Hydrochemical characteristics of the groundwater in Trans-Yamuna Alluvial aquifer, Palwal District, Haryana, India

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Abstract
Hydrochemical processes have been evaluated for the groundwater regime in Trans-Yamuna alluvial aquifer, Palwal District, Haryana. The groundwater belongs to the Na+–Mg+2 and Cl−–SO4
−2 facies, and solute acquisition processes indicated that the rock weathering/evaporation is a major mechanism that characterizes the hydrochemistry. It is also indicated that dissolution and reverse ion exchange processes are playing a major role in determining the groundwater chemistry in the study area. The varied climate in Ganga plains is responsible for the importance of different hydrogeochemical processes that impact on hydrochemistry of groundwater. Groundwater quality parameters were tested for drinking and irrigation purposes. Water quality index shows that 13%, 31%, 34% and 21% fall in good, poor, very poor and unsuitable water category, respectively, for drinking purposes. On the basis of SAR and Na%, the groundwater indicated that it is safe for irrigation purposes. But high TDS of few samples suggested the salinity hazard while using it for irrigation purposes for a longer period.

Keywords Hydrochemical characteristics · Seasonal variations · Trans-Yamuna River

Introduction
The success of the green revolution resulted in unprecedented development in the state of Haryana in India. It was assisted by groundwater as a key source of irrigation that resulted in an increase in agriculture productivity exponentially. A general increase in wealth of population due to high agriculture productivity subsequently resulted in rural–urban migration, industrialization and economic development in the last 50 years in urban–rural areas of India. These activities are putting huge pressure on natural resources. A unique geological and climatic condition in the Trans-Yamuna area supported less development of the groundwater due to hydrometeorological and geological conditions. Therefore, less-water-required agricultural practices were adopted in this region. But in the last 50 years, groundwater is being continuously used to irrigate types of crops that need huge irrigation. It has resulted in environmental degradation in terms of groundwater and soil resources in the region.

During the last few decades, it is also observed that groundwater has been polluted drastically because of changes in agricultural expansion, industrialization, improper solid and toxic waste management practices throughout India (Ramesh and Soorya 2012; Kumar et al. 2009, 2011). Numbers of studies on groundwater quality deterioration and geochemical evolution of groundwater have been carried out in different parts of India as well as in other parts of the world (Jalali 2006, Jalali 2007, Gupta et al. 2008; Irfan and Said 2008; Kumar et al. 2009; Srinivasamoorthy et al. 2010; Zhang et al. 2011; Vasanthavigar et al. 2012). It is found that several regions in India have encountered degradation in groundwater quality too due to an increase in population growth, change in land use/land cover and rapid urbanization (Brindha and Elango 2010; Ramesh and Elango 2005).

The present study area of Trans-Yamuna aquifer is characterized by high population growth, urbanization, industrialization and the rapid increase in agricultural productivity. The impact of such circumstances may adversely affect the future sustainability of the groundwater in the area. Therefore, the present study...
was carried out for the assessment of hydrogeochemical characteristics in the area facing environmental stresses due to groundwater overexploitation in recent years. The findings of this study will help to protect the quality of groundwater for the present and to prepare future groundwater for sustainable water supply in the region.

**Study area**

Palwal District of Haryana lies between 27°50′:28°15′ N latitudes and 77°05′:77°33′ E longitudes, covering an area of about 1364.55 Km² with an average elevation of 195 amsl. The district comprises river flood plains, low lying plains, depressions, sand dunes and hills. Geologically, the area is situated in the Yamuna sub-basin of the Ganga basin in India (Fig. 1).

**Climate**

This area shows tropical steppe, semiarid and arid climatic condition. The climate exhibits the following characteristics: (a) seasonal rhythm, (b) cool winter, (c) hot summer, (d) mostly dry weather except for two to three months (July to September), (e) unreliable rainfall (f) meager rainfall and (g) high annual range of temperature. The study area is very hot in summer (up to 49 °C) and cold in winters (down to 1 °C). The hottest months are May and June, and the coldest being December and January. With the onset of March, the temperature begins to increase rapidly and goes up to 49 °C in May and June. From April onwards, hot dust-laden winds locally known as Loo blows and weather is unpleasant.

Rainwater resource plays an important role in every aspect of human activity. Rainfall is markedly restricted in season, and drought is a usual occurrence in this area.

![Fig. 1 Location map of the study area along with the sample locations](image-url)
Variation in rainfall from year to year is considerable. The distribution of rainfall is irregular in both time and space, and water deficiency is a problem in most of the area. About 80% of the rainfall occurs in the monsoon season (July to September) and sometimes causes local flooding. The annual rainfall including monsoon of the region is about 300–500 mm which is unevenly distributed over the area. During 3 months from the last week of June to September, the moist air of oceanic origin penetrates into the region and causes high humidity, cloudiness and monsoon rainfall.

Geology

The basement of the area is composed of quartzite and slate of Delhi Supergroup of Achaean age. It is overlain by sediments of older alluvium (upland unit of the area) of the Pleistocene age. Lowland areas near the flood plain are newer alluvium of Holocene age overlain on older alluvium. Newer alluvium is confined within floor plains of Yamuna River and disconformably overlies the older alluvium. The newer alluvium is devoid of calcareous nodules, while the older alluvium consists of calcareous Kankar. The northwest part of the area is covered by quaternary eolian sediment (Fig. 2).

The lithological character and water-bearing characteristics of formations are summarized as follows:

| Geological age       | Litho unit         | Morpho unit     |
|----------------------|--------------------|-----------------|
| (Quaternary) Holocene| Newer alluvium     | Lowland unit    |
| Quaternary (Eolian)  | Disconformities    |                 |
| (Quaternary) Pleistocene| Older alluvium | Up land unit    |
| Unconformity Proterozoic| Delhi Supergroup | Denuded hill unit |

(After CGWB 2006)

Soil cover

The alluvium and eolian soil are the main extensive cover area in the area. The texture of the soil is sand to loamy in recent Yamuna flood plains, sandy loam for older plains, sandy loam to clay loam for alluvial plains, and clay loam/silty clay for low lying plains and depressions. The spatial distribution shows coarse loamy–calcareous soil in the northern part, fine loamy in southwest and calc–sandy in the eastern part, respectively (NBSS and LUP 1993).

Hydrogeology

The district is occupied by the Gangetic alluvial plain of Quaternary age and falls in the Yamuna sub-basin of the Ganga basin. The permeable granular zones are comprised of fine- to medium-grained sand and occasionally coarse sand and gravel. Groundwater occurs in alluvium and the underlying weathered/fractured quartzite. Alluvium comprises sand silt, Kankar and gravel, which form the principal groundwater-bearing horizon. In quartzite formation, occupying the northwestern part of the district, groundwater occurs in weathered and jointed fractured horizons (CGWB 2013). The depth to the water table in the area ranges from 2.00 to 20.75 mbgl during the pre-monsoon period and from 2 to 9.40 mbgl during the post-monsoon period and the average gradient of the water table is of the order of 1 m/km with groundwater flow from north to south direction (Fig. 3).

Fig. 2 Geology of the Trans-Yamuna region, Palwal District, Haryana

Fig. 3 Spatial distribution of the average groundwater depth in Trans-Yamuna region, Palwal District
Land use and land cover

The land use pattern broadly constitutes built-up land as a habitat, agriculture land, industrial land and water bodies, forest, scrubland, wasteland and urban land. The forest area covers 2197 ha, built-up area 7436 ha, agriculture land 130,056 ha, wasteland 1344 ha, water bodies 1673 and other 369 ha. A small number of water bodies are considered in Silauthi, Aurangabad, Sholaka and Dighaut, while the mining areas are found in Sarai, Tumsara and Sugar mill side (Dept. of Town and Country Planning 2013).

Methodology

The present study is designed to evaluate the hydrogeochemical processes that are responsible for hydrogeochemical characteristics for the groundwater in Trans-Yamuna alluvial plain, Palwal District, Haryana. The grid sampling method was adopted to collect the samples from the study area, and the samples were collected in post-monsoon 2015 and pre-monsoon 2016. Hydrochemical parameters, i.e., pH, EC (electrical conductivity) and concentrations of Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Na\textsuperscript{+}, K\textsuperscript{+}, Cl\textsuperscript{−}, HCO\textsubscript{3}\textsuperscript{−}, Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}−, in groundwater were determined. The groundwater samples were collected from hand-pumps-fitted boreholes at different locations of Palwal District, Haryana. About 30–50 L of water was drawn from hand pumps before collecting the samples in plastic bottles and analyzed as per standard method (APHA 1998) and the summary of these methods is presented in Table 1. The groundwater depth data were downloaded from India-WRIS Web GIS Web site, and the rates of change in groundwater depth in m/year were determined using groundwater depth time series data from 1994 to 2016. Spatial and temporal coverage of the settlement area has been downloaded for the Palwal City from Bhuvan ISRO’s Geoportal. The growth of the settlement area has been determined using PCI Geomatica 9.1. Population data of Palwal District for the periods 1991 and 2011 were obtained from India Census. The comparative analysis has been conducted using the hydrochemical data for Bareilly District from Ahmad and Mazhar (2020) and data from the Aligarh Doab region from Wasim et al. (2014).

Results and discussion

The details of the parameters for the groundwater samples in pre-monsoon and post-monsoon period and the average of these parameters are presented in Tables 2, 3 and 4. A comprehensive observation is as follows: pH value 8 ± 0.28 (7.4–8.4), HCO\textsubscript{3}− 384 ± 208 (49–1281) mg/l, Mg\textsuperscript{2+} 184 ± 22 (455–103 mg/l) and SO\textsubscript{4}\textsuperscript{2−} 423 ± 509 (2183–9) mg/l. Cl\textsuperscript{−} shows 776 ± 668 (3302–105) mg/l,

| Table 1 | Detailed methodology used in determining the hydrochemical characteristics of the groundwater |
|---------|------------------------------------------------------------------------------------------------|
| Parameter | Instrument and reagents | References |
| **General** | | |
| pH | pH meter (pH 4 and 9.2) | APHA (1998) |
| EC | EC meter (KCl) | APHA (1998) |
| TDS | Heating at 180 °C, laboratory | APHA (1998) |
| TH | EDTA titrimetric (EDTA, ammonia buffer and Eriochrome Black T (EBT) indicator) | APHA (1998) |
| **Major cations** | | |
| Ca\textsuperscript{2+} | EDTA titrimetric (EDTA, sodium hydroxide and murexide) | APHA (1998) |
| Mg\textsuperscript{2+} | Calculation (MgH = TH-CaH; Mg = MgH X Eq. Wt of Mg X normality of EDTA) | APHA (1998) |
| Na\textsuperscript{+} | Flame photometric (NaCl) | APHA (1998) |
| K\textsuperscript{+} | Flame photometric (KCl) | APHA (1998) |
| **Major anions** | | |
| HCO\textsubscript{3}− | Titrimetric (H\textsubscript{2}SO\textsubscript{4}, phenolphthalein and methyl orange) | APHA (1998) |
| Cl\textsuperscript{−} | Titrimetric, silver nitrate (AgNO\textsubscript{3}), potassium chromate | APHA (1998) |
| F\textsuperscript{−} | Spands (NaF) | APHA (1998) |
| SO\textsubscript{4}\textsuperscript{2−} | Turbidity—UV–visible spectrophotometer method (HCl, ethyl alcohol, NaCl, barium chloride, sodium sulfate) | APHA (1998) |
and the Ca\(^{2+}\) concentration is 102 ± 103 mg/l (890–24) mg/l. The Na\(^{+}\) concentration is 337 ± 355 (1716–19) mg/l, whereas the K\(^{+}\) concentration is 81 ± 355 (263–14) mg/l. It is found that monsoonal activity resulting in recharge of groundwater reflected in a decrease in TDS, pH and Na\(^{+}\) values and increase in K\(^{+}\), HCO\(_3\)\(^{-}\) and NO\(_3\)\(^{-}\) due to leaching. The order of anions is characterized by Cl\(^{-}\) > SO\(_4\)\(^{2-}\) > HCO\(_3\)\(^{-}\) > F\(^{-}\) and Cl\(^{-}\) > HCO\(_3\)\(^{-}\) > SO\(_4\)\(^{2-}\) > F\(^{-}\), and the anions were in the order of Na\(^{+}\) > Mg\(^{2+}\) > Ca\(^{2+}\) > K\(^{+}\) and K\(^{+}\) > Mg\(^{2+}\) > Ca\(^{2+}\) > Na\(^{+}\) in pre- and post-monsoon periods, respectively.

The Piper plot of chemical data on a diamond-shaped trilinear diagram reveals that the majority of groundwater samples fall in the fields of 3 and 4, i.e., Na\(^{+}\)–Mg\(^{2+}\)–Cl\(^{-}\)–SO\(_4\)\(^{2-}\) type, suggesting that alkaline exceeds in most of the water samples. However, few groundwater samples fall in no-dominant type (Fig. 4). A comparative analysis has been conducted for a water sample from different parts of the Ganga–Yamuna aquifer. It indicated that the groundwater facies of the Ramganga aquifer in the Bareilly District show dramatically changes with seasons. But, the groundwater facies from Doab (interfluves) aquifer of Ganga–Yamuna and Trans-Yamuna aquifer do not show any significant change with seasons (Fig. 5). It suggests that the high permeability of aquifer material and slope facilitates the flushing of old groundwater from the Ramganga aquifer and causes a significant change in groundwater chemistry during the post-monsoon season. But a change in hydrochemical characteristic has not been indicated by the groundwater samples from Palwal and Aligarh districts.

An assessment of the relative importance of different hydrochemical processes was performed in Ramganga–Ganga–Yamuna aquifer area using Durov diagram (Fig. 6). The diagram indicates a systematic change in different hydrochemical processes identified from NE to SW in the Ganga basin. The ion exchange process was dominant in Ramganga aquifer; dissolution action was prominent in Ganga–Yamuna Doab region. But in Trans-Yamuna aquifer, most of the samples are indicating dissolution and few samples are exhibiting a reverse ion exchange as a dominant process. The northeast region is characterized by high rainfall and less evapotranspiration, while in the south on the present study area the climate becomes more arid. It is also revealed by a continuous change in hydrochemical processes that are reflected in a change in hydrogeochemical characteristics from NE to SW.

The base-exchange processes can be determined through base-exchange index R\(_1\) (Soltan 1999) and computing using Eq. 1. It reveals the dominant processes and classifies the groundwater as Na\(^{+}\)–HCO\(_3\)\(^{-}\) and Na\(^{+}\)–SO\(_4\)\(^{2-}\) types if R\(_1\) < 1 or > 1, respectively. In the present study, it is found that most of the samples are Na\(^{+}\)–HCO\(_3\)\(^{-}\) type except one sample. Meteoric genesis index R\(_2\) can be used to determine whether the sources of groundwater samples are deep meteoric water percolation type or shallow meteoric water percolation type. If R\(_2\) < 1, the sources of groundwater are of deep meteoric water percolation type. If R\(_2\) > 1, it shows the sources of groundwater are shallow meteoric water percolation type. Meteoric genesis index R\(_2\) can be computed by using Eq. 2. The results indicated that most of the groundwater samples fall under deep meteoric water percolation type. The semi-arid climate along with the continuous overexploitation of groundwater resulted in steep fall in groundwater levels, which leads to deep meteoric percolation as a source of groundwater.

\[
R_1 = \frac{Na^+ - Cl^-}{SO_4^{2-}} \text{ where all values are in meq/l.} \tag{1}
\]

\[
R_2 = \frac{(K^+ + Na^+)}{Cl^-} - \frac{SO_4^{2-}}{SO_4^{2-}} \text{ where all values are in meq/l.} \tag{2}
\]

**Sources of solute in groundwater**

Gibbs (1970) proposed the boomerang envelope model to describe the dynamics of chemical compositions of water and classified the controlling factors into three types, namely atmospheric precipitation, rock weathering and evaporation. The weight ratio Na\(^{+}/(Na^{+} + Ca^{2+})\) as a function of TDS has been plotted (Fig. 7). It is inferred from the figure that all samples belong to rock weathering and moderate evaporation processes.

The sources and mechanisms controlling groundwater chemical composition have been further evaluated by applying the mass balance approach through scatter diagrams (Stallard and Edmond 1983). Analysis based on stoichiometric relationships demonstrates that in the present groundwater, Ca\(^{2+}\) + Mg\(^{2+}\) together accounts for 47% of the total cations. The plot of Ca\(^{2+}\) + Mg\(^{2+}\) versus HCO\(_3\)\(^{-}\) illustrates that equal numbers of groundwater samples show position above and below the 1:1 line of Ca\(^{2+}\) + Mg\(^{2+}\) and HCO\(_3\)\(^{-}\) ion concentration. It implies that the part of Ca\(^{2+}\) and Mg\(^{2+}\) could be through silicate and carbonate weathering. Furthermore, moderate (Ca\(^{2+}\) + Mg\(^{2+}\))/(Na\(^{+}\) + K\(^{+}\)) and (Na\(^{+}\) + K\(^{+}\))/Tz\(^{+}\) equivalent ratio indicates that the mixed type (silicate and carbonate weathering) could be a major source of dissolved ions in the groundwater in the area (Fig. 8).
### Table 2 Hydrochemical characteristics of the groundwater in the Trans-Yamuna aquifer in post-monsoon, Palwal District (2015)

| S. no. | EC  | TH  | pH  | HCO₃⁻ | SO₄²⁻ | NO₃⁻ | Cl⁻ | F⁻ | Ca²⁺ | Mg²⁺ | Na⁺ | K⁺ | TDS | Er% |
|--------|-----|-----|-----|--------|--------|-------|-----|----|------|------|-----|----|------|-----|
| 1      | 0.85 | 0.3 | 7.5 | 377    | 140    | 6,855 | 438 | 0.5| 54   | 121  | 44  | 152 | 1.3 | 8   |
| 2      | 0.84 | 0.2 | 7.4 | 754    | 54     | 4,135 | 161 | 1.6| 26   | 64   | 73  | 168 | 1.3 | 10  |
| 3      | 0.64 | 0.3 | 7.1 | 195    | 70     | 3,756 | 449 | 0.6| 45   | 105  | 39  | 86  | 1.0 | 8   |
| 4      | 0.95 | 0.5 | 7.9 | 533    | 341    | 147.9 | 72  | 0.7| 35   | 205  | 29  | 116 | 1.5 | −1  |
| 5      | 0.79 | 2.8 | 7.6 | 377    | 137    | 0.589 | 228 | 0.5| 96   | 84   | 77  | 228 | 1.2 | −10 |
| 6      | 1.72 | 2.0 | 7.1 | 273    | 10     | 25.4  | 1368| 1.2| 237  | 55   | 126 | 584 | 2.7 | 9   |
| 7      | 1.56 | 0.7 | 7.6 | 663    | 1      | 3,087 | 1152| 1.2| 32   | 327  | 10  | 240 | 2.4 | 10  |
| 8      | 0.76 | 0.2 | 7.2 | 338    | 34     | 19.08 | 426 | 1.1| 48   | 62   | 44  | 216 | 1.2 | 10  |
| 9      | 0.32 | 0.1 | 6.9 | 169    | 31     | 11.84 | 133 | 0.3| 55   | 19   | 3   | 75  | 0.5 | 9   |
| 10     | 0.40 | 0.0 | 7.5 | 169    | 113    | 8.966 | 228 | 0.5| 96   | 84   | 77  | 228 | 1.2 | −10 |
| 14     | 1.37 | 0.7 | 6.9 | 364    | 143    | 7,916 | 864 | 0.7| 289  | 310  | 29  | 132 | 2.1 | −10 |
| 51     | 1.38 | 0.6 | 7.4 | 377    | 416    | 1.127 | 778 | 1.1| 61   | 152  | 37  | 248 | 2.2 | 10  |
| 52     | 0.53 | 0.3 | 7.1 | 0      | 81     | 0.012 | 187 | 1.5| 55   | 80   | 46  | 124 | 1.0 | 8   |
| 53     | 0.54 | 0.4 | 7.2 | 182    | 51     | 11.05 | 461 | 0.6| 77   | 47   | 26  | 152 | 0.8 | 8   |
| 55     | 0.48 | 1.1 | 7.2 | 221    | 123    | 5,374 | 216 | 0.5| 77   | 64   | 10  | 28  | 0.7 | 10  |
| 56     | 1.34 | 0.8 | 7.3 | 468    | 111    | 0.468 | 781 | 1.7| 87   | 67   | 40  | 202 | 2.1 | 10  |
| 57     | 1.33 | 0.6 | 6.8 | 234    | 134    | 1.658 | 907 | 0.7| 620  | 91   | 63  | 28  | 2.1 | 10  |
| 58     | 0.92 | 1.0 | 7.2 | 403    | 377    | 2,386 | 288 | 0.9| 97   | 96   | 46  | 124 | 1.4 | 10  |
| Avg    | 1.03 | 0.7 | 7.3 | 410.87 | 151    | 21.82 | 542 | 1.0| 100  | 53   | 53  | 173 | 1.6 | 4   |
| Max.   | 2.28 | 2.8 | 7.9 | 1040   | 680    | 164.1 | 1613| 1.7| 620  | 573  | 488 | 584 | 3.6 | 11  |
| Min.   | 0.32 | 0.0 | 6.7 | 0      | 1      | 0.012 | 72  | 0.1| 26   | 19   | 3   | 24  | 0.5 | −11 |
| Std.   | 0.59 | 0.6 | 0.3 | 205.05 | 162    | 42.48 | 383 | 0.4| 113  | 114  | 76  | 118 | 0.7 | 9   |

All the values are in ppm except EC and pH, EC (µS/cm.), EC, TDS and TH in thousands.
Table 3 Hydrochemical characteristics of the groundwater in the Trans-Yamuna aquifer during pre-monsoon, Palwal District 2016

| S. no. | EC  | TH  | pH  | HCO$_3^-$ | SO$_4^{2-}$ | NO$_3^-$ | Cl$^-$ | Ca$^{2+}$ | Mg$^{2+}$ | Na$^+$ | K$^+$ | TDS | Er% |
|--------|-----|-----|-----|-----------|-------------|----------|-------|----------|----------|-------|------|------|-----|
| 1      | 1.01| 0.4 | 8.6 | 286       | 152         | 4.2      | 568   | 0.8      | 35       | 144   | 345  | 44   | 1.6 − 10 |
| 2      | 1.43| 0.1 | 9.3 | 1456      | 3           | 3        | 128   | 0.6      | 29       | 35    | 496  | 76   | 2.2 − 0  |
| 3      | 0.37| 0.2 | 8.1 | 130       | 33          | 3.3      | 213   | 0.4      | 45       | 60    | 40   | 47   | 0.6 − 6  |
| 4      | 1.25| 0.3 | 8.9 | 390       | 277         | 19.5     | 710   | 0.5      | 38       | 123   | 312  | 80   | 2.0 − 9  |
| 5      | 0.74| 0.3 | 9.0 | 429       | 32          | 5.4      | 320   | 0.3      | 19       | 144   | 184  | 27   | 1.2 − 10 |
| 6      | 0.66| 0.3 | 9.0 | 260       | 75          | 5.1      | 355   | 0.6      | 19       | 115   | 180  | 16   | 1.0 − 8  |
| 7      | 1.83| 0.6 | 8.1 | 195       | 300         | 2.2      | 1287  | 0.8      | 513      | 94    | 200  | 270  | 2.9 − 3  |
| 8      | 1.58| 0.7 | 8.4 | 143       | 415         | 11.3     | 1136  | 0.6      | 96       | 304   | 332  | 37   | 2.5 − 2  |
| 9      | 0.45| 0.3 | 8.5 | 169       | 213         | 0.3      | 77    | 90       | 76       | 30    | 312  | 47   | 0.6 − 10 |
| 10     | 0.75| 0.4 | 8.5 | 156       | 147         | 4.3      | 355   | 0.5      | 58       | 160   | 272  | 21   | 1.2 − 10 |
| 11     | 0.78| 0.2 | 9.0 | 273       | 163         | 6.5      | 355   | 0.6      | 48       | 98    | 260  | 15   | 1.2 − 10 |
| 12     | 0.78| 0.2 | 8.9 | 273       | 165         | 6.5      | 350   | 0.6      | 48       | 98    | 260  | 15   | 1.2 − 10 |
| 13     | 0.77| 0.2 | 8.7 | 275       | 161         | 6.5      | 349   | 0.6      | 48       | 96    | 255  | 18   | 1.2 − 10 |
| 14     | 1.41| 1.0 | 8.2 | 130       | 511         | 9.9      | 710   | 0.8      | 160      | 390   | 272  | 21   | 1.2 − 10 |
| 15     | 5.87| 5.8 | 8.2 | 390       | 2516        | 72.9     | 3195  | 0.6      | 1106     | 427   | 1376 | 92   | 9.2 − 0  |
| 16     | 1.82| 0.4 | 9.1 | 585       | 272         | 67.7     | 639   | 0.5      | 32       | 160   | 1056 | 27   | 2.8 − 10 |
| 17     | 1.06| 0.3 | 9.0 | 390       | 284         | 255      | 0.5   | 38       | 133      | 296   | 15   | 1.7 − 2  |
| 18     | 1.43| 0.5 | 8.9 | 364       | 327         | 8.1      | 852   | 0.5      | 71       | 242   | 352  | 23   | 2.2 − 3  |
| 19     | 0.63| 0.3 | 9.0 | 312       | 97          | 2.3      | 213   | 0.5      | 19       | 134   | 164  | 49   | 1.0 − 10 |
| 20     | 1.12| 0.3 | 9.1 | 585       | 92          | 1.5      | 426   | 0.8      | 22       | 133   | 224  | 264 | 1.7 − 9  |
| 21     | 1.13| 0.3 | 9.1 | 377       | 363         | 2.5      | 497   | 0.6      | 48       | 127   | 312  | 35   | 1.8 − 2  |
| 22     | 0.85| 0.6 | 8.6 | 247       | 131         | 15.2     | 497   | 0.4      | 64       | 180   | 172  | 18   | 1.3 − 10 |
| 23     | 0.72| 0.6 | 8.1 | 218       | 75          | 5.1      | 355   | 0.6      | 19       | 115   | 180  | 16   | 1.0 − 8  |
| 24     | 1.58| 0.7 | 8.4 | 143       | 415         | 11.3     | 1136  | 0.6      | 96       | 304   | 332  | 37   | 2.5 − 2  |
| 25     | 0.45| 0.3 | 8.5 | 169       | 213         | 0.3      | 77    | 90       | 76       | 30    | 312  | 47   | 0.6 − 10 |
| 26     | 1.83| 0.6 | 8.1 | 195       | 300         | 2.2      | 1287  | 0.8      | 513      | 94    | 200  | 270  | 2.9 − 3  |
| 27     | 1.58| 0.7 | 8.4 | 143       | 415         | 11.3     | 1136  | 0.6      | 96       | 304   | 332  | 37   | 2.5 − 2  |
| 28     | 0.45| 0.3 | 8.5 | 169       | 213         | 0.3      | 77    | 90       | 76       | 30    | 312  | 47   | 0.6 − 10 |
| 29     | 1.83| 0.6 | 8.1 | 195       | 300         | 2.2      | 1287  | 0.8      | 513      | 94    | 200  | 270  | 2.9 − 3  |
| 30     | 1.58| 0.7 | 8.4 | 143       | 415         | 11.3     | 1136  | 0.6      | 96       | 304   | 332  | 37   | 2.5 − 2  |

All the values are in ppm except EC and pH, EC (µS/cm.) EC, TDS and TH in thousands
Table 4  Average hydrochemical characteristics of the groundwater in the Trans-Yamuna aquifer, Palwal District

| S. no. | EC  | TH  | pH  | HCO₃⁻ | SO₄²⁻ | NO₃⁻ | Cl⁻ | Ca²⁺ | Mg²⁺ | Na⁺ | K⁺ | TDS | Er% |
|--------|-----|-----|-----|--------|--------|-------|-----|------|------|-----|----|-----|-----|
| 1      | 1.16| 0.3 | 8.0 | 309    | 460    | 4.5   | 484 | 0.8  | 40   | 143 | 298| 71  | 1.8 | 1   |
| 2      | 1.29| 0.1 | 8.4 | 1281   | 30     | 3.3   | 136 | 0.9  | 28   | 42  | 390| 99  | 2.0 | 2   |
| 3      | 0.43| 0.2 | 7.6 | 146    | 60     | 3.2   | 249 | 0.4  | 45   | 72  | 40 | 57  | 0.7 | -2  |
| 4      | 1.22| 0.4 | 8.4 | 426    | 378    | 46.1  | 550 | 0.6  | 38   | 143 | 241| 89  | 1.9 | 10  |
| 5      | 0.81| 1.5 | 8.3 | 416    | 93     | 4.0   | 287 | 0.4  | 38   | 161 | 185| 77  | 1.3 | 10  |
| 6      | 0.90| 1.2 | 8.1 | 263    | 61     | 9.2   | 568 | 0.8  | 74   | 100 | 167| 158 | 1.4 | -3  |
| 7      | 1.76| 0.7 | 7.9 | 312    | 226    | 2.2   | 1249| 0.9  | 393  | 152 | 153| 263 | 2.7 | 0   |
| 8      | 1.52| 0.5 | 7.8 | 192    | 329    | 12.2  | 1172| 0.6  | 84   | 244 | 260| 82  | 2.4 | 7   |
| 9      | 0.42| 0.2 | 7.7 | 169    | 62     | 6.8   | 192 | 0.3  | 71   | 72  | 58 | 23  | 0.7 | 10  |
| 10     | 0.68| 0.2 | 8.0 | 159    | 167    | 5.0   | 303 | 0.4  | 58   | 138 | 209| 26  | 1.1 | 10  |
| 11     | 0.84| 0.3 | 8.1 | 263    | 61     | 9.2   | 568 | 0.8  | 74   | 100 | 167| 158 | 1.4 | -3  |
| 12     | 1.22| 0.4 | 8.4 | 426    | 378    | 46.1  | 550 | 0.6  | 38   | 143 | 241| 89  | 1.9 | 10  |
| 13     | 0.81| 1.5 | 8.3 | 416    | 93     | 4.0   | 287 | 0.4  | 38   | 161 | 185| 77  | 1.3 | 10  |
| 14     | 0.90| 1.2 | 8.1 | 263    | 61     | 9.2   | 568 | 0.8  | 74   | 100 | 167| 158 | 1.4 | -3  |
| 15     | 1.76| 0.7 | 7.9 | 312    | 226    | 2.2   | 1249| 0.9  | 393  | 152 | 153| 263 | 2.7 | 0   |
| 16     | 1.52| 0.5 | 7.8 | 192    | 329    | 12.2  | 1172| 0.6  | 84   | 244 | 260| 82  | 2.4 | 7   |
| 17     | 0.42| 0.2 | 7.7 | 169    | 62     | 6.8   | 192 | 0.3  | 71   | 72  | 58 | 23  | 0.7 | 10  |
| 18     | 0.68| 0.2 | 8.0 | 159    | 167    | 5.0   | 303 | 0.4  | 58   | 138 | 209| 26  | 1.1 | 10  |
| 19     | 0.78| 0.2 | 8.2 | 351    | 179    | 5.8   | 304 | 0.9  | 46   | 89  | 196| 47  | 1.2 | -2  |
| 20     | 1.22| 0.4 | 8.4 | 426    | 378    | 46.1  | 550 | 0.6  | 38   | 143 | 241| 89  | 1.9 | 10  |
| 21     | 0.81| 1.5 | 8.3 | 416    | 93     | 4.0   | 287 | 0.4  | 38   | 161 | 185| 77  | 1.3 | 10  |
| 22     | 0.90| 1.2 | 8.1 | 263    | 61     | 9.2   | 568 | 0.8  | 74   | 100 | 167| 158 | 1.4 | -3  |
| 23     | 1.76| 0.7 | 7.9 | 312    | 226    | 2.2   | 1249| 0.9  | 393  | 152 | 153| 263 | 2.7 | 0   |
| 24     | 1.52| 0.5 | 7.8 | 192    | 329    | 12.2  | 1172| 0.6  | 84   | 244 | 260| 82  | 2.4 | 7   |
| 25     | 0.42| 0.2 | 7.7 | 169    | 62     | 6.8   | 192 | 0.3  | 71   | 72  | 58 | 23  | 0.7 | 10  |
| 26     | 0.68| 0.2 | 8.0 | 159    | 167    | 5.0   | 303 | 0.4  | 58   | 138 | 209| 26  | 1.1 | 10  |

All the values are in ppm except EC and pH, EC (µS/cm.), TH, EC and TDS in thousands
Correlation matrix

The statistical analysis has been carried out by correlation coefficient between different pairs of groundwater quality parameters of groundwater to assess the mechanism of solute acquisition processes in the area. The values of the coefficient of correlation were determined using SPSS software version 13 at probability ($p$) of < 0.01. Relationships during pre-monsoon and post-monsoon seasons showed positive and negative correlations among the parameters and significant relation are presented as bold numbers in the Table 5. The strong positive correlation of $\text{HCO}_3^-$ with $\text{Na}^+$ ($R^2 = 0.77$) and that of $\text{Cl}^-$ with $\text{Na}^+$ ($R^2 = 0.87$) in pre-monsoon indicate the importance of the silicate weathering and evaporation. This relationship changes in post-monsoon due to recharge of the groundwater by monsoon rainfall; the strong positive correlation coefficient of $\text{HCO}_3^-$ with $\text{Na}^+$ ($R^2 = 0.71$) and $\text{Na}^+$ with $\text{Cl}^-$ ($R^2 = 0.84$) is maintained. The leaching of $\text{SO}_4^{2-}$ associated with $\text{Mg}^{2+}$ and $\text{Na}^+$ is clearly indicated in the post-monsoon period. High input of $\text{KNO}_3$ is being used as artificial fertilizer in the area, and leaching in the post-monsoon period shows a strong coefficient relationship ($R^2 = 0.61$) between $\text{K}^+$ and $\text{NO}_3^-$. A strong relationship between $\text{Na}^+$ and $\text{Cl}^-$ in the post-monsoon in groundwater indicates the dissolution of the salt which precipitated due to high evaporation in a dry climate and leaches during monsoonal recharge.

Principal Component Analysis (PCA)

The PCA technique has been used to recognize the important parameters that determine the water quality in many studies (Akbal et al. 2011; Varol and Davraz 2014). On investigating the existing water quality data using PCA, we attempt to find the governing factors that establish the quality of water by taking out important principal components (PCs). These components identify the processes that are associated with parameters showing the same behavior. These components explain 74% of the total variance in the pre-monsoon hydrochemical data and 70% of the total variance in the post-monsoon hydrochemical data (Table 6). The bold numbers in this table are showing significant contributions by the parameters towards the particular component.

During pre-monsoon, the first PC accounts for 36% of the total variance and it has a high correlation with $\text{NO}_3^-$, $\text{Cl}^-$, $\text{F}^-$, hardness, $\text{Mg}^{2+}$ and TDS. The second component
Fig. 5 Piper’s diagram (Piper 1953) for groundwater in Bareilly, Palwal and Aligarh districts.

Fig. 6 Durov diagram for groundwater in Bareilly, Palwal and Aligarh districts.
is associated with pH, $SO_4^{2-}$ and $Mg^{2+}$ probably contributed by the dissolution of $MgSO_4$ and subsequent change in pH. The third component is associated with $Na^+$ and TDS as a proxy to strong evapotranspiration. The fourth component explains about 8% of the total variance that is associated with only $HCO_3^-$. The first four PCs during post-monsoon explain the less total variance than pre-monsoon. The first component explains 29% of the total variance and is associated with hardness, $HCO_3^-$, $F^-$ and TDS. The second component is associated with pH, $Na^+$ and $K^+$. The third component includes $Na^+$ and $NO_3^-$ in association with inverse relationships to the second component. It indicates that leaching results in an increase in $NO_3^-$ and decrease in $Na^+$ concentration in groundwater during monsoonal recharge. The fourth component is related to $SO_4^{2-}$, $Cl^-$ and $Mg^{2+}$ as dissolution of Mg salts during monsoonal recharge.

**Drinking water quality analysis**

The suitability of the groundwater has been assessed for drinking purposes using BIS (2012) standards. It is found that most of the samples have a high degree of magnesium content. Undesirably high $SO_4^{2-}$, $Cl^-$, EC, $F^-$ and $Ca^{2+}$ values were found in 22%, 18%, 10%, 8% and 3% of the samples.
samples, respectively. It is observed that region of bad water quality lies in highly urbanized areas and localities along the Yamuna River. That is heavily affected by agriculture activities assisted by dense canal network system along with the industrial activity. High fluoride content was observed in the northwest and southeast side of the district dominated by the metamorphic rock of Aravalli Mountains and low lying region of Yamuna River. The difference in nitrate concentration in the post- and pre-monsoon indicates higher values near city due to leaching from sewage and intense fertilizers-supported vegetable crops near city areas. But in the south of the district this fluctuation is negative that indicates the utilization of enhanced nitrate in the pre-monsoon by the pre-monsoon crop.

The water quality index for the groundwater samples was determined to rank these samples from the drinking purpose. The water quality index provides an inclusive interpretation of the quality of surface and groundwater and its suitability for drinking purposes. The main purpose of WQI is to change the complex water quality data into understandable and usable information by which common people can know the status of water sources in a particular region (Akoteyon et al. 2011; Vasanthavigar et al. 2010). The weighted arithmetic index method is used in the present case for the calculation of WQI using 11 water quality characteristics, namely turbidity, pH, total hardness, bicarbonate, chloride, total dissolved solids, calcium, magnesium, sulfate, nitrate and fluoride. A detailed distribution of WQI suggests that 13% fall in good category, 31% and 34% of the total water samples were found with poor and very poor water quality standard, 21% fall under the very poor category and 3% samples are unsuitable water quality standard (Table 7).

Irrigation water quality analysis

The groundwater is also being heavily used for irrigation purposes in the area due to the absence of large surface bodies. In view of irrigation utility, the groundwater samples were also analyzed for their suitability and usefulness to meet the irrigational needs of farmers. The suitability of water for irrigation purposes has been evaluated through three parameters, namely SAR (sodium adsorption ratio), sodium percent (Na%) and RSC (residual sodium carbonate).

Table 5 Matrix of correlation for the hydrochemical parameters in groundwater

|                | pH | EC  | HCO₃⁻ | SO₄²⁻ | NO₃⁻ | Cl⁻ | F⁻ | Na⁺ | K⁺ | Ca²⁺ | Mg²⁺ | TDS |
|----------------|----|-----|-------|-------|------|-----|----|-----|----|-----|------|-----|
| **Post-monsoon** 2016 |    |     |       |       |      |     |    |     |    |     |       |     |
| pH             | 1.00 |     |       |       |      |     |    |     |    |     |       |     |
| EC             | 0.25 | 1.00 |       |       |      |     |    |     |    |     |       |     |
| HCO₃⁻          | 0.27 | 0.92 | 1.00 |       |      |     |    |     |    |     |       |     |
| SO₄²⁻          | 0.01 | 0.70 | 0.47 | 1.00 |      |     |    |     |    |     |       |     |
| NO₃⁻           | 0.14 | 0.05 | 0.08 | 0.10 | 1.00 |     |    |     |    |     |       |     |
| Cl⁻            | 0.02 | 0.78 | 0.58 | 0.62 | 0.04 | 1.00 |    |     |    |     |       |     |
| F⁻             | 0.29 | 0.08 | 0.09 | 0.02 | 0.23 | −0.11 | 1.00 |    |    |    |       |     |
| Na⁺            | 0.01 | 0.85 | 0.77 | 0.65 | 0.00 | 0.87 | 0.00 | 1.00 |    |    |       |     |
| K⁺             | 0.37 | 0.59 | 0.39 | 0.52 | 0.61 | 0.48 | 0.27 | 0.43 | 1.00 |    |       |     |
| Ca²⁺           | 0.17 | 0.59 | 0.50 | 0.17 | 0.06 | 0.44 | 0.07 | 0.41 | 0.34 | 1.00 |     |     |
| Mg²⁺           | 0.19 | 0.65 | 0.42 | 0.81 | −0.01 | 0.57 | 0.02 | 0.49 | 0.46 | 0.06 | 1.00 |     |
| TDS            | 0.25 | 1.00 | 0.92 | 0.70 | 0.05 | 0.78 | 0.08 | 0.85 | 0.59 | 0.59 | 0.65 | 1.00 |
| **Pre-monsoon** 2017 |    |     |       |       |      |     |    |     |    |     |       |     |
| pH             | 1.00 |     |       |       |      |     |    |     |    |     |       |     |
| EC             | −0.50 | 1.00 |       |       |      |     |    |     |    |     |       |     |
| HCO₃⁻          | −0.40 | 0.87 | 1.00 |       |      |     |    |     |    |     |       |     |
| SO₄²⁻          | 0.18 | 0.03 | 0.00 | 1.00 |      |     |    |     |    |     |       |     |
| NO₃⁻           | −0.24 | 0.30 | 0.09 | −0.09 | 1.00 |     |    |     |    |     |       |     |
| Cl⁻            | −0.38 | 0.83 | 0.53 | −0.02 | 0.17 | 1.00 |    |     |    |     |       |     |
| F⁻             | −0.14 | 0.21 | 0.31 | −0.04 | 0.03 | 0.09 | 1.00 |    |    |    |       |     |
| Na⁺            | −0.51 | 0.93 | 0.71 | 0.07 | 0.27 | 0.84 | 0.16 | 1.00 |    |    |       |     |
| K⁺             | −0.48 | 0.71 | 0.55 | −0.05 | 0.37 | 0.56 | 0.02 | 0.57 | 1.00 |    |       |     |
| Ca²⁺           | −0.19 | 0.31 | 0.28 | −0.27 | 0.11 | 0.40 | 0.10 | 0.16 | 0.15 | 1.00 |     |     |
| Mg²⁺           | −0.21 | 0.33 | 0.13 | −0.03 | 0.34 | 0.25 | −0.13 | 0.37 | 0.44 | −0.50 | 1.00 |     |
| TDS            | −0.50 | 1.00 | 0.87 | 0.03 | 0.30 | 0.83 | 0.21 | 0.93 | 0.71 | 0.31 | 0.33 | 1.00 |
Sodium Adsorption Ratio (SAR)

Sodium adsorption ratio is used to evaluate the excess of sodium with calcium and magnesium (Richards 1954). In general, the permeability of soil reduces due to excessive sodium content in irrigation water. The use of water having a high SAR level continuously can lead to the increase...
in Na% level over the time, which in turn can adversely affect soil infiltration and percolation rates. Fine-textured soils, especially those high in clay, are most subject to this action. Certain amendments may be required to maintain soils under high SARs. Calcium and magnesium, if present in the soil in large enough quantities, will counter the effects of sodium and help to maintain good soil properties (Fipps 2003). In addition to this, the excessive SAR levels of irrigation water can also cause soil crusting, poor seedling and poor aeration (Lesch and Suarez 2009). The SAR of groundwater samples is calculated, and the results of SAR were found within the range 0.8–17.85 with an average value of 3.6. Based on classification (Richards 1954), it is observed that the groundwater of the study area was excellent and good for irrigation purposes. The Wilcox diagram has been prepared to determine the suitability of the groundwater for irrigation purposes (Fig. 9). It is showed that 62% of the samples belong to good water category (C3S1, C2S1), 14% samples belong to moderate water category (C3S2, C3S3), 7% samples fall under bad category (C4S3, C4S2) and 5% samples fall under very bad quality category (C4S4).

**Sodium Percentage (Na%)**

Sodium percentage is a parameter to evaluate the water quality for irrigation purposes. Excess of sodium in water reacts with soil, reduces soil permeability and supports little or no plant growth (Wilcox 1955). Na+% in groundwater ranged from 9 to 60% with an average of 25%. The calculated Na% shows that 87% of all samples fall within the excellent/good for irrigation category and 12.5% fall under permissible category (Table 7).

**Residual sodium carbonate (RSC)**

The sodium hazard also increases, if the water contains a higher concentration of bicarbonate ions. As the soil solution becomes more concentrated, there is a tendency for calcium and magnesium to precipitate as carbonates, thereby increasing the relative proportion of sodium as a consequence. In the present case, RSC was used to quantify the effect of the carbonate and bicarbonate (Eaton 1950) as RSC. Distribution of samples based on RSC value indicated that the majority of the samples fall under doubtful and unsuitable categories for irrigation purposes.

**Impact of land use/land cover change on groundwater depth**

A rapid increase in population has been observed from 59,168 in 1991 and 131,926 in 2011 with the 122% growth (Census of India 1991, 2011). During this period, the settlement area of the main Palwal City has been increased by 177% (Fig. 10). The increased population and associated services withdraw water from local aquifer, resulting in a decline of groundwater level. Time series of the groundwater depths were assessed using the linear regression line method at few locations. The average declining trends of the groundwater level vary from 0.10 to 0.40 m/year, and the spatial trends show minimum decline near the Yamuna flood plain and maximum decline near the Palwal City (Fig. 11). However, the areas near Bhagola village along the canal show a decrease in groundwater depth with a rate of 0.05 m/year. The declining groundwater depth will result in decreasing well productivity in the near future. Deep groundwater is normally associated with solute-enriched groundwater, and this will be further detrimental to the suitability of groundwater for irrigation, drinking and other purposes.

**Conclusions**

Groundwater in the study area is characterized by deep origin as revealed by meteoric genesis index $R_2$. The source of chemical in groundwater is mainly controlled by rock
weathering and evaporation processes. The major portion of ions in groundwater is derived by combined weathering of carbonate and silicate rocks. Durov diagram indicated that dissolution and reverse ion exchange are the major processes that control the hydrochemistry. Spatial variation in the contribution of ion exchange, dissolution and reverse exchange processes is mainly controlled by climatic conditions in the Ganga basin.

Spatial distribution of the fluoride is controlled by rock type and low lying areas, while high Mg$^{2+}$ and SO$_4$$^{2-}$ distribution is associated with urban and peri-urban areas. Groundwater quality index suggested that a fair percentage of water samples fall under the category of very poor (34%) and unsuitable (21%) for drinking purposes. Most of the samples are suitable for irrigation purposes on the basis of SAR. However, continuous usage of groundwater with high TDS with moderate Na% may result in the development of salinity in soil.

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