Geochemical assessment of groundwater quality in vicinity of Bhalswa landfill, Delhi, India, using graphical and multivariate statistical methods

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Abstract A geochemical assessment of groundwater quality and possible contamination in the vicinity of the Bhalswa landfill site was carried out by using a hydrochemical approach with graphical and multivariate statistical methods with the objective of identifying the occurrence of various geochemical processes and understanding the impact of landfill leachates on groundwater quality. Results indicate that nitrate, fluoride and heavy metal pollution are in an alarming state with respect to the use of groundwater for drinking purposes. Various graphical plots and statistical analyses have been applied to the chemical data based on the ionic constituents, water types, and hydrochemical facies to infer the impact of the landfill on groundwater quality. The statistical analysis and spatial and temporal variations indicate the leaching of contaminants from the landfill to the groundwater aquifer system. The concentrations of heavy metals in the landfill leachates are as follows: Fe (22 mg/l), Mn (−20 mg/l), Cu (−10 mg/l), Pb (−2 mg/l), Ni (0.25 mg/l), Zn (−10 mg/l), Cd (−0.2 mg/l), Cl (−4,000 mg/l), SO4 (−3,320 mg/l), PO4 (−4 mg/l), NO3 (30 mg/l) and fluoride (−50 mg/l); all were much higher than the standards. The study reveals that the landfill is in a depleted phase and is affecting groundwater quality in its vicinity and the surrounding area due to leaching of contaminants.

Keywords Landfill · Heavy metals · Leachates · Delhi · Hydrogeochemistry · Groundwater quality

Introduction

The study of hydrogeochemical processes in subsurface water in the vicinity of an unplanned landfill (Bhalswa), Delhi, India, was carried out to understand the impact of the landfill leachates on groundwater quality, which is used for drinking, agriculture and industrial purposes. It helps to understand and distinguish between the rock–water interactions and anthropogenic influences. The geochemical processes occurring within the groundwater and the reaction with aquifer minerals have a profound effect on water quality, and further leaching of pollutants from the landfill causes changes in groundwater quality (Matthess 1982). Groundwater chemically evolves by interaction with aquifer minerals or internal mixing of different groundwaters along subsurface flow-paths (Domenico 1972; Wallick and Toth 1976; Toth 1984). Therefore spatial distribution of chemical species gives some idea about the direction of groundwater movement. Schultz and Kjeldsen (1986) indicate that increases in solute concentration in the groundwater were caused by spatial recharge governed by microtopographic control. Several conventional methods of data analysis are available for simple interpretation and presentation of results (Back 1961; Matthess 1982; Hem 1989), e.g. histograms, trilinear and semilogarithmic diagrams. Multivariate analyses, such as factor analysis, are used simply as a numerical method for discovering variables that are more important than other data for representing parameter variations or demonstrating hydrochemical processes.

As per an estimate of the Central Pollution Control Board (CPCB), the landfills of the National Capital
Territory (NCT), Delhi, cumulatively generate a significant amount of leachates annually, which is alarming in terms of groundwater (CPCB 2001). In many parts of India, especially in the arid and semiarid regions, due to the vagaries of monsoons and scarcity of surface water, dependence on the groundwater resource has increased tremendously in recent years. Viewed from the international standard that "<1,700 m³/person/year" qualifies as water-stressed and "<1,000 m³/person/year" as water-scarce, India is water-stressed today and is likely to face severe water scarcity by 2050 (CPCB 2001). Delhi, as the rapidly growing capital city of Asia, is facing problems in terms of both the groundwater quality and quantity.

The geology of the study area, an older alluvium, makes it more susceptible to leaching. Hence, more attention is needed to understand the processes happening in and around this specific landfill site. A vast amount of literature is available on the presence of heavy metals in the solid wastes (Terao et al. 1993; Tisdell and Breslin 1995; Shivhare and Pandey 1996) and on the acidity of the soil solution and solubility of metals that are closely related (Taylor et al. 1987). According to Taylor et al. (1987), the acidity of soil increases three- to fivefold with an increase in metal concentration. This causes heavy leaching of hazardous metals (Blais et al. 1993). Solid waste that contains metals at low pH has a high pollution potential to contaminate groundwater (Olaninya et al. 1991). In the study area, there has been no documented scientific study on the impact of the Bhalswa landfill leachate on groundwater. Although there are some unpublished reports on fluorosis and major ions by CPCB (2001), no published information with systematic data presentation is available to indicate the impact on the population that is exposed to contaminated groundwater in the surrounding area of the Bhalswa landfill.

Hence, this systematic study was carried out for the first time with the objective of studying the impact of the landfill on groundwater quality, identifying the hydrogeochemical processes related to groundwater quality, conducting a hydrochemical evaluation of the aquifer system and delineating the various factors controlling the water chemistry and general suitability of the groundwater for domestic and drinking purposes in the vicinity of landfill site.

**Study area**

Sampling was carried out for 2 years for an approximately 28-km² area around the Bhalswa landfill, which is located in one of the most urbanized areas of Delhi between latitudes 28°42′30″ and 28°45′N and longitudes 77°07′30″ and 77°11′54″E (Fig. 1). The geology of the study area is mainly alluvium (Fig. 2). Groundwater flow direction in the vicinity of the Bhalswa landfill is shown in Fig. 3a, and a vertical cross-section of unconfined aquifer is shown in Fig. 3b. There are several small patches of aquifers shown in the figures, but scientifically all these comprise a single aquifer system in Delhi (CGWB 1995). The area of the landfill is about 5 ha.

The Delhi region is a part of the Indo-Gangetic Alluvial Plains, at an elevation ranging from 198–220 m above mean sea level. Lithologically, the area is transected by a quartzite rocky ridge—a prolongation of the Aravalli Hills extending along the southern border of Delhi and ending to the north on the west bank of the Yamuna River (Fig. 2). The climate is of semi-arid nature due to marked diurnal differences in temperature, high saturation deficit and low-moderate rainfall. The climate is markedly periodic and is characterized by a dry and gradually increasingly hot season between March and June, a dry and cold winter from October to February and a warm, monsoon period from July to September. The average rainfall is 721 mm/year [Indian Meteorological Department (IMD) 1990–2004, unpublished]. The minimum (average) and maximum (average) temperatures are 19.2 and 31.5°C, respectively, with daily maximum temperatures during the hottest months commonly exceeding 41.2°C.

Physiographically, the region shows major variations, including the Delhi Ridge—an extension 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 bedrock have different natures on either side of the ridge. The nearly closed Chattarpur alluvial basin covering an area about 48 km² is composed of the alluvium derived from the adjacent quartzite ridge alluvial plains on the eastern and western sides of the ridge and Yamuna flood plain deposits. These are of recent origin, also termed newer alluvium. The newer alluvium is characterized by the absence of permanent vegetation due to periodic flooding and lack of kankar.

The thickness of the 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 the alluvium in the region of the Yamuna River on the east side of the ridge is about 165 m (CGWB 2003).

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 calcrite depositions in places (Wadia 1981). The alkaline soils contain sodium bicarbonate and carbonate among the soluble salts, while the saline soils are impregnated with sodium chloride and sulphate as the main soluble salts. The distribution of these soils divides the
study region into geographical subregions. The northwest region is covered by calcareous, silt clay loam; the northeast soils are calcareous, silt, and clay; and the southern parts are sandy-loam type.

**Methodology**

To understand the general variation in groundwater chemistry over the study area, a well inventory survey was carried out during March 2004; electrical conductivity (EC), pH and temperature (°C) were measured. A Garmin global positioning system (GPS) was used for location and elevation readings and cross-checked against topographic sheets made available by the Geological Survey of India (GSI). These data were used to select the representative wells and hand pumps for groundwater sampling. Sampling wells were selected to represent different geological formations, land-use patterns, and the varying topography of study area. Sampling was done for an area about 28 km² around the landfill two times a year as the monsoon period changes in India. The sampling was done pre- and post-monsoon in 2004 and 2005 (2 years). The sampling locations were chosen carefully in order to get maximum representation of the variation in and around the landfill on the basis of the different land-use patterns with due consideration to the hydrogeological set-up.

Groundwater samples were collected in 500-ml clean bottles and capped airtight. The parameters [pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS) and temperature] were analyzed or measured in the field at the time of sampling by using a water-analyzer kit and cross-checked in laboratory. For cations, 100-ml samples were filtered using 0.45-μm filter paper and preserved on site with ultra pure nitric acid (boric acid was used as a preservative for nitrate), and stored at 4°C to avoid any major chemical alteration (APHA 1995). Sodium and potassium were analyzed by an AIMIC, PE I Flame photometer following the standard method (APHA1995). An atomic absorption spectrophotometer (AAS-900) was used for analysis of heavy metals (Mn, Fe, Cu, Ni and Zn) and alkaline earth metals (Mg and Ca). Anions (SO$_4^{2-}$, NO$_3^-$, F$^-$ and silicate) were analyzed by using a JENWAY 6505.
UV/Vis spectrophotometer, using the standard method as given in APHA (1995). HCO$_3^-$ and Cl$^-$ were analyzed by titration method using the standard procedure as given in APHA (1995). The landfill leachates were collected according to standard procedure as explained by Kumar and Alappat (2005) and Christensen et al. (2001) and analyzed in the School of Environmental Sciences, Jawaharlal Nehru University, India.

**Results and discussion**

The distribution pattern of major cations and anions in groundwater in the vicinity of the landfill in all seasons was as follows: Na$^+$ >> Ca$^{2+}$ > Mg$^{2+}$ > K$^+$ and Cl$^-$ >> SO$_4^{2-}$ > HCO$_3^-$ > F$^-$.

The analytical precision of the data was measured using the normalized inorganic charge balance (Huh et al. 1998), which is defined as $|\left(\sum^+ - \sum^-\right)/\left(\sum^+ + \sum^-\right)|$ and represents the fractional difference between the total cations and total anions (Edmond et al. 1995). Most of the groundwater samples showed good charge balance with ±5.0% error, which is generally considered acceptable because it is very difficult to analyze all cations and anions (Berner-Kay and Berner 1987; Edmond et al. 1995; Huh et al. 1998). According to Huh et al. (1998), the analysis of major ions (Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, HCO$_3^-$) is generally enough to give a charge balance because it represents maximum concentrations of available dissolved ions in freshwater.

Most of the water samples showed a charge balance mainly with positive-charge excess except for a few
samples with some negative-charge deficit. Positive-charge excess greater than 5% agrees with the database on the dissolved load near the Yamuna River (Sharma et al. 2004). The negative-charge deficit could be related to the fact that no analysis was made for organic matter (Berner-Kay and Berner 1987; Edmond et al. 1995; Huh et al. 1998).

Water chemistry and leachate composition

The average, maximum, minimum and standard deviation for each water quality parameter analyzed for both pre-monsoon and post-monsoon samples for year 2004 and 2005 are shown in Table 1. The average concentrations of various anions, cations, and heavy metals in the groundwater aquifer at radial distances from the landfill are shown in Table 2. The data indicate the landfill as the point source for all the contaminants because groundwater flow is outward away from the Bhalswa landfill (Fig. 3a), and the concentration of pollutants decreases radially as we move away from the landfill along the groundwater flow (Table 2). Groundwater flow helps in dispersion and diffusion of leached contaminants in the groundwater aquifer system, but there is variation at different depths of water samples because leachate movements in groundwater vary with hydraulic gradient much faster in the X–Y coordinate in comparison to the Z coordinate.

Groundwater pH around Bhalswa landfill is slightly alkaline due to the influx of HCO₃⁻ ions in subsurface water with rainwater through various ion-exchange processes in the aquifer system (Table 1). Figure 4a indicates an unexpected rise in DO over a short period of observation (600 days) due to the high inorganic activity/content in the water, which is believed to inhibit the consumption of oxygen by microorganisms (Srivastava and Ramanathan 2006).

The spatial and temporal variation in EC around the landfill is shown in Fig. 5b₁,b₂. The variation occurs due to spatial and temporal changes in the migration of contaminants from landfill leachates, indicated by the clustering of contour lines in and around the landfill. A few samples in Bhalswa Dairy village, which is located close to the landfill where the landfill leachates quickly seep into the groundwater, showed exceptionally high EC, i.e., 2,800 µS/cm (Fig. 5b₁,b₂). In general EC is high in Bhalswa Dairy village, and other areas, including Shalimar Village, J. J. Colony, Badali and Ramgarh, showed comparatively high EC values in their groundwater samples. Chloride and sulphate concentrations were also highest in this region, i.e., around 1,000 and 550 mg/l, respectively. The contour lines indicate high concentrations around Bhalswa Lake because it is acting as a pond to receive leachates from Bhalswa landfill.

The average values for chloride and other anions (SO₄²⁻, NO₃⁻, F⁻) are higher post-monsoon than pre-monsoon perhaps due to the rise in the water table post-monsoon, which allows salts coated in soil to dissolve in rainwater (Ramesam 1982; Ballukray and Ravi 1999; Jalali 2005) (Table 1). The other source of these anions is leachates that seep along with the rainwater, a hypothesis that is
Table 1  Summary of statistics of chemical parameters pre- and post-monsoon

| Parameter | Year 2004 | | | Year 2005 | | | |
|-----------|-----------|-----------|------------|-----------|-----------|------------|-----------|
|           | Pre-monsoon | Post-monsoon | Pre-monsoon | Post-monsoon | Pre-monsoon | Post-monsoon | |
|           | Min | Max | Avg | SD | Min | Max | Avg | SD | Min | Max | Avg | SD | Min | Max | Avg | SD |
| Temperature (°C) | 22.5 | 35.1 | 26.8 | NA | 22.7 | 36.2 | 27.8 | NA | 19.2 | 28.4 | 23.4 | NA | 144 | 188 | 167.27 | 9.80 |
| pH | 6.34 | 7.87 | 7.06 | 0.26 | 6.29 | 7.64 | 7.17 | 0.29 | 6.61 | 7.91 | 7.56 | 0.26 | 7.09 | 8.49 | 7.82 | 0.35 |
| Eh (mV) | 140 | 178 | 160.27 | 9.6 | 146 | 177 | 161.57 | 19.64 | 144 | 188 | 167.27 | 9.80 | 165 | 186 | 167.21 | 9.76 |
| EC (µS/cm) | 748 | 3,256 | 1,839.6 | 812.63 | 694 | 2,974 | 1,670.87 | 724.33 | 768 | 3,600 | 2,139.66 | 842.63 | 648 | 3,171 | 1,691.21 | 784.75 |
| TDS (mg/l) | 477 | 2,042 | 1,170.6 | 502.55 | 464 | 2,014 | 1,149.12 | 502.37 | 487 | 2,059 | 1,183.6 | 502.55 | 494 | 2,064 | 1,183.78 | 506.81 |
| Cl⁻ (mg/l) | 142.4 | 1,019.7 | 434.04 | 225.55 | 133.49 | 1,174.75 | 445.55 | 241.5 | 162.41 | 1,129.7 | 467.04 | 214.5 | 73.15 | 313.16 | 168.12 |
| SO₄²⁻ (mg/l) | 61.45 | 551.47 | 238.9 | 129.01 | 58.45 | 591.47 | 222.14 | 118.19 | 58.45 | 591.47 | 222.14 | 118.19 | 58.45 | 591.47 | 222.14 | 118.19 |
| HCO₃⁻ (mg/l) | 8.03 | 43.46 | 19.98 | 9.62 | 9.52 | 46.46 | 29.90 | 10.62 | 10.02 | 55.16 | 33.72 | 10.96 |
| NO₃⁻ (mg/l) | 4.98 | 41.66 | 22.02 | 10.09 | 3.71 | 49.66 | 28.02 | 9.09 | 6.07 | 45.05 | 27.47 | 11.08 |
| Mg²⁺ (mg/l) | 14.45 | 48.07 | 24.98 | 9.34 | 11.3 | 42.41 | 20.66 | 8.49 | 15.45 | 58.07 | 34.98 | 9.54 | 13.44 | 51.48 | 33.32 | 8.95 |
| Ca²⁺ (mg/l) | 68.94 | 215.49 | 101.08 | 40.88 | 88.94 | 315.49 | 156.08 | 60.88 | 73.46 | 291.84 | 146.49 | 49.19 |
| Mn (mg/l) | 0.02 | 1.00 | 0.51 | 0.57 | 0.02 | 1.61 | 0.44 | 0.48 | 0.02 | 1.00 | 0.51 | 0.57 | 0.02 | 1.00 | 0.51 | 0.57 |
| Fe (mg/l) | 0.01 | 0.12 | 0.05 | 0.09 | 0.01 | 0.60 | 0.13 | 0.15 | 0.01 | 0.22 | 0.09 | 0.13 | 0.01 | 0.22 | 0.09 | 0.13 |
| Zn (mg/l) | 0.01 | 0.12 | 0.05 | 0.09 | 0.01 | 0.60 | 0.13 | 0.15 | 0.01 | 0.22 | 0.09 | 0.13 | 0.01 | 0.22 | 0.09 | 0.13 |
| Cu (mg/l) | 0.01 | 0.12 | 0.05 | 0.09 | 0.01 | 0.60 | 0.13 | 0.15 | 0.01 | 0.22 | 0.09 | 0.13 | 0.01 | 0.22 | 0.09 | 0.13 |
| Ni (mg/l) | 0.01 | 0.12 | 0.05 | 0.09 | 0.01 | 0.60 | 0.13 | 0.15 | 0.01 | 0.22 | 0.09 | 0.13 | 0.01 | 0.22 | 0.09 | 0.13 |

Min Minimum, Max maximum, Avg average, SD standard deviation
Table 2 Cation, anion and heavy-metal concentrations at radial distances from landfill

| Cation/anion/heavy metal | \( \leq 75 \text{ m} \) | \( 75 < X \leq 500 \text{ m} \) | \( 500 < X \leq 1,000 \text{ m} \) | \( 1,000 < X \leq 1,500 \text{ m} \) | \( 1,500 < X \leq 2,000 \text{ m} \) | \( 2,000 < X \leq 2,500 \text{ m} \) |
|--------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| EC (\( \mu \text{S/cm} \)) | 3,540 | 2,673 | 2,349 | 2,102 | 1,487 | 789 |
| Cl\(^-\) (mg/l) | 1,174.20 | 1,032.24 | 845.45 | 543.12 | 324.23 | 135.36 |
| SO\(_4^{2-}\) (mg/l) | 610.22 | 534.13 | 411.89 | 265.23 | 100.12 | 56.12 |
| HCO\(_3^-\) (mg/l) | 307.56 | 277.56 | 196.04 | 123.56 | 76.43 | 65.12 |
| NO\(_3^-\) (mg/l) | 53.45 | 44.23 | 36.13 | 24.03 | 11.23 | 8.03 |
| F\(^-\) (mg/l) | 9.43 | 7.23 | 6.71 | 5.86 | 3.21 | 2.01 |
| Na\(^+\) (mg/l) | 776.20 | 623.12 | 567.34 | 403.12 | 192.45 | 45.46 |
| K\(^+\) (mg/l) | 46.65 | 32.02 | 23.45 | 19.23 | 8.92 | 3.71 |
| Mg\(^{2+}\) (mg/l) | 57.53 | 48.76 | 29.34 | 25.32 | 15.23 | 11.3 |
| Ca\(^{2+}\) (mg/l) | 312.54 | 273.06 | 211.77 | 165.93 | 99.61 | 40.88 |
| Mn (mg/l) | 2.60 | 2.55 | 1.97 | 1.32 | 0.76 | 0.01 |
| Fe (mg/l) | 7.04 | 6.53 | 5.11 | 3.61 | 1.73 | 0.64 |
| Zn (mg/l) | 3.37 | 3.27 | 2.14 | 1.11 | 0.56 | 0.09 |
| Cu (mg/l) | 0.10 | 0.08 | 0.06 | 0.05 | 0.02 | 0.01 |
| Ni (mg/l) | 0.43 | 0.32 | 0.22 | 0.13 | 0.06 | 0.02 |

X Distance from landfill

Fig. 4 Temporal variation in EC, DO, pH, Fe\(^{2+}\), SO\(_4^{2-}\) and other cations and anions in groundwater around landfill.
supported by the variation in the different parameters with distance (Table 2). The high-concentration contour lines for the anions around the landfill indicate possible anthropogenic input of these contaminants, i.e. leaching of these anions from the landfill. The landfill leachates contain high concentrations of $\text{Cl}^-$ ($\sim$4,000 mg/l), $\text{NO}_3^-$ ($\sim$30 mg/l), $\text{F}^-$ ($\sim$50 mg/l) and $\text{PO}_4^{3-}$ ($\sim$4 mg/l), values that are higher than the values recommended by the Central Pollution Control Board (CPCB 2001), Delhi, India. The Bhalswa Dairy Village, Ramgarh and Yadva Nagar show comparatively high concentrations, perhaps due to migration of contaminant plume with groundwater flow.

Generally the major sources for nitrate in groundwater include domestic sewage, runoff from agricultural fields, and leachates from landfill sites (Lee et al. 2003; Jalali 2005). The groundwater samples collected around the landfill show that the nitrate concentration in the groundwater is very close to the concentration observed in Fig. 5 Spatial distribution of different anions and heavy metals in groundwater around landfill.
leachate (Tables 1, 3). This indicates that the vertical soil profile of the landfill is highly saturated with nitrate, which enables a large quantity of nitrate to seep out from the landfill to the groundwater. The hypothesis that the landfill serves as a point source for nitrate is also justified by the study of nitrate levels with distance from the landfill as shown in Table 2; statistical analysis supports this view. In general, Bawana and J. J. Colony show very high concentrations of nitrate, indicating anthropogenic input in the groundwater aquifer system (Jalali 2005). The spatial and temporal variations in nitrate concentration around the landfill indicate possible leaching of contaminants from the landfill because the Bhalswa landfill is the only known point source in this area (Fig. 5d1, d2).

The concentration of fluoride in groundwater is principally governed by climate, the composition of the host rock
The major source of fluoride in the study area is the fluorite minerals in the bedrock of the Aravalli ridge, which is located very close to the Bhalswa landfill and passes midway through Delhi. Areas with a semiarid climate, crystalline rocks and alkaline soils are mainly affected by fluoride (Handa 1975). This is probably due to higher TDS in groundwater resulting in an increased ionic strength and higher fluorite (CaF$_2$) solubility. Fluorite is the principal bearer of fluoride and is found in granite, gneiss, and pegmatite (Rama Rao 1982). Fluoride is released to the soil and groundwater by the process of weathering of primary rock or leaching of landfill contaminants (Sujatha 2003). When fluoride is released into the soil and groundwater, the concentration may increase until saturation is reached (Handa 1975). The alkaline water can mobilize fluoride from fluorite (CaF$_2$) with the simultaneous precipitation of CaCO$_3$ because the solubility of CaF$_2$ increases with an increase in NaHCO$_3$ rather than with salts NaCl, Na$_2$SO$_4$, MgCl$_2$, and MgSO$_4$ (Ramamohan Rao et al. 1993; Saxena and Ahmad 2001, 2003).

Minerals rich in CaCO$_3$ can also favor the dissociation of fluoride from fluorine-containing minerals, as given below:

\[
\text{CaF}_2 + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2
\]  
(1)

\[
\text{CaF}_2 + 2\text{NaHCO}_3 \leftrightarrow \text{CaCO}_3 + 2\text{Na}^+ + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2
\]  
(2)

where K is an equilibrium constant and a is the activity. It is evident that if the pH is constant, the activity of fluoride is directly proportional to bicarbonate. Fluorite and mica bedrock are the major sources in Delhi of fluoride, which is released by an ion-exchange process between the OH$^-$ ion from water and the F$^-$ ion from the mica bed (CGWB 1995). The spatial distributions indicate the landfill is one of the sources of fluoride in the groundwater aquifer system in the study area (Fig. 5c). It is also possible that the evaporation/weathering process would cause an increase in concentrations of all species in groundwater, but in practice, the spatial distribution of these species shows that the major source of chloride, nitrate, fluoride and other heavy metals is the landfill leachates.

The Bhalswa landfill leachates contain more than 3,000 mg/l of sodium (Table 3). Sodium concentration variation in the groundwater aquifer in the vicinity of the landfill for 600 days is shown in Fig. 4, which shows a

**Table 3** Heavy-metal, cation and anion concentration analyzed in Delhi landfill leachates

| Parameters    | Observed concentrations (2004) | Observed concentrations (2005) | Recommended | References |
|---------------|--------------------------------|--------------------------------|-------------|------------|
| pH            | 4–13                           | 5–13                           | 4–12        | CPCB 2001  |
| Iron          | 20 mg/l                        | 22 mg/l                        | –           | Not available |
| Lead          | <2 mg/l                        | <2.2 mg/l                      | <2 mg/l     | CPCB 2001  |
| Cadmium       | 0.2 mg/l                       | 0.25 mg/l                      | <0.2 mg/l   | CPCB 2001  |
| Copper        | <10 mg/l                       | <12 mg/l                       | <10 mg/l    | CPCB 2001  |
| Nickel        | <3 mg/l                        | <3.5 mg/l                      | <3 mg/l     | CPCB 2001  |
| Zinc          | <10 mg/l                       | <11 mg/l                       | <10 mg/l    | CPCB 2001  |
| Manganese     | 20 mg/l                        | 25 mg/l                        | –           | Not available |
| Sodium        | 2,640 mg/l                     | 3,150 mg/l                     | –           | Not available |
| Calcium       | 687 mg/l                       | 703 mg/l                       | –           | Not available |
| Magnesium     | 151 mg/l                       | 167 mg/l                       | –           | Not available |
| Potassium     | 119 mg/l                       | 132 mg/l                       | –           | Not available |
| Fluoride      | <50 mg/l                       | <54 mg/l                       | <50 mg/l    | CPCB 2001  |
| Sulphate      | 3,320 mg/l                     | 3,375 mg/l                     | –           | Not available |
| Nitrate       | <30 mg/l                       | <45 mg/l                       | <30 mg/l    | CPCB 2001  |
| Chloride      | 4,000 mg/l                     | 4,500 mg/l                     | –           | Not available |
| Phosphate     | 4 mg/l                         | 4.4 mg/l                       | –           | Not available |
| Bicarbonate   | 412 mg/l                       | 431 mg/l                       | –           | Not available |
consistent increase in sodium concentration in groundwater with time, indicating possible anthropogenic input via landfill leachates. Our study shows comparatively less K⁺ because the study area (Delhi) soils have significant amounts of illite, which fixes K⁺ from water. Hence groundwater in Delhi has low K⁺ values (Subramanian and Saxena 1983).

Hydrogeochemical evaluation

The geochemical variations in the ionic concentrations in the groundwater can easily be understood when they are plotted along an X–Y coordinate (Guler et al. 2002). Results from the chemical analyses were used to identify the geochemical processes and mechanisms in the groundwater aquifer system. Most of the samples have an Na/Cl ratio around or above 1 pre-monsoon and less than 1 post-monsoon, indicating that an ion-exchange process is prevalent in the study area (Fig. 6a) (Kumar et al. 2006).

The graph of Ca²⁺ + Mg²⁺ versus SO₄²⁻ + HCO₃⁻ will feature a nearly 1:1 line if dissolutions of calcite, dolomite and gypsum are the dominant reactions in the system. Ion exchange tends to shift the points right because of the excess of SO₄²⁻ + HCO₃⁻ ions, which may be due to anthropogenic input in the groundwater system (Cerling et al. 1989; Fisher and Mulican 1997). The graph of Ca²⁺ + Mg²⁺ versus SO₄²⁻ + HCO₃⁻ shows most of samples fall above the 1:1 ratio line except for a few post-monsoon samples, indicating the predominance of the ion-exchange process in the groundwater system, which indicates possible leaching of these anions from the landfill (Fig. 6b) (Kumar et al. 2006).
The graph of $\text{Na}^+$ versus NO$_3$ shows most of the groundwater samples scattered and falling above the equilene 1:1, which suggests anthropogenic input into the groundwater system because nitrate is released in groundwater mainly from anthropogenic sources (Lee et al. 2003; Subba Rao 2002) (Fig. 6c). Since a major source of pollutants in this area is the Bhalswa landfill, an assumption of possible leaching of nitrate from the landfill is justified by the nitrate contour lines around the landfill.

The source of Ca and Mg in the groundwater can be deduced from the $m(\text{Ca}^{2+} + \text{Mg}^{2+})/m(\text{HCO}_3^\text{-})$ ratio. If calcium and magnesium originate solely from dissolution of carbonate in the aquifer from the weathering of accessory pyroxenes and amphibole minerals, the ratio would be about 0.5 (Sami 1992). The fact that this ratio increases with salinity shows that Ca and Mg are released into the groundwater aquifer faster than bicarbonate, indicating some anthropogenic input in the aquifer system (Kumar et al. 2006) (Fig. 6d).

The graph of $\text{TZ}^+$ (total cation) versus $\text{Ca}^{2+} + \text{Mg}^{2+}$ shows most of the samples far below the theoretical line (1:1) (Fig. 6e), indicating an increasing contribution of alkalis to the major ions, which indicates anthropogenic input in the groundwater (Subba Rao and Devadas 2003). The increase in alkalis with a simultaneous increase in Cl$^-$ + SO$_4^{2-}$, which suggests a common source of these ions, as well as the presence of Na$_2$SO$_4$ and K$_2$SO$_4$ in the soils indicates leaching of these ions from landfill leachates (Datta et al. 1996) (Fig. 6f). The dominance of $\text{Na}^+$, an index of weathering, suggests that the ions result from dissolution of soil salts or are derived from landfill leachates, which also suggests that the higher concentration of alkalis is from sources other than precipitation (Singh and Hasnain 1999). All this indicates a significant effect of landfill leachates on the hydrogeochemical process occurring in groundwater aquifer systems in the vicinity of Bhalswa landfill.

Heavy metals in leachates and groundwater

Heavy-metal concentrations in groundwater and landfill leachates are shown in Tables 1 and 3, respectively, while spatial and temporal variation of heavy metals in the groundwater around the landfill is shown in Fig. 5e$1$, e$_2$, f$1$, f$_2$. The contour lines around the landfill show a high concentration of heavy metals around Bhalswa Lake because it works like a leachate pond for the Bhalswa landfill, while the temporal variation indicates a consistent increase in heavy metals in groundwater.

The major anthropogenic source of iron and other iron-containing alloys in groundwater is steel industry waste, which is dumped in the landfill without prior treatment (European Commission Report 2002). The steel industry generally dumped their effluents in nearby landfills that contain high concentrations of iron; over time, the iron seeps into groundwater from landfills with rainwater in monsoon period. The iron can be released into the groundwater by natural processes such as oxidation-reduction reactions, ion-exchange processes and other physiochemical reactions in the groundwater aquifer system (Roger 1996; Drever 1997). The spatial distribution shows some areas are highly contaminated, including the Badali Industrial Area, Rajasthan Industrial Area, and Bhalswa Dairy village, because all these areas are located very close to the landfill, which acts as a point source for these heavy metals because landfill leachates contain high concentrations of heavy metals (Fig. 5e$1$, e$_2$). The hypothesis that the heavy metals originate from the landfill is also justified because there is no known natural source of these heavy metals in the study area. High concentrations of other heavy metals (Mn, Ni, Cu, Zn Pb) were observed, which is hazardous for health (Table 1).

Statistical analysis

Numerical analysis of hydrogeochemical data has been attempted to determine the geochemical parameters of groundwater (Lawrence and Upchurch 1982). Correlation and factor analysis are widely used in statistical or numerical concepts for parametric classification of modeling studies (Balasubramanian et al. 1985). Statistical data generally provide a better representation than graphical data because (1) there is a finite number of variables that can be considered, (b) variables are generally limited by convention to major ions, and (c) superior relationships may be deduced by use of certain procedures.

Correlation matrix

The correlation matrix for groundwater samples collected around the Bhalswa landfill is shown in Table 4. Good correlation was observed between TDS and EC, $\text{F}^-$ and EC, $\text{Na}^+$ and EC, $\text{K}^+$ and EC, HCO$_3^-$ and EC, $\text{Zn}$ and EC, $\text{Ca}^{2+}$ and Cl$^-$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$, $\text{Ca}^{2+}$ and $\text{Na}^+$, $\text{Ca}^{2+}$ and SO$_4^{2-}$, $\text{Ca}^{2+}$ and $\text{K}^+$, $\text{Na}^+$ and $\text{Mg}^{2+}$, $\text{Mg}^{2+}$ and Cl$^-$, $\text{Mg}^{2+}$ and SO$_4^{2-}$, $\text{Ca}^{2+}$ and $\text{F}^-$, $\text{Na}^+$ and Cl$^-$, $\text{Na}^+$ and $\text{F}^-$, $\text{Na}^+$ and SO$_4^{2-}$, and $\text{Na}^+$ and $\text{K}^+$, indicating that all of them have the same origin (Chidambram and Ramanathan 2000) (Table 4). Almost all analyzed metals showed good correlation with conductivity because conductivity increases with dissolution of metals through ion exchange or oxidation-reduction reaction in a groundwater aquifer system (Subba Rao 2002).
Sodium showed good correlation with chloride (0.99), indicating anthropogenic input in groundwater, and moderate correlation with fluoride (0.56), zinc (0.78) and iron (0.55), indicating input of heavy metals including fluoride in groundwater through leaching of landfill (Kumar and Alappat 2005) (Table 4). Chloride showed moderate correlation with HCO₃⁻ (0.54). Calcium showed quite good correlation with sulphate (0.92), indicating that a major source of calcium in groundwater is gypsum, as the geology of the study area also contains a high concentration of gypsum (Fig. 2), while both calcium and magnesium showed moderate correlation with sodium and potassium, indicating a possible ion-exchange process in the groundwater aquifer system (Drever 1997; Mahlknecht 2003). Nitrate showed moderate correlation with bicarbonate (0.56), indicating some ion-exchange process in the groundwater aquifer system. Nitrate also showed moderate correlation with copper (0.44), indicating some anthropogenic source (Table 4).

EC and TDS (0.99) showed a good correlation in pre-monsoon as well as post-monsoon samples because conductivity increases as the concentration of all dissolved constituents/ions increases, while seasonal variation occurs due to dilution of the groundwater in differing proportions during the monsoon period (Rajmohan and Elango 2004). EC showed good correlation with Zn (0.75), HCO₃⁻ (0.71), F⁻ (0.78) and moderate correlation with Fe (0.58), Na (0.52), K (0.51), Cl⁻ (0.51) and Cu (0.48), indicating most of the ions are involved in various physiochemical reactions, such as oxidation–reduction and ion exchange in the groundwater aquifer system (Subba Rao 2002). Zinc (0.79) and iron (0.61) showed good correlation with chloride, indicating that a possible anthropogenic source may be the leaching alloy or salt present in industrial effluent dumped in the landfill (Mahlknecht et al. 2004). Iron showed good correlation with chloride (0.61) and zinc (0.68), indicating leaching of steel and alloys from an anthropogenic source. But this correlation also indicates anthropogenic input into the groundwater system because its value is just average, indicating free dumping of iron material into the groundwater system.

The negative correlation between ORP and TDS and EC and ORP indicates the input of additional ions from multiple sources (Drever 1997). EC-ORP correlation (~0.90) pre-monsoon and post-monsoon indicates dissolution of metal ions in a reducing atmosphere (Subba Rao 2002). In general, highly polluted groundwater samples have low oxidation-reduction potential because of the reducing atmosphere. Most of the samples in the vicinity of the Bhalswa landfill show low oxidation-reduction potential, which indicates a reducing atmosphere in the groundwater in the vicinity of the Bhalswa landfill.

Factor analysis

Factor analysis is one of the most important statistical methods for interpretation of hydrochemistry of groundwater (Subba Rao 2002). Mahlknecht (2003) presented molar relationships to elucidate factors controlling geochemical reactions in the groundwater aquifer. In our study, factor analyses

| Table 4 Correlation matrix |
|-----------------------------|
| ORP | EC | TDS | Na⁺ | K⁺ | Mg²⁺ | Ca²⁺ | Mn²⁺ | Fe²⁺ | Zn²⁺ | Cu²⁺ | Ni²⁺ | F⁻ | Cl⁻ | SO₄²⁻ | NO₃⁻ | HCO₃⁻ | PO₄³⁻ |
| ORP | 1  |     |     |     |     |     |     |     |     |     |     |     |     |     |       |       |       |       |
| EC  | -0.91 | 1  |     |     |     |     |     |     |     |     |     |     |     |     |       |       |       |       |
| TDS | -0.92 | 0.99 | 1  |     |     |     |     |     |     |     |     |     |     |     |       |       |       |       |
| Na⁺ | -0.45 | 0.52 | 0.50 | 1  |     |     |     |     |     |     |     |     |     |     |       |       |       |       |
| K⁺  | -0.39 | 0.51 | 0.48 | 0.48 | 1  |     |     |     |     |     |     |     |     |     |       |       |       |       |
| Mg²⁺| 0.02  | 0.02 | 0.01 | 0.38 | 0.28 | 1  |     |     |     |     |     |     |     |     |       |       |       |       |
| Ca²⁺| 0.06  | -0.07 | -0.07 | 0.37 | 0.24 | 0.96 | 1  |     |     |     |     |     |     |     |       |       |       |       |
| Mn²⁺| 0.02  | 0.16 | 0.12 | 0.26 | 0.10 | 0.37 | 0.34 | 1  |     |     |     |     |     |     |       |       |       |       |
| Fe²⁺| -0.42 | 0.58 | 0.47 | 0.55 | 0.33 | 0.51 | 0.48 | 0.53 | 1  |     |     |     |     |     |       |       |       |       |
| Zn²⁺| -0.63 | 0.75 | 0.69 | 0.78 | 0.57 | 0.29 | 0.25 | 0.38 | 0.68 | 1  |     |     |     |     |       |       |       |       |
| Cu²⁺| -0.36 | 0.48 | 0.39 | 0.02 | 0.11 | -0.38 | -0.39 | -0.37 | -0.16 | -0.01 | 1  |     |     |     |       |       |       |       |
| Ni²⁺| 0.08  | -0.11 | -0.12 | 0.29 | -0.11 | 0.01 | -0.09 | 0.30 | 0.11 | 0.09 | -0.36 | 1  |     |     |       |       |       |       |
| F⁻ | -0.72 | 0.78 | 0.79 | 0.56 | 0.52 | 0.02 | 0.01 | 0.11 | 0.47 | 0.53 | 0.48 | -0.27 | 1  |     |       |       |       |       |
| Cl⁻ | -0.45 | 0.51 | 0.48 | 0.99 | 0.44 | 0.46 | 0.41 | 0.25 | 0.61 | 0.79 | 0.01 | 0.29 | 0.49 | 1  |       |       |       |       |
| SO₄²⁻| 0.13 | -0.10 | -0.10 | 0.28 | 0.30 | 0.91 | 0.92 | 0.24 | 0.54 | 0.19 | -0.36 | -0.12 | -0.01 | 0.35 | 1  |       |       |       |
| NO₃⁻| -0.33 | 0.39 | 0.37 | 0.22 | 0.31 | -0.29 | -0.32 | -0.26 | -0.03 | 0.18 | 0.44 | 0.18 | 0.22 | 0.15 | -0.29 | 1  |       |       |
| HCO₃⁻| -0.58 | 0.71 | 0.70 | 0.54 | 0.65 | -0.01 | -0.06 | 0.14 | 0.39 | 0.76 | 0.20 | -0.03 | 0.58 | 0.54 | -0.12 | 0.56 | 1  |       |
| PO₄³⁻| 0.57 | -0.48 | -0.49 | -0.35 | -0.03 | 0.27 | 0.22 | -0.02 | -0.29 | -0.33 | -0.31 | -0.11 | -0.58 | -0.35 | 0.28 | -0.16 | -0.29 | 1  |
were used as an alternative tool for corroboration of the concept obtained from molar calculation. Factor analyses allow for determination of basic independent dimensions of variables (Chidambaram and Ramanathan 2000). The factor analysis in this study was carried out by using SPSS. The software provides a numerical value resulting from different variants as components and initial eigenvalues for each species (Table 5). With the help of linear combinations, an originally large number of variables can be reduced to a few factors. These factors can be interpreted in terms of new variables. There exist numerous solution methods and variations for determination of factors (Mahlknecht et al. 2004).

Principal component analyses (PCA), which aim to load most of the total variance into one factor, are used in the present case, and factors were extracted through the principal extraction method (Mahlknecht et al. 2004). The varimax rotation-one factor, which explains mostly one variable, was selected. In order to limit the number of factors to be extracted, only factors with eigenvalues higher than one were taken into consideration (Kaiser normalization). Creating a distribution map of the factor scores in this way tests the usefulness of the results, and the factor scores are a measure of the statistical weight of each case on the extracted factors.

Factor analysis as applied to widely differing sets of groundwater hydrogeochemical data appears to be moderately successful as a statistical tool for revealing hydro-chemical and hydrogeological features (Mahlknecht et al. 2004). The aim of the factor analysis of the hydrogeochemical data is to explain the observed relationship in simple terms expressed as a new set of variables called factors. The factor analysis model is assumed to represent an overall variance of the data set and structure expressed in the pattern of variance and covariance between the variables and the similarities between the observations (Davis 1986). Contribution of a factor is said to be significant when the corresponding eigenvalue is greater than unity (Briz Kishore and Murali 1992). In general, the factor will be related to the largest eigenvalue and will explain the greatest amount of variance in the data set. The factor analysis of groundwater data around the Bhalswa landfill is shown in Table 5.

Factor I of the principal component factor matrix of groundwater data around the Bhalswa landfill is characterized by the strong loading of Ca$^{2+}$, Mg$^{2+}$ and SO$_4^{2-}$ ions, which accounts for 22.29% of the variance in pre-monsoon samples and 19.72% of total variance in post-monsoon samples. The strong loading of Ca$^{2+}$ and SO$_4^{2-}$ indicates weathering of gypsum, which is believed to be available in the geology of Delhi.

Factor II of the principal component factor matrix of groundwater data around the Bhalswa landfill is characterized by the strong loading of Na$^+$, K$^+$ and F$^-$ ions with alkali and alkaline earth metals indicates anthropogenic input in the groundwater system, it may be due to leaching of industrial effluents from the landfill (Kumar and Alappat 2005). The strong loading of HCO$_3^-$ ions with alkali and alkaline earth metals supports the view of natural weathering sources. The high variance in Na$^+$, K$^+$ and F$^-$ indicates an anthropogenic input into the aquifer system (Mahlknecht et al. 2004). There were no known natural sources of fluoride in Bhalswa landfills; the hypothesis of anthropogenic input is also justified by the spatial distribution of F$^-$ ions around the landfill (Fig. 5c1, c2).

Factor IV is characterized by the strong loading of NO$_3^-$ ions, indicating an anthropogenic input in the groundwater system due to leaching of fertilizer from agriculture land (Mahlknecht et al. 2004) or leaching from the municipal landfill (Kumar and Alappat 2005), while spatial distribution of NO$_3^-$ around the landfill indicates possible leaching of NO$_3^-$ from the landfill (Fig. 5d1, d2). Factor V indicates groundwater chemistry is controlled by the pH variation in the aquifer system.

Classification of water types

According to Wilcox (1955), water samples can be divided into five divisions on the basis of the percentage of Na and the EC value, as shown in Table 6. Based on the Na %, about 42.42% of our groundwater samples were within permissible limits, 48.48% were doubtful, 3.03% were unsuitable and 6.06% were good. On the basis of EC, 63.64% of our groundwater samples were permissible, 30.30% were doubtful and 6.06% were good. Seasonal variations in groundwater quality were also seen but were very small.

Richard (1954) classified water quality on the basis of sodium absorption ratio (SAR) as shown in Table 6. According to Richard’s classification, 81.81% of our groundwater samples were excellent and 18.19% were good. Stuyfzand (1989) classified water on the basis of Cl$^-$ ion concentration into eight divisions as shown in
According to Stuyfzand, 63.64% of our groundwater samples were brackish, 27.27% were fresh-brackish, 6.06% were fresh and 3.03% were brackish-salt on the basis of Cl− concentration. USSL (1954) classification is based on the concentration of total dissolved solids as shown in Table 6. According to USSL classification, 60.60% of our groundwater samples showed total dissolved solids concentrations in the range of 500–1,500 mg/l, 36.36% were in the range of 1,500–3,000 mg/l and 3.03% were in the range of 200–500 mg/l. Eaton also classified water quality on the basis of percentage of Na in water. According to the Eaton Classification (Eaton 1954), 48.48% of our groundwater samples were safe, while 51.52% were unsafe for use.

Graphical representation of water quality data

Most of the graphical methods are designed to simultaneously represent the total dissolved solids concentrations and the relative proportions of certain major ionic species (Hem 1989). All graphical methods use a limited number of parameters, usually a subset of the available data, unlike the statistical methods that can utilize all the available parameters. The Schoeller semilogarithmic diagram (Schoeller 1956, 1967) allows the major ions of many samples to be represented on a single graph, in which samples with similar patterns can be easily discerned (Cetindag and Okan 2003). The Schoeller diagram shows the total concentration of major ions in log-scale, while Schoeller classification (Schoeller 1965) is based on the physical and chemical importance of hydrochemical parameters. Schoeller (1965) has presented classifications based on several viewpoints. Since the Schoeller diagram is useful for a few samples only, we used other graphical methods like the Piper and Durov diagram for interpretation of groundwater quality. The main purpose of graphical representation of the water quality data is to gain better insight into the processes.

Table 5

| Parameter | Pre-monsoon | Post-monsoon |
|-----------|-------------|--------------|
| pH        | –0.39 0.14 0.33 0.35 0.69 | 1 0.88 0.64 0.10 0.36 0.31 1 0.67 |
| ORP       | –0.71 0.49 0.09 0.02 –0.32 | 1 0.84 –0.82 0.32 0.01 0.11 1 0.75 |
| EC        | 0.78 –0.48 –0.07 –0.09 0.29 | 1 0.94 0.88 –0.33 –0.001 –0.11 1 0.84 |
| TDS       | 0.79 –0.49 –0.10 –0.12 0.25 | 1 0.95 0.88 –0.33 –0.003 –0.1 1 0.81 |
| Na        | 0.83 0.09 0.25 0.18 –0.09 | 1 0.80 0.74 0.35 0.25 0.28 1 0.66 |
| K         | 0.73 –0.06 0.21 0.21 –0.27 | 1 0.70 0.79 –0.04 –0.06 0.11 1 0.82 |
| Mg        | 0.46 0.81 –0.11 0.13 0.19 | 1 0.94 0.25 0.52 –0.65 0.23 1 0.87 |
| Ca        | 0.37 0.84 –0.24 0.15 0.16 | 1 0.95 0.31 0.77 –0.34 0.26 1 0.82 |
| Mn        | 0.38 0.47 0.23 –0.39 0.04 | 1 0.58 0.31 0.47 0.57 –0.42 1 0.77 |
| Fe        | 0.69 0.35 0.01 –0.31 0.15 | 1 0.72 0.70 0.43 0.13 –0.26 1 0.83 |
| Zn        | 0.92 –0.02 0.09 –0.15 –0.12 | 1 0.89 0.87 0.18 0.19 –0.06 1 0.67 |
| Cu        | 0.02 –0.7 –0.36 –0.03 0.23 | 1 0.67 0.27 –0.69 –0.34 0.02 1 0.81 |
| Ni        | 0.11 0.1 0.91 –0.01 –0.09 | 1 0.85 0.02 0.17 0.87 0.19 1 0.83 |
| Fluoride  | –0.19 –0.07 0.24 –0.57 0.29 | 1 0.50 0.81 –0.29 –0.24 –0.17 1 0.82 |
| Chloride  | 0.84 0.16 0.23 0.13 –0.07 | 1 0.80 0.78 0.38 0.18 0.18 1 0.90 |
| Sulphates | 0.32 0.84 –0.3 0.12 0.13 | 1 0.92 0.17 0.84 –0.39 –0.03 1 0.83 |
| Nitrate   | 0.27 –0.48 0.26 0.62 0.09 | 1 0.76 0.31 –0.48 0.12 0.70 1 0.67 |
| Bicarbonate | 0.77 –0.32 0.03 –0.01 –0.27 | 1 0.77 0.77 –0.23 0.11 0.10 1 0.67 |
| Total     | 6.43 4.01 1.58 1.26 1.16 | 1 6.60 3.35 2.24 1.18 |
| % of variance | 35.74 22.29 8.77 6.98 6.43 | 1 38.80 19.72 13.20 6.92 |
| Cumulative % | 35.74 58.03 66.80 73.78 80.21 | 1 38.80 58.52 71.72 78.64 |

Table 6

According to Stuyfzand, 63.64% of our groundwater samples were brackish, 27.27% were fresh-brackish, 6.06% were fresh and 3.03% were brackish-salt on the basis of Cl− concentration. USSL (1954) classification is based on the concentration of total dissolved solids as shown in Table 6. According to USSL classification, 60.60% of our groundwater samples showed total dissolved solids concentrations in the range of 500–1,500 mg/l, 36.36% were in the range of 1,500–3,000 mg/l and 3.03% were in the range of 200–500 mg/l. Eaton also classified water quality on the basis of percentage of Na in water. According to the Eaton Classification (Eaton 1954), 48.48% of our groundwater samples were safe, while 51.52% were unsafe for use.

Piper and Durov

The Piper diagram (Piper 1944) is the most widely used graphical form and is quite similar to the diagram proposed by Hill (Hill 1940). The central diamond-shaped field (quadrilateral field) is used to show the overall chemical character of the water (Hill 1942; Piper 1944). Back (1961) and Back and Hanshaw (1965) defined the subdivisions of the diamond field that represent water-type categories.
form the basis for one common classification scheme for natural waters.

Piper’s (1944) tri-linear diagram has been used to decipher the geochemical evaluation of groundwater. The diagram consists of two triangular fields and a central diamond-shaped field. In the two triangular fields, percentage epm values of major cations and anions are plotted separately and then projected onto the central field for the representation of overall characteristics of water. This plot reveals useful properties and relationships for large sample groups. The highlighted sample points indicate samples that are selected in the database and are also highlighted on all other open graphical displays. The Durov diagram is an alternative to the Piper diagram. The Durov diagram (Durov 1948) plots the major ions as percentages of milliequivalents in two base triangles. The main purpose of the Durov diagram (Durov 1948) is to show clustering of data points to indicate samples that have similar compositions.

### Table 6  Water classification

| Classification scheme | Categories | Ranges | Percent of samples |
|-----------------------|------------|--------|--------------------|
| EC (Wilcox 1955)      | Excellent  | <250   | 0                  |
|                       | Good       | 250–750| 6.06               |
|                       | Permissible| 750–2,250| 63.64          |
|                       | Doubtful   | 2,250–5,000| 30.30         |
|                       | Unsuitable | >5,000 | 0                  |
| RSC (Richard 1954)    | Good       | <1.25  | 100                |
|                       | Medium     | 1.25–2.5| 0                |
|                       | Bad        | >2.5   | 0                  |
| Na% (Wilcox 1955)     | Excellent  | 0–20   | 0                  |
|                       | Good       | 20–40  | 6.06               |
|                       | Permissible| 40–60   | 42.42              |
|                       | Doubtful   | 60–80  | 48.48              |
|                       | Unsuitable | >80    | 3.03               |
| Na% (Eaton 1950)      | Safe       | <60    | 48.48              |
|                       | Unsafe     | >60    | 51.52              |
| TDS classification (USSL 1954) |      | < 200  | 0                  |
|                       |           | 200–500| 3.03               |
|                       |           | 500–1,500| 60.60          |
|                       |           | 1,500–3,000| 36.36       |
| Cl– classification (Stuyfzand 1989) | Extremely fresh | <0.14 | 0                |
|                       | Very fresh | 0.14–0.85 | 0             |
|                       | Fresh     | 0.85–4.23| 6.06          |
|                       | Fresh brackish | 4.23–8.46 | 27.27         |
|                       | Brackish | 8.46–28.21| 63.64         |
|                       | Brackish-salt | 28.21–282.06 | 3.30           |
|                       | Salt     | 282.06–564.13| 0          |
|                       | Hypersaline | >564.13 | 0                |
| SAR (Richard 1954)    | Excellent | 0–10   | 81.81              |
|                       | Good      | 10–18  | 18.18              |
|                       | Fair      | 18–26  | 0                  |
|                       | Poor      | >26    | 0                  |

Chemical facies that determine the water type are calculated by first converting the concentration (meq/l) of the major cations (Na+, K+, Ca2+, Mg2+) and anions (Cl–, SO42–, HCO3–) to percentages (Guler et al. 2002). All ions with concentrations surpassing 10% of the molar concentration in the solution are considered to be major ions (Guler et al. 2002).

The diagram indicates dominance of the major ions Na+, K+ and Cl–, while other ions, such as Ca2+, Mg2+, SO42– and HCO3–, are comparatively less represented, indicating anthropogenic input in the groundwater system (Cetindag and Okan 2003). The groundwater samples collected pre-monsoon and post-monsoon, with similar results with some spatial and seasonal variation, indicate anthropogenic input into the groundwater system along with leachates or dilution of groundwater in various proportions with rainwater. Concentrations of major cations and major anions are classified as
Most of the samples show decreasing order of cation facies order with \( \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ \), while a few samples show a different trend, indicating some localized...
changes in quality. This is possible only in cases of anthropogenic input in the groundwater system (Guler et al. 2002). The other possible hydrochemical facies based on major cation concentrations in the groundwater aquifer system in the vicinity of Bhalswa landfill are as follows: Na\(^+\) > Ca\(^{2+}\) > Mg\(^{2+}\) > K\(^+\) (73.45\%), Na\(^+\) > Mg\(^{2+}\) > Ca\(^{2+}\) > K\(^+\) (13.45\%), and Ca\(^{2+}\) > Na\(^+\) > Mg\(^{2+}\) > K\(^+\) (13.10\%). Most samples showed decreasing order of anions in groundwater samples as Cl\(^-\) > SO\(_4^{2-}\) > HCO\(_3^-\), while a few samples showed different trends, indicating some localized changes in quality. The other possible hydrochemical facies based on major anion concentrations in the groundwater aquifer system in the vicinity of the Bhalswa landfill are as follows: Cl\(^-\) > SO\(_4^{2-}\) > HCO\(_3^-\) (73.45\%), Cl\(^-\) > HCO\(_3^-\) > SO\(_4^{2-}\) (23.45\%), SO\(_4^{2-}\) > Cl\(^-\) > HCO\(_3^-\) (3.10\%).

The Piper and Durov diagrams indicate most of the samples were classified as Ca–Na type of cation facies and Cl\(^-\) type of anion hydrochemical facies, while samples BH11, BH15 and BH24 showed Cl\(^-\)–SO\(_4^{2-}\)–HCO\(_3^-\) type of anion hydrochemical facies (Chidambaram and Ramanathan 2000). The Piper and Durov diagram shows temporal variation of these ions, indicating an increase in concentration of chloride ions because of anthropogenic input from the landfill, since there is no known natural source of chloride in the study area. A total of 90.91% of groundwater samples collected around the landfill showed Ca–Na type cation hydrochemical facies and Cl\(^-\) type of anion hydrochemical facies in pre-monsoon, whereas 9.09% of groundwater samples showed Ca–Na type cation hydrochemical facies and Cl\(^-\)–SO\(_4^{2-}\)–HCO\(_3^-\) type of anion hydrochemical facies in pre-monsoon.

The situation is changed post-monsoon due to the addition of various ions from rainwater and further dilutions in various proportions (Rajamohan and Elango 2004). Post-monsoon only 87.88% samples showed Ca–Na type of cation hydrochemical facies and Cl\(^-\) type of anion hydrochemical facies, and 12.12% groundwater samples showed Ca–Na type cation hydrochemical facies and Cl\(^-\)–SO\(_4^{2-}\)–HCO\(_3^-\) type of anion hydrochemical facies (Chidambaram and Ramanathan 2000). The results indicate that groundwater samples collected from Rajasthan Industrial Area (BH11), Haidur Pur (BH15) and J. J. Colony (BH24) showed Cl\(^-\)–SO\(_4^{2-}\)–HCO\(_3^-\) type hydrochemical facies in pre-monsoon period (Table 7). This indicates a change in water quality because of localized anthropogenic inputs in this area along with input of contaminants from the landfill.

Conclusions

A 28-km\(^2\) area was selected for this study that is suspected to be influenced by landfill dumping; the area has the same lithology and aquifer systems, and extends in an approximately 3-km radius from the Bhalswa landfill site. Sampling sites in the vicinity of the landfill were chosen in such a way as to indicate possible influences from the past, present and future. The Bhalswa landfill is located in one of the most urbanized areas of Delhi, and its influences on the huge population are inevitable in the capital city of India, because it is unplanned, lying in flood plain of the Yamuna River, and its alluvial lithology makes it more susceptible to contamination by leaching of pollutants.

The studies, further justified by statistical interpretation, indicate high contamination of groundwater due to leaching of pollutants from the landfill with temporal and spatial variations in groundwater quality around the landfill. Most of the samples reported had high conductivity, high heavy-metal concentration, chloride, nitrate and other cations and anions, indicating anthropogenic input, i.e. leaching of pollutants from the landfill. The pollutant concentrations decrease in the direction of the groundwater flow along the radius as we move away from landfill, indicating that the Bhalswa landfill acts as a point source of contamination. Various graphical plots and statistical analyses have been applied to the chemical data based on the ionic constituents, water types, and hydrochemical facies to deduce the impact of the landfill on groundwater quality. The statistical analysis and spatial and temporal variations indicate leaching of contaminants from the landfill into the groundwater aquifer system. The concentrations of heavy metals in the leachates were much higher than the standards.

The study suggests that the landfill influenced the groundwater chemistry of the aquifer system. It is high time to check it and plan for a possible alternative site. The site developed for future dumping should have a planned engineering structure to control and minimize the impact of landfill leachates on groundwater quality around the landfill.

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