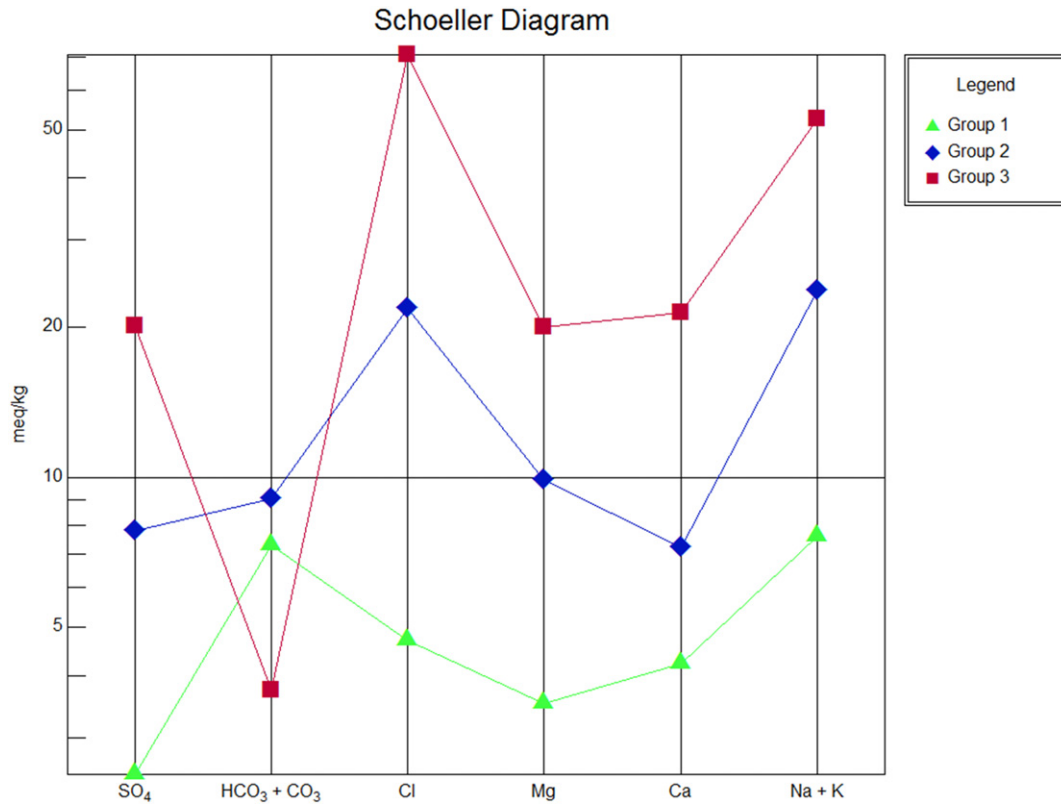


Fig. 6. Schoeller Plot for the three clusters obtained as a result of HCA.

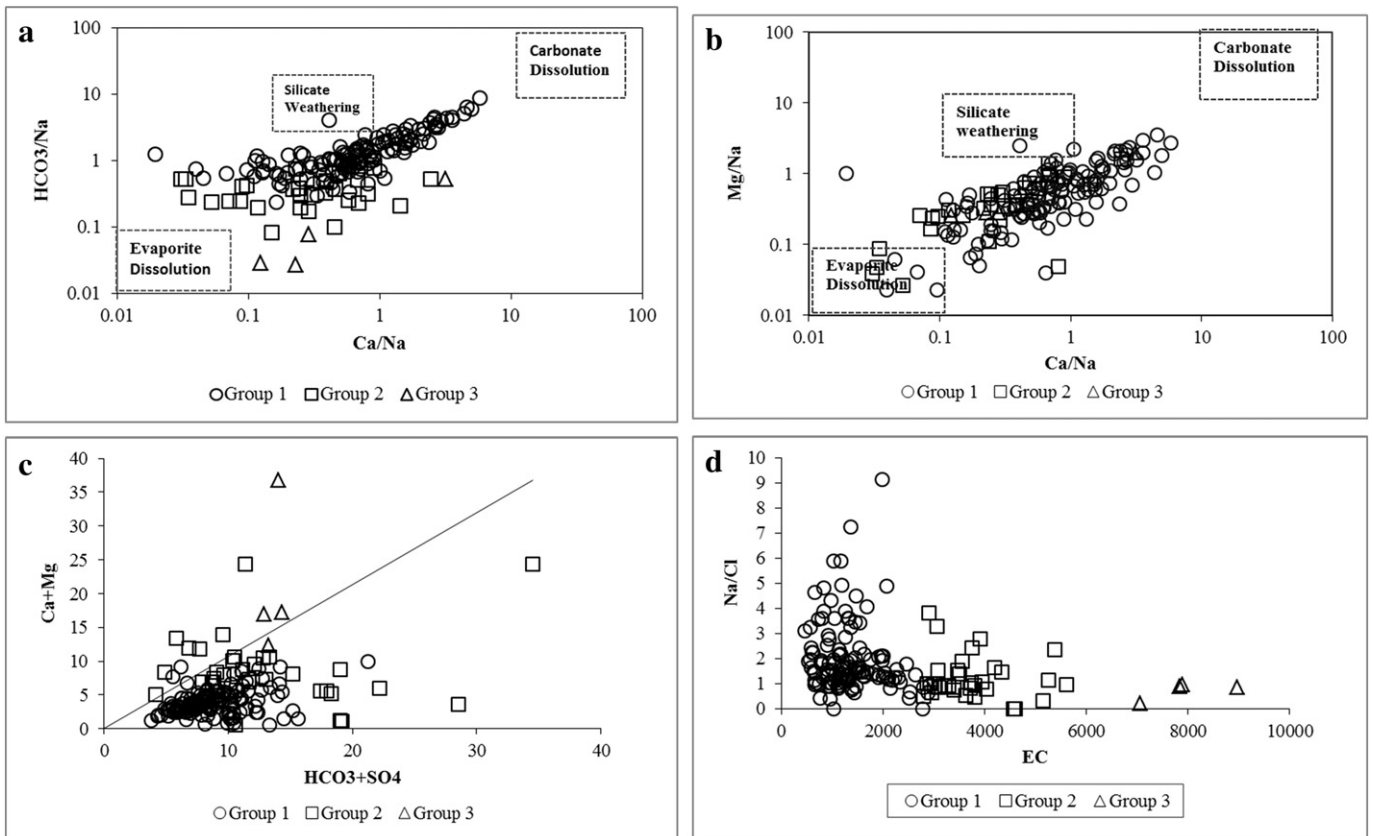


Fig. 7. a Na<sup>+</sup> normalized Ca<sup>2+</sup> vs HCO<sub>3</sub><sup>-</sup> scatter plot b Na<sup>+</sup> normalized Ca<sup>2+</sup> vs Mg<sup>2+</sup> scatter plot c Ca<sup>2+</sup> + Mg<sup>2+</sup> vs SO<sub>4</sub><sup>2-</sup> + HCO<sub>3</sub><sup>-</sup> scatter plot d Na<sup>+</sup>/Cl<sup>-</sup> vs EC scatter plot e Scatter plot between Na<sup>+</sup> vs Cl<sup>-</sup> f Scatter plot between Na<sup>+</sup> + K<sup>+</sup> vs Cl<sup>-</sup> g Scatter plot between Ca<sup>2+</sup> + Mg<sup>2+</sup> vs Cl<sup>-</sup>.



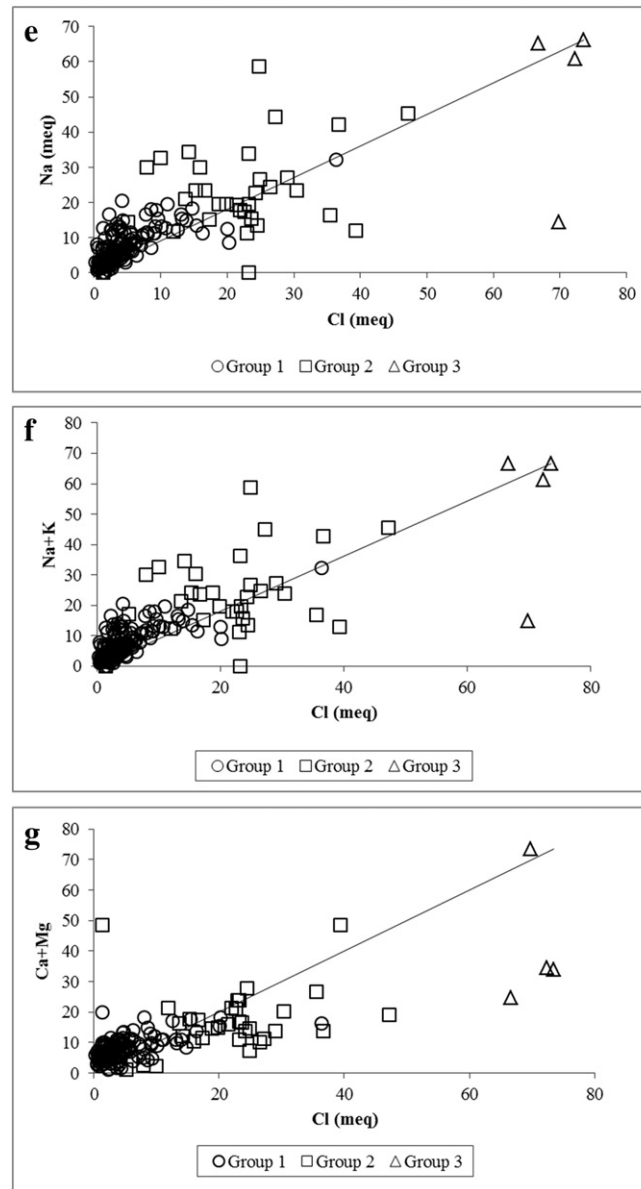


Fig. 7 (continued).

few spatially spread patches. The highest concentration of  $\text{Ca}^{2+}$  is observed at SW and southern part where agriculture and dense vegetation are dominant. Highest concentration of  $\text{Mg}^{2+}$  is found in the central parts while high concentration of  $\text{K}^{+}$  is found at NW part along the River Yamuna. High  $\text{HCO}_3^-$  is found in the NW and southern part while the highest concentration is observed in central part along with the Najafgarh drain.

Table 1 depicts that standard deviation of some of the parameters are higher than the mean value indicating that the geochemistry of study area is not homogenous.

Among anions  $\text{HCO}_3^-$  is the most dominant anion followed by  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Concentration of  $\text{HCO}_3^-$  varies from 93 mg/L to 2023 mg/L with an average value of 479 mg/L, while  $\text{Cl}^-$  varies from 9.9 mg/L to 2610 mg/L with an average of 339.8 mg/L. High  $\text{Cl}^-$  concentration might be due to high evaporation rate in the region (Singh et al., 2013a). High  $\text{HCO}_3^-$  concentration indicates presence of carbonate containing minerals. Weathering of silicate and carbonate minerals along with degradation of organic matter might contribute high concentration

of  $\text{HCO}_3^-$  ions in groundwater (Rina et al., 2012). High concentration of  $\text{Cl}^-$  is found in NE region where the agriculture is prominent. High concentration of  $\text{NO}_3^-$  is found in western and central parts while  $\text{SO}_4^{2-}$  is found to be high in the NW parts of study area.

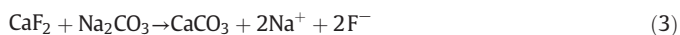
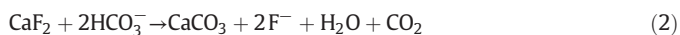
Fluoride concentration varies from bdl–12.5 mg/L with an average of 1.5 mg/L. Concentration of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  varies from bdl to 1220 mg/L and bdl to 600 mg/L with an average value of 190.5 mg/L and 51 mg/L respectively. 23% of the samples are found to have high  $\text{SO}_4^{2-}$  concentration, while 29.7% have high  $\text{NO}_3^-$  concentration above WHO limits for drinking water. Dissolution of gypsum and anhydrite might contribute  $\text{SO}_4^{2-}$  in groundwater while fertilizers and leaching of municipal waste or agricultural runoff might contribute high concentration of  $\text{NO}_3^-$  in groundwater.

### 3.1.1. Contaminants of public health concern:

3.1.1.1. Nitrate. 29% of the groundwater samples show high concentration of  $\text{NO}_3^-$  against the WHO standards of 45 mg/L.  $\text{NO}_3^-$  in

groundwater is mostly associated with anthropogenic activities along with some natural processes (Walvoord et al., 2003). High concentration and wide variation in  $\text{NO}_3^-$  concentration indicates both point and non-point source of contamination. The spatial distribution of  $\text{NO}_3^-$  indicates that highest concentration is found in central Delhi (Fig. 4). This area has dense built-up and septic tank leakages might be a potential source of  $\text{NO}_3^-$  in groundwater. High concentration of  $\text{NO}_3^-$  in some pockets in east and SW parts indicate the impacts of agricultural activities. Najafgarh drain, a major drain that carries enormous amount of pollutant load runs through SW part of Delhi, the seepages from the drain might also contribute an increase  $\text{NO}_3^-$  concentration. Along with septic tanks and fertilizer use,  $\text{NO}_3^-$  can be contributed by animal waste, crop residues, sewage and food processing units (Williams, 1998; Liu et al., 2005; Avtar et al., 2013; Elisante and Muzuka, 2015).

**3.1.1.2. Fluoride.** A daily intake of 0.5 mg of  $\text{F}^-$  is essential for formation of bones and enamel of teeth's but when the concentration increases above 1.5 mg/L (WHO standards) it affects adversely. Out of total 170 samples 27% of samples have high  $\text{F}^-$  compared to WHO guideline and thus is unfit for drinking and domestic use. In arid and semi-arid region evaporation due to high temperature play an important role in distribution of  $\text{F}^-$  (Farooqi et al., 2007). Lower pH prevents dissolution of fluorite mineral (Adriano, 1986). Spatial variation of  $\text{F}^-$  suggests high concentrations in Western part of the study area (Fig.4). In alkaline environment hydroxyl ions ( $\text{OH}^-$ ) replaces  $\text{F}^-$  ions from fluorite minerals and high TDS enhances the ionic strength of water which increases the solubility of fluorite (Singh et al., 2011b; Xing et al., 2013). Ions and minerals present in groundwater and aquifer system along with high pH influences the dissolution of fluorite. Dissolution of fluorite takes place as



Along with high pH high  $\text{Na}^+$  and  $\text{HCO}_3^-$  is found making it favourable for dissolution of fluorite (Singh et al., 2012, 2013b).

### 3.2. Chemometric analysis

Correlations among water quality variables give insight of major hydro-geochemical process which controls its chemicals characteristics. The value of  $R > 0.7$  indicates strong correlation, while  $R$  value 0.5–0.7 indicates moderate correlation between the parameters. EC is also strongly correlated with  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  ions and moderately correlated with  $\text{Ca}^{2+}$ . Correlation indicates that EC of groundwater is mostly controlled by these ions.  $\text{Na}^+$ - $\text{SO}_4^{2-}$  are strongly correlated while  $\text{SO}_4^{2-}$ - $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ - $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ - $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$  are moderately correlated. Strong and positive correlation between  $\text{Na}^+$ - $\text{Cl}^-$  indicates similar source of these ions. Fluoride is not much significant but positively correlated with pH (Table 2).

The concentration of these ions might be high due to dissolution of evaporitic minerals (Singh and Mukherjee, 2015). Ionic strength of water increases because of dissolution of evaporite minerals and favours the dissolution of sulphate salts which increases the concentration of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in groundwater (Alaya et al., 2014).

PCA results show (Fig. 5a) shows that four principle components (PCs) have eigen values  $> 1$  and it explains around 77% of total variance of the data. PC1 explains 43.83% of total variance whereas; PC2, PC3 and PC4 explain 14.44%, 9.96% and 8.75% of total variance respectively (Table 3). The component loading of  $> 0.6$  has been use for further interpretation (Singh et al., 2011b). There is significant loading of EC, TDS,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  in PC1 (Table 3). High loading of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  indicates dissolution of evaporitic minerals. High loading of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  is due to soil water interaction and dissolution of Na-bearing minerals (Yakubo et al., 2009). Significant loading of  $\text{Na}^+$  and  $\text{Cl}^-$  together in PC1 also indicates similar source of these ions.  $\text{F}^-$

solubility from fluoride bearing minerals is high in alkaline environment as exchange of ions takes place between  $\text{OH}^-$  ions and  $\text{F}^-$  which increases the concentration of  $\text{F}^-$  in water. PC2, high loading of pH and F indicates the dissolution of fluorite ( $\text{CaF}_2$ ) at high pH value (Singh et al., 2011b) which establishes the fact that alkaline pH favours high  $\text{F}^-$  in groundwater as indicated in previous section. Negative loading of  $\text{Ca}^{2+}$  in PC2 indicates that the dissolution  $\text{F}^-$  is limited through the solubility of the  $\text{CaF}_2$  (Appelo and Postma, 1993; Guo et al., 2012). It is apparent that the high concentration of  $\text{F}^-$  is more likely in low  $\text{Ca}^{2+}$  containing groundwater.  $\text{Na}^+$  although not significant but shows positive loading in PC2 indicating that there might be exchange of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  on the surface of clay which might be responsible for low concentration of dissolved  $\text{Ca}^{2+}$  and high concentration of  $\text{F}^-$  in groundwater (Table 3).  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  are found to be high in PC3. High concentration of  $\text{NO}_3^-$  might be associated with the anthropogenic input, as fertilizers used in agriculture, crop residues and seepage from septic tanks which might contributes to  $\text{NO}_3^-$  enrichment (Williams, 1998, Kumari et al., 2013a), which is also evident from spatial distribution of  $\text{NO}_3^-$  which is found to be high in agriculture occupied regions. High loading of  $\text{K}^+$  alone in PC4 indicates the impact of agricultural activities as potassium is mostly used as fertilizers in agriculture. The factor loading plot between PC1 and PC2 is presented in Fig. 5b.

Q-mode hierarchical cluster analysis (HCA) of the hydro-chemical data indicates three major associations between 12 water quality variables. The 3 groups obtained as a result of HCA has been used for further investigation of processes responsible for water quality, where in general the samples have been clustered on the basis of concentration of major ions which contributes to overall EC of the samples. Group 1 comprises 133 samples, while Group 2 has 33 samples and Group 3 comprises of 4 samples. The uniqueness of these three Group is that the average concentrations of physico-chemical parameters of all three clusters in general follow an increasing trend as Group 1 < Group 2 < Group 3. Average of chemical parameter has been represented by Schoeller diagram (Fig. 6).  $\text{Na-HCO}_3$  seems as the most dominant water type in Group 1, while in Group 2 and 3  $\text{Na-Cl}$  is found as the dominant water type. EC depends on the concentration of dissolved ions it has been found that the average value of EC varies in order of Group 1 < Group 2 < Group 3. Group 1 average EC is 1344  $\mu\text{S/cm}$  while it increases in Group 2 to 3763  $\mu\text{S/cm}$  and in Group 3 to 7950  $\mu\text{S/cm}$ . These Groups have been further used to understand the hydro-geo-chemical process influencing the water quality in the study area.

## 4. Hydrogeochemical process

### 4.1. Weathering and dissolution

Plot between  $\text{Ca}^{2+}/\text{Na}^+$  and  $\text{HCO}_3^-/\text{Na}^+$  i.e.  $\text{Na}^+$  normalized  $\text{Ca}^{2+}$  vs  $\text{HCO}_3^-$  graph is used to identify the influence of silicate weathering, evaporate dissolution or carbonate weathering on groundwater chemistry. Fig. 7a indicates that chemical characteristics of most of water samples from Group 1 are influenced by silicate weathering to carbonate dissolution. In Group 2 and 3, samples are influenced by evaporate dissolution to silicate weathering. In Fig. 7b  $\text{Na}^+$  normalized  $\text{Ca}^{2+}$  vs  $\text{Mg}^{2+}$

**Table 4**  
Detailed water type and number of samples.

Group 1		Group 2		Group 3	
Water type	No of samples	Water type	No of samples	Water type	No of samples
Ca-HCO <sub>3</sub>	39	Ca-Mg-HCO <sub>3</sub>	2	Na-Cl	3
Ca-Cl	2	K-SO <sub>4</sub>	1	Ca-Cl	1
Mg-HCO <sub>3</sub>	13	Mg-Cl	2		
Mg-Cl	2	Mg-HCO <sub>3</sub>	1		
Na-Cl	18	Na-Cl	20		
Na-HCO <sub>3</sub>	58	Na-SO <sub>4</sub>	3		
Na-SO <sub>4</sub>	1	Na-HCO <sub>3</sub>	4		

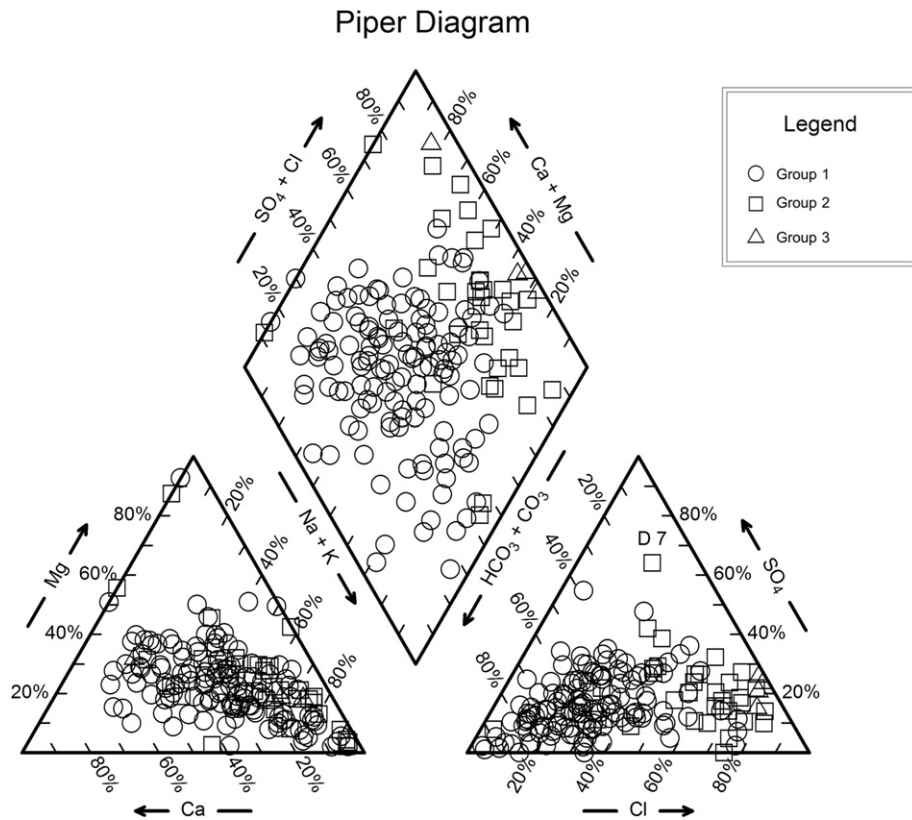


Fig. 8. Piper diagram.

graph indicates that most of the  $Mg^{2+}$  in Group 1 is derived from carbonate dissolution. In Group 2 and 3 it is weathering of silicate minerals which might contribute  $Mg^{2+}$  in groundwater. The study of  $Ca^{2+}/Mg^{2+}$  ratio of groundwater indicates about the dissolution of calcite and dolomite. The value of  $Ca/Mg$  below 1 indicates dissolution of dolomite while the value  $>1$  indicates dissolution of calcite as the major controlling factor. The  $Ca^{2+}/Mg^{2+}$  ratio indicates that in most of the samples in Group 1, dissolution of calcite is the dominant process. Out of 133 samples in Group 1, 93 sample have  $Ca^{2+}/Mg^{2+}$  value  $>1$ . In Group 2 and 3 dissolution of dolomite seems as the dominant process as out of 33 samples, 24 samples have  $Ca^{2+}/Mg^{2+}$  value  $>1$  and 2 out of 4 sample in Group 3 have  $Ca^{2+}/Mg^{2+}$  value  $>1$ .

The scattered plot between  $Ca^{2+} + Mg^{2+}$  and  $SO_4^{2-} + HCO_3^-$  identifies the ion-exchange process. The samples close to equiline (1:1 line) indicates the dissolution of dolomite, calcite or gypsum as the dominant process in the aquifer (Fig. 7c). Reverse ion-exchange tends to shift the points left to equiline due to excess of  $Ca^{2+} + Mg^{2+}$  while if ion-exchange is the major process it will shift the points away from the equiline i.e. towards right (Singh et al., 2013a). The scatter plot between  $Ca^{2+} + Mg^{2+}$  and  $SO_4^{2-} + HCO_3^-$  for groundwater samples shows that most of the samples in Groups 1 and 2 have high values of  $SO_4^{2-} + HCO_3^-$ . High concentration of  $SO_4^{2-} + HCO_3^-$  indicates that ion-exchange and silicate weathering is the most dominant process at these sampling locations, whereas in Group 3, three out of four samples have excess value of  $Ca^{2+} + Mg^{2+}$ , which indicates that at these locations reverse ion-exchange is the dominant process and is influenced by carbonate weathering (Kumari et al., 2013b). When atmospheric  $CO_2$  interacts with water it forms carbonic acid ( $H_2CO_3$ ). Presence of  $H_2CO_3$  in groundwater enhances the dissolution of minerals in groundwater.

#### 4.2. Evaporation

Climatic factor such as evaporation may contribute high concentration of all form of ions in groundwater.  $Na^+/Cl^-$  vs EC plot is the

effective indicator of evaporation (Fig. 7d). In case of halite dissolution  $Na^+/Cl^-$  ratio is approximately 1, greater values of  $Na^+/Cl^-$  indicates release of  $Na^+$  due to silicate weathering. In present study the ratio of  $Na^+/Cl^-$  varies from 0.00 to 9.13. Some of the samples in Group 1 have high value of  $Na^+/Cl^-$  which indicates silicate weathering. 57.5% of samples in Group 2 and all 4 samples in Group 3 have  $Na^+/Cl^-$  values around 1 which indicates evaporation as dominant process at these locations (Fig. 7e).

Scattered plot ( $Na^+ + K^+$ ) vs Cl indicates that most of the samples in Group 1 and 2 are above 1:1 line (Fig. 7f). It suggests that excess of cations due to silicate weathering or may be due to presence of saline soils. The plot indicates that there is abundant presence of alkali in this region which might take part in formation of alkali carbonates or sulphates. Interestingly high concentration of  $Na^+$  is observed over  $K^+$  which might be because of resistance of potassium to chemical weathering. It also suggests that beside halite dissolution and ion-exchange,  $Na^+$  is also being contributed by anthropogenic activities.

#### 4.3. Ion exchange

The  $Na^+$  vs  $Cl^-$  graph indicates that most of the samples in Group 1 lie slightly above 1:1 line. It indicates that silicate weathering is the dominant process and also the reason behind the excess of  $Na^+$  in groundwater. Points below equiline indicate evaporation dominance and thus increase in  $Cl^-$  concentration.  $Ca^{2+} + Mg^{2+}$  vs  $Cl^-$  plot indicates that most of the samples in Group 1 lies above the equiline indicating dominance of ion-exchange (Fig. 7g).

### 5. Geochemical modeling

#### 5.1. Hydrochemical facies

Hydro-chemical facies reflect the overall chemical characteristics of aquifer system. Facies indicates the effects of interaction between

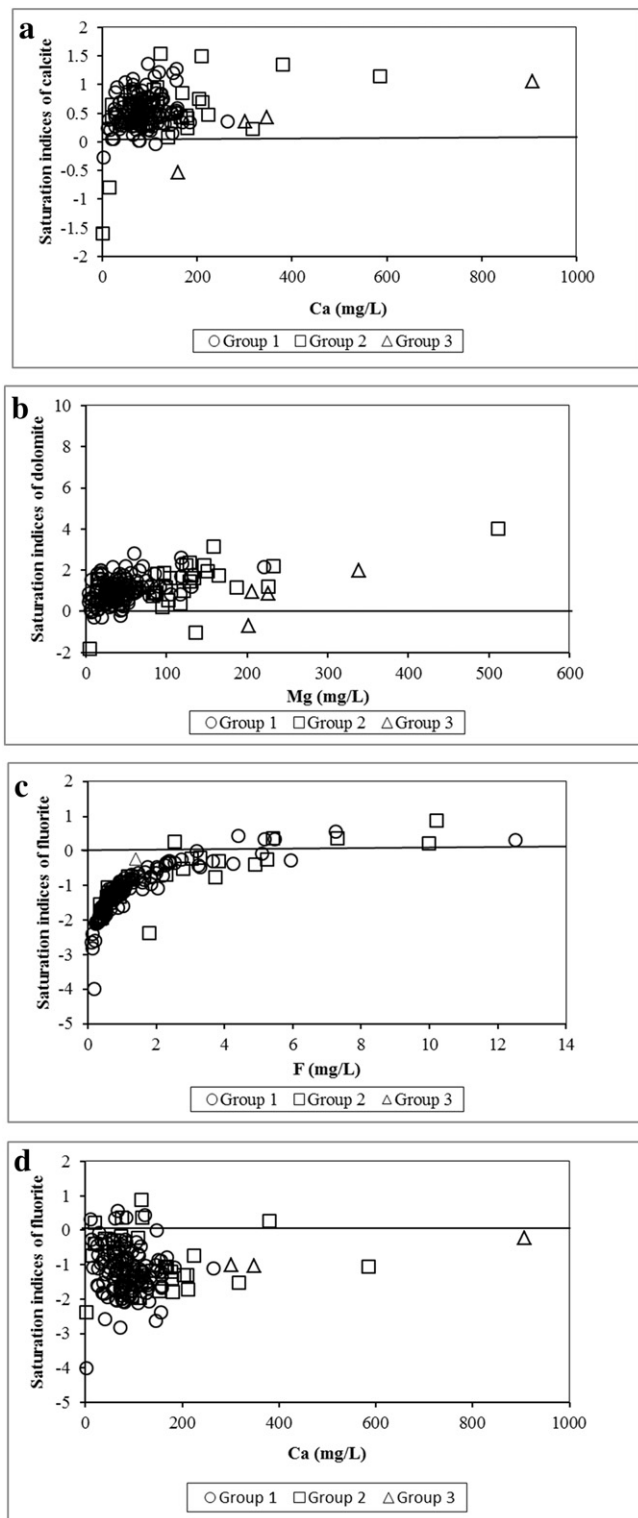


Fig. 9. a  $SI_{\text{calcite}}$  vs  $Ca^{2+}$  b  $SI_{\text{dolomite}}$  vs  $Mg^{2+}$  c  $SI_{\text{fluorite}}$  vs  $F^{-}$  d  $SI_{\text{fluorite}}$  vs  $Ca^{2+}$ .

water and aquifer minerals within lithological framework. Flow path, residence time, rock-water interaction and chemical processes within the aquifer systems are the major factor which determines the water facies. Na-HCO<sub>3</sub> is the dominant facies present in the region. In Group 1, 58 samples have Na-HCO<sub>3</sub> type water facies, 39 samples belong to Ca-HCO<sub>3</sub>, and 18 samples have Na-Cl facies (Table 4). In Group 2, Na-Cl is found as the dominant facies followed by Na-HCO<sub>3</sub> and Na-SO<sub>4</sub>. In Group 3 Na-Cl is dominant water type. Piper (1944) trilinear diagram

suggests that cationic species Ca<sup>2+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> and anionic species HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> are dominant in groundwater aquifers (Fig. 8). Thus majority of the water type in study area belongs to Na<sup>+</sup>/Ca<sup>2+</sup> or Mg-HCO<sub>3</sub>/Cl type. Most of the water contains high Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> and belongs to Na-HCO<sub>3</sub> water type which is considered favourable for dissolution of fluorite minerals.

## 5.2. Saturation indices

Saturation indices (SI) are important to determine the reactivity of minerals in groundwater. A positive value of SI for particular mineral indicates oversaturation and thus precipitation will occur whereas a negative value indicates undersaturation and dissolution of mineral will take place. The SI value for calcite and dolomite indicates that most of the samples are oversaturated with respective minerals (Fig. 9a and b). The study region lies under semi-arid climate with high evaporation, less rainfall which might be responsible for the precipitation of calcite and dolomite in groundwater (Kumar and Singh, 2015). Oversaturation of these minerals indicates that water has enough residence time to reach up to equilibrium (Fig. 9b). Negative value of SI for fluorite, halite and gypsum indicates that groundwater is under saturated with these minerals (Fig. 9c and d). The dissolution of fluorite is major factor controlling F<sup>-</sup> enrichment in groundwater of the region. Fig. 9c indicates SI value of fluorite and concentration of F<sup>-</sup> in groundwater.

In Group 1, F<sup>-</sup> concentration varies from bdl to 12.52 mg/L. Out of total 133 samples in Group 1, 31 samples had F<sup>-</sup> higher than the WHO guideline i.e. 1.5 mg/L whereas in Group 2, 15 samples have high F<sup>-</sup> which ranges between bdl to 10.52 mg/L. The samples showing high F<sup>-</sup> belong to Na-HCO<sub>3</sub> type water facies. Calcite precipitation in alkaline environment favours dissolution of fluorite (Adriano, 1986). Due to oversaturation of calcite, Ca<sup>2+</sup> ions resist the solubility of fluorite. Dissolution of fluorite is concealed by common ion effect and thus a negative correlation exists between Ca<sup>2+</sup> and F<sup>-</sup> ions (Handa, 1975). In our study Ca<sup>2+</sup> and F<sup>-</sup> also shows negative correlation ( $r = -0.183$ ), although not significant but it suggests that F<sup>-</sup> concentration is mainly governed by oversaturation of calcite and ion-exchange of Ca<sup>2+</sup>.

## 6. Conclusion

The multivariate statistical methods along with conventional plots and geochemical modeling are found to be effective for characterization of hydro-geochemical processes and thus the water chemistry of the region. The hydro-geochemical composition of groundwater in the national capital of India is affected not only by geogenic process but also has an impact of anthropogenic inputs. Four principal components (PC1-PC4) were found to explain 76% of the dataset when subjected to PCA. PCA indicates ion exchange, soil mineralization and weathering processes, fluoride enrichment, impact of anthropogenic activities such as fertilizer use, leakages from septic tanks and canals as few of the factors governing the overall geochemistry of groundwater in the region. The groundwater is mostly Na-HCO<sub>3</sub> type, which is also a factor responsible for fluoride enrichment. The scatter plots between the ions also indicate about the processes such as ion-exchange, halite dissolution and silicate and carbonate weathering which substantiates the information inferred from statistical methods. High concentration of nitrate and fluoride is a serious concern for public health. Climatic condition coupled with high temperature and less rainfall along with the alkaline environment is the reason for high concentration of fluoride in groundwater. The enrichment of fluoride is also supported by the fact that saturation index, for calcite indicates oversaturation and undersaturation for fluorite. High concentration of nitrate is the result of anthropogenic activities. In agricultural area excessive use of fertilizer contributes nitrate and potassium in groundwater, while seepages from septic tanks also contributes nitrate in dense built-up areas. Thus a sustainable



water management and conservation practices should be adopted before the situation aggravates further.

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