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Hydrogeochemistry for the assessment of groundwater quality in Varanasi: a fast-urbanizing center in Uttar Pradesh, India

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Abstract The hydrogeochemical parameters for groundwater samples of the Varanasi area, a fast-urbanizing region in India, were studied to evaluate the major ion chemistry, weathering and solute acquisition processes controlling water composition, and suitability of water quality for domestic and irrigation uses. Sixty-eight groundwater samples were collected randomly from dug wells and hand pumps in the urban Varanasi area and analyzed for various chemical parameters. Geologically, the study area comprises Quaternary alluvium made up of an alternating succession of clay, silty clay, and sand deposits. The Total dissolved solids classification reveals that except two locations, the groundwater samples are desirable for drinking, and all are useful for irrigation purposes. The cationic and anionic concentrations indicated that the majority of the groundwater samples belong to the order of Na > Ca > Mg > K and $HCO_3 > Cl > SO_4$ types, respectively. Geochemical classification of groundwater based on the Chadha rectangular diagram shows that the majority (81%) of groundwater samples belong to the calcium–bicarbonate type. The $HCO_3/(HCO_3 + SO_4)$ ratio (0.87) indicates mostly carbonic acid weathering process due to presence of *kankar* carbonate mixed with clay/fine sand. The high nitrate concentration (>45 mg/l) of about 18% of the groundwater samples may be due to the local domestic sewage, leakage of septic tanks, and improper management of sanitary landfills. In general, the calculated values of sodium adsorption ratio, percent sodium, residual sodium carbonate, and permeability index indicate good to permissible use of water for irrigation, and only a few locations demand remedial measures for better crop yields.

Keywords Major ion chemistry · Groundwater quality · Solute acquisition process · Hydrochemical indices · Irrigation use · Urbanization · Varanasi

Introduction

In recent times, there has been a tremendous increase in demand for freshwater and water shortage in arid and semiarid regions due to population

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increase, urbanization, industrialization, and intense agricultural activities in many parts of world. Due to inadequate supply of surface waters, most of the people in India are depending mainly on groundwater resources for drinking and domestic, industrial, and irrigation uses. Innumerable large towns and many cities in India derive water supply from groundwater for different uses through municipality network and also from large number of private boreholes. Hence, knowledge on hydrochemistry of freshwater is important to assess the quality of groundwater in any basin and/or urban area that influences the suitability of water for domestic, irrigation, and industrial needs. Important hydrogeologic factors such as rainfall, mineral weathering, topographic relief, and biological activity in a given basin are important for controlling recharge and hydrogeochemical reactions responsible for chemical constituents contaminating the groundwater. Because of the importance of groundwater in drinking and in other uses, its environmental aspects such as contamination transport have been significantly studied. Many researchers have focused on hydrochemical characteristics and contamination of groundwater in different basins as well as in urban areas that resulted due to anthropogenic intervention mainly by agricultural activities and industrial and domestic wastewater (Umar et al. 2006; Raju 2007; Singh et al. 2008). The water quality may yield information about the inner geologic environments through which the water has circulated. The chemical alteration of rainwater depends on several factors such as soil–water interaction, dissolution of mineral species, and anthropogenic activities (Faure 1998; Raju et al. 2009). The overexploitation of groundwater has detrimentally affected its quality and quantity.

The source of about 90% of drinking and irrigation water is from groundwater resources in Varanasi environs. However, this water resource is facing problems including quality hazard in many areas where the exposure to pollution from agriculture and other metal pollution in shallow groundwater aquifers makes the water unfit for human consumption. Land use for urbanization and agricultural purpose in the Varanasi City environs has increased at an alarming rate during the last few decades. Borehole sediments revealed that multistoried sand bodies generated, as a result of channel migration provide, excellent aquifers confined by a thick zone of muddy sediments near the surface in Varanasi City (Shukla and Raju 2008). In complex multilayered alluvial formations, the shallowest phreatic aquifer is often most vulnerable to anthropogenic pollution and most susceptible to saline intrusion. Raju et al. (2009) have studied groundwater quality in the lower Varuna River basin in Varanasi district and found high nitrate concentrations at few locations due to intense anthropogenic activity and inadequate sewage system. The study of a relatively large number of groundwater samples from a given area offers clues to various chemical alterations that the meteoric groundwater undergoes before acquiring distinct chemical characteristics. The aim of the study was to assess the spatial distribution of hydrogeochemical parameters for suitability of groundwater resources and geochemical process controlling the water composition based on the major ion chemistry of 68 groundwater samples in the Varanasi urban area.

Study area

The Ganga is the principal river of Varanasi flowing incised into its narrow valley from south to north direction. In the study area, it has two tributaries, namely, Assi-nala on the southern flank and Varuna River in the north eastern side of the city. Varanasi City and its environs are located at an average height of about 76 m above the mean sea level and have largely even topography with a low relief kilometer scale undulations. The study area covers an about 100-km^2 area in and around Varanasi City and lies between the latitude 25°15′0″ N–25°20′22″ N and 82°56′44″ E–83°4′10″ E. Geomorphologically, the study area is located in the central Ganga Plain of the Indian subcontinent (Fig. 1). Its climate is tropical with a marked monsoonal effect. The area receives about 80% of its annual rainfall of 1,020 mm from the southwest monsoon during the month of July to August. In summer, the maximum temperature rises to 47°C, and in winter, the minimum temperature drops to 4°C with the average annual temperature being 24°C.

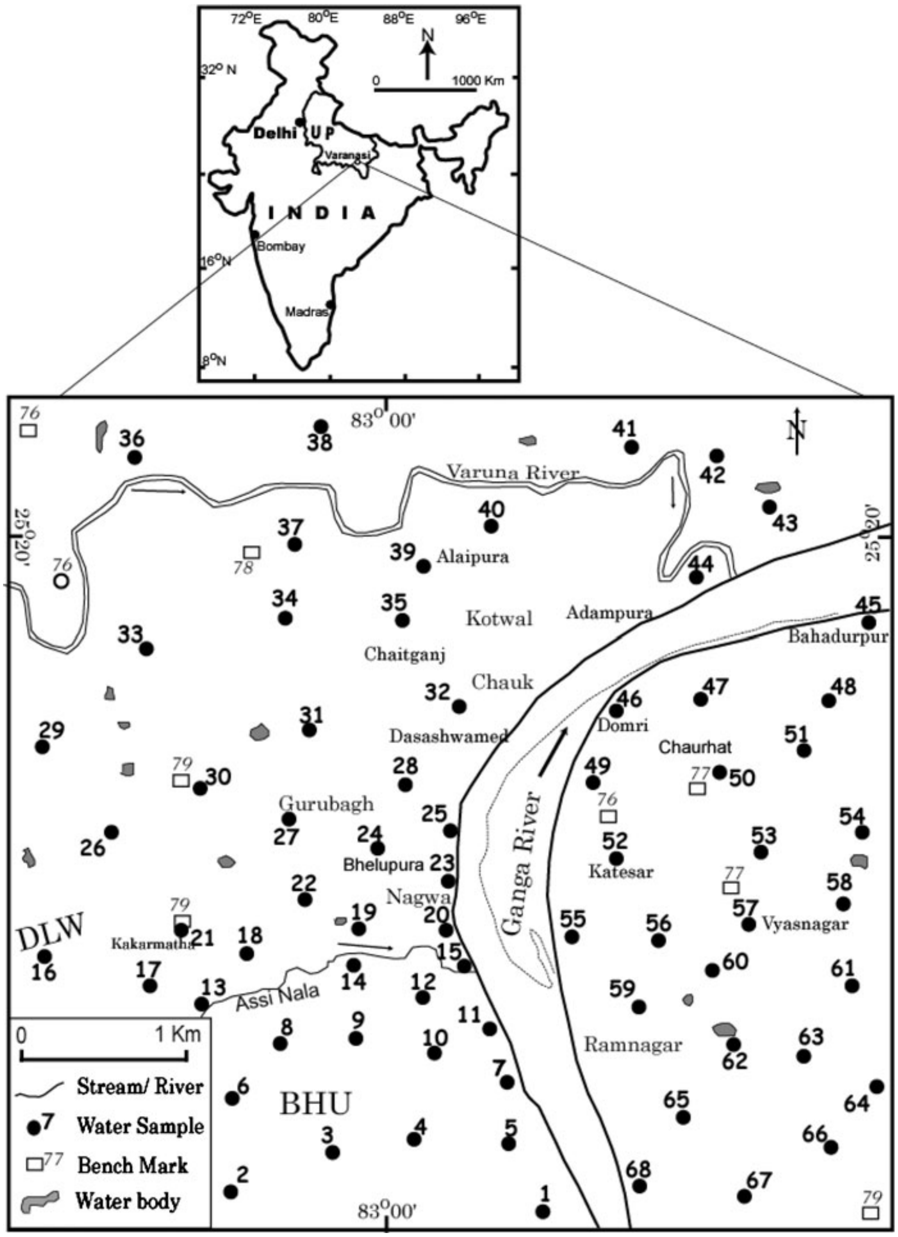


Fig. 1 Physiographic and groundwater sample location map of Varanasi urban area. *1* Malahia, *2* Hyderabad gate (BHU), *3* Agricultural farm (BHU), *4* Chittupur, *5* Madarwa, *6* Jagainpur, *7* Samneghat, *8* Karaundi, *9* IMS (BHU), *10* Bhagavanpur, *11* Nagwa Chungi, *12* Lanka, *13* Sunderpur, *14* Saketnagar, *15* Nagwa, *16* Bhulanpur, *17* Bikharipur, *18* Sarainandan, *19* Ravindrapuri, *20* Assighat, *21* Kakarmitha, *22* Kheiriya, *23* Shivala, *24* Belupur, *25* Sonarpura, *26* Sivadaspur, *27* Koluwaa, *28* Kamachha, *29* Chandpura, *30* Manduadi, *31* Gurubagh, *32* Jangambadi, *33* Koharpur, *34* Railway station (Cant.), *35* Sonia Pokhara, *36* Central Prison, *37* Nadeshwar, *38* Rajanhia, *39* Samskrat Viswavidyala, *40* Railway station (City), *41* Rasulgarh, *42* Kapildara, *43* Kotwara, *44* Rajghat, *45* Bahadurpur, *46* Domari, *47* Ratanpur, *48* Madhiya, *49* Semra, *50* Bhojpur, *51* Jalilpur, *52* Kateswar, *53* Bhakhara, *54* Nibupur, *55* Kodupur, *56* Wajidpur, *57* Nathupur, *58* Nathupur, *59* Kutulupur, *60* Sultanpur, *61* Mannapur, *62* Kabirpur, *63* Dariyapur, *64* Parawara, *65* Bhiti, *66* Dahiya, *67* Tangara, *68* Rathupur

Geology

The Varanasi urban area spreading over 100 km^2 is part of the Indo-Gangetic Plain underlain by Quaternary alluvial sediments of Pleistocene to recent times. The earliest phase of the geologic history of the Indo-Gangetic Plain commenced with the formation of fore-deep concurrent with uplift of the Himalayan mountain system. In the area studied, however, unconsolidated sediments form a sequence of clay, silt, and sands of various grades. The presence of *kankar* carbonates is at times intercalated with the clays and sands and forms potential aquifers at various depths. Throughout the central Ganga Plain, the top few meters show a distinctive fining upward sequence terminating with clay-rich sediments. Optically stimulated luminescence (OSL) dated between 59 ± 6 ka at the base to 7 ± 1 ka near the top has been performed on an about 20-m-thick fine-grained sedimentary sequence exposed on the eastern bank of River Ganga near Ramnagar (Fig. 1). The origin of sand, silt, and clays is from alluvial deposits, and formation of the kankar may be the precipitation of the calcium carbonate from the groundwaters. The Quaternary alluvial deposits are divided into older and newer alluviums (Shukla and Raju 2008). In the Varanasi area, the older alluvial deposit consists of fairly consolidated clay with kankar and polycyclic sequence of fine to medium sand with little gravel. The thick unit of the older alluvium is developed throughout the study area and is predominated by gray micaceous sand in the west and yellowish concretized clay in the east side. The gray sands consist of clear angular quartz with small amounts of altered alkali feldspar, micas, hornblende, garnet, kyanite, hypersthene, tourmaline, and zircon indicating Himalayan sources (Shukla and Raju 2008). The sandy horizons indicate profound fluvial activity in the region, and thick clay horizons indicate the low-energy fluvial phase. Clay found associated with kankar indicates a dry spell of nondepositional phase. The newer alluvium occurs adjacent to the drainage courses of the river Ganga, and the area is subjected to flood during rainy season each year, which deposits a mat of fresh silt, clay, and loam. It occurs in mainly narrow belts and is affected by the action of water currents.

Hydrogeology

The unconsolidated near-surface Pleistocene to recent fluvial sediments underlying most of the Gangetic plains are generally potential aquifers. The development of groundwater resources has increased manifold in the highly productive Gangetic plains having thick Quaternary deposits, forming multitier aquifer system. The availability of groundwater in these alluvial zones is controlled by the relative thickness of sand and clay horizons. Sand layers form the most important aquifers, and their potentiality clearly increases with its degree of assortment. The alternating sand and clay layers have created a multitiered aquifer system in the Varanasi area (Shukla and Raju 2008). The sand beds with or without kankar in the area form the main aquifer zones of the multitier aquifer system. As compared to shallow groundwater under phreatic condition, the deeper aquifers are in semiconfined to confined conditions. The confined aquifer is made up of moderately well-sorted sand and reflects a fluviatile environment of deposition. Both dug wells and bore wells are used for groundwater extraction for different uses in the study area. The dug well diameter ranges from 2 to 8 m and ranges in depth from 7 to 30 m. The shallow bore wells (hand pumps) and dug wells puncturing unconfined aquifers at an about 20- to 60-m depth have water level fluctuations from 9 to 12 m. Such unconfined aquifers are made up of recycled interfluve silt and silty sand forming lensoid units capped by relatively thin and impersistent mud layers showing kankar development (Shukla and Raju 2008). The general depth of deep bore wells ranges from 60 to 250 m below ground level, and the deep wells penetrate below 60–70 m and have an enormous yield of 750 to 3,500 l/min. The total thickness of the good water yielding sand strata varies from 20 to 80 m or more in tube wells, with an average depth of about 100 m (Bilas 1980). The intensive pumping of water due to population increase and urbanization factors in Varanasi shows a lowering trend of the water level in some parts of the study area. The average fall of groundwater level in the last 15 years in the Varanasi environs is about 1.43 m (Sinha 2003). The nature of occurrence and availability of groundwater in the study area has been assessed by conducting hydrogeologic investigations.

Materials and methods

A total of 68 groundwater samples have been collected (Fig. 1) from dug wells and bore wells (hand pumps) during May and June 2006 and analyzed to understand the chemical variations of water quality parameters using standard methods (APHA 1995). Precleaned (acid-washed) polyethylene containers of 1-l capacity were used for groundwater sample collection. Each of the groundwater samples were analyzed for pH, electrical conductivity (EC), major cation, and anions. pH (Cyber Scan pH meter) and EC (Eco Scan Con-6) were analyzed using portable meters. Total hardness and calcium were estimated by ethylenediaminetetraacetic acid titrimetric method and magnesium estimated by the difference in the hardness and calcium. Total alkalinity, carbonate, and bicarbonate and also chloride were estimated by titrimetric methods. Sodium and potassium were estimated by flame photometer. The sulfate estimations were done by the gravimetric method. The nitrate was analyzed by the UV–spectrophotometer. Fluoride was estimated by using an ion-selective electrode (ISE) with a pH/ISE meter (Orion 4-Star meter). Iron is estimated by atomic absorption spectroscopy. Total dissolved solids (TDS) were estimated by calculation method. The accuracy of the chemical analysis was verified by calculating ion-balance errors where the errors were generally within 5%.

Results and discussion

Chemical quality of groundwater

Range limits of physicochemical analytical results of the 68 groundwater samples are presented in Table 1. The pH of the analyzed samples varies from 6.9 to 8.2 with a mean value of 7.6 in the study area. In general, pH of groundwater samples was slightly alkaline in nature. The EC values vary from 400 to 2,150 μS/cm with an average value of 928 μS/cm. Total dissolved solids (TDS) varied from 232 to 1,175 mg/l with a mean of 526 mg/l. Based on total dissolved solids, groundwaters are classified (Davis and De Wiest 1966) into desirable for drinking (up to 500 mg/l), permissible for drinking (500–1,000 mg/l), useful for agricultural purposes (up to 3,000 mg/l), and unfit for drinking and irrigation (above 3,000 mg/l). Out of the 68 groundwater samples, 66 samples are within the desirable and two are within the permissible limits of drinking, and all samples are useful for irrigation purposes. Spatial distribution of TDS concentration in the groundwater is illustrated in Fig. 2. The high concentration of total dissolved solids was observed in northern (city station), eastern (Mannapur), and south-central (Karaundi) parts of the area. This may be due to untreated domestic sewage and high agricultural activities. The variation in the TDS, EC, and ionic concentrations in the groundwater may be attributed to variation in geochemical process and anthropogenic activities (Raju et al. 2009).

Among the cationic concentrations, sodium is the dominant ion, having a range of 14 to 252 mg/l (mean value of 75 mg/l), followed by calcium, magnesium, and potassium ion ranges of 10–183 (mean, 62.8 mg/l), 0.4–127 (mean, 45.4 mg/l), and 0.6–75 mg/l (mean, 8.1 mg/l), respectively (Table 1). The cation chemistry is dominated by sodium, constituting 39% of the total cations (TZ^+) followed by calcium (33%) and magnesium (24%) with a minor contribution (4%) from potassium ion. The cation chemistry indicated that 25% of the groundwater samples are $Na > Ca > Mg > K$, while 24%, 20%, 16%, and 12% belong to $Ca > Na > Mg > K$, $Na > Mg > Ca > K$, $Ca > Mg > Na > K$, and $Mg > Na > Ca > K$, respectively. Only 4% of the samples are $Mg > Ca > Na > K$ type. In general weathering, dissolution and base-exchange processes control the levels of cationic concentrations in groundwater. High sodium waters can be explained by the combination of dilution factors, ion exchange, and sulfate reduction (Krothe and Oliver 1982). Among the anionic concentrations, bicarbonate is the dominant ion, having a range of 145–720 mg/l (mean, 374 mg/l), followed by chloride and sulfate, which have ranges of 12–397 (mean, 93 mg/l) and 2.5–180 mg/l (mean, 43 mg/l), respectively (Table 1). The anionic chemistry of the study area shows

Table 1 Ranges of chemical parameters and their comparison with the WHO and the Indian standards for drinking water

Chemical parameter	Concentrations of ions		Ranges of standards (desirable–permissible)		Sample numbers exceeding desirable limits	
	Range	Mean	WHO (1997)	BIS (1991)	WHO (1997)	BIS (1991)
pH	6.9–8.2	7.6	7.0–9.2	6.5–9.2	1–38, 40–68	1–68
EC (μS/cm)	400–2,150	928	—	—	—	—
TDS (mg/l)	232–1,175	526	500–1,500	500–2,000	4, 8, 12, 20, 21, 22, 24, 25–28, 30–34, 36, 37, 40, 42, 44, 48, 49, 54, 55, 59–65, 67	4, 8, 12, 20, 21, 22, 24, 25–28, 30–34, 36, 37, 40, 42, 44, 48, 49, 54, 55, 59–65, 67
Ca^{2+} (mg/l)	10–183	62.8	75–200	75–200	2, 4, 6, 19, 37, 39, 40, 44–50, 52, 55–57, 59, 64	2, 4, 6, 19, 37, 39, 40, 44–50, 52, 55–57, 59, 64
Mg^{2+} (mg/l)	0.4–127	45.4	30–150	30–100	1, 3–5, 7–18, 20–38, 40, 42, 44, 48, 50, 52, 54, 55, 59–64, 66, 67	1, 3–5, 7–18, 20–38, 40, 42, 44, 48, 50, 52, 54, 55, 59–64, 66, 67
Na^{+} (mg/l)	14–252	75	50–200	—	2, 4, 6, 8, 10–13, 17, 18, 20, 21–32, 34–38, 40, 42–44, 54–56, 59–67	—
K^{+} (mg/l)	0.6–75	8.1	10–12	—	23–25, 28, 32, 44, 59, 61	—
HCO$_3^-$ (mg/l)	145–720	374	300–600	300–600	1, 2, 4–6, 8, 10–18, 20, 22–25, 27–30, 32–34, 36–40, 42–50, 52, 54–57, 59–67	1, 2, 4–6, 8, 10–18, 20, 22–25, 27–30, 32–34, 36–40, 42–50, 52, 54–57, 59–67
SO$_4$$^{2-}$ (mg/l)	2.5–180	43	200–600	200–400	within limit	within limit
Cl$^-$ (mg/l)	12–397	93	250–600	250–1,000	40, 61	40, 61
NO$_3^-$ (mg/l)	0.8–106	21	50	45–100	21, 26, 29, 30, 31, 33, 34, 40, 43, 44	21, 26, 29–31, 33, 34, 38, 40, 41,
F$^-$ (mg/l)	0.3–1.3	0.7	0.9–1.5	1.0–1.5	1, 9, 11, 12, 32, 34, 35, 38, 45, 47–49, 52, 55, 58, 60, 61, 66, 68	11, 32, 34, 38, 45, 48, 49, 53, 55, 58, 60
Fe (mg/l)	0.1–6.9	0.9	0.3	0.3	4, 5, 7, 8, 9, 11, 12, 15, 16, 21, 23, 25–68	4, 5, 7, 8, 9, 11, 12, 15, 16, 21, 23, 25–68
TH (mg/l)	169–694	341	100–500	300–600	1–68	8–10, 12–17, 20–22, 24, 26, 28, 30, 31, 33, 36, 40, 44–50, 52, 54, 55, 59–61,63, 64,66

EC electrical conductivity, *TH* total hardness, *TDS* total dissolved solids

bicarbonate ion is dominant, constituting 71% of the total anions (TZ$^-$), followed by chloride (17%) and sulfate (8%) with minor contribution (<3%) from nitrate and fluoride ions. The anionic chemistry indicates that 83% of the groundwater samples are $\mathrm{HCO_3} > \mathrm{Cl} > \mathrm{SO_4}$, while 16% belongs to the $\mathrm{HCO_3} > \mathrm{SO_4} > \mathrm{Cl}$ type. Only 1% samples belongs to the $\mathrm{Cl} > \mathrm{HCO_3} > \mathrm{SO_4}$ type.

The concentration of nitrate in the study area varies from 0.8 to 106 mg/l with an average value of 21 mg/l (Table 1). The nitrate concentration was relatively high in some of the groundwater samples. Spatial distribution of the nitrate concentration in the groundwater is illustrated in Fig. 3. The concentration of nitrate was relatively high in western, northern, and north-eastern

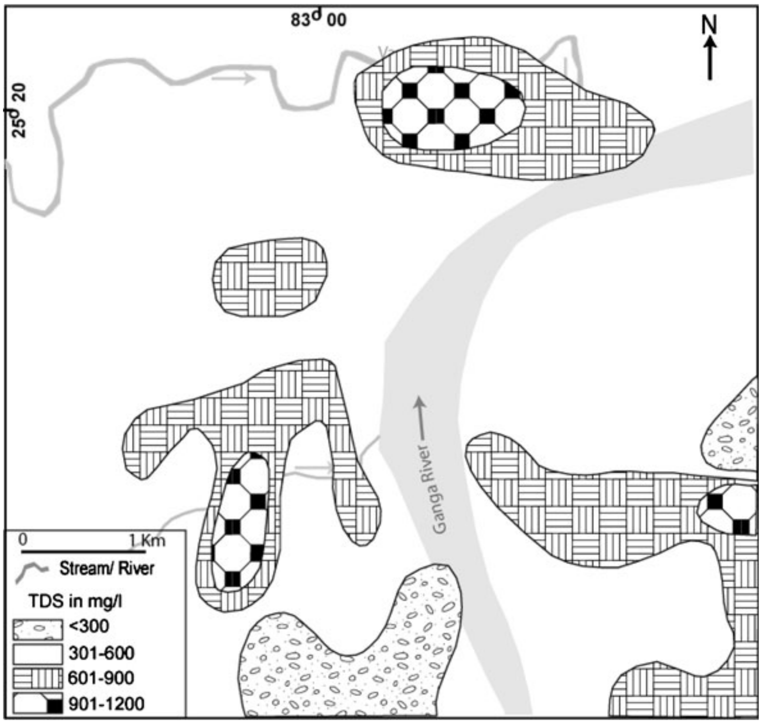


Fig. 2 Spatial distribution of TDS concentration

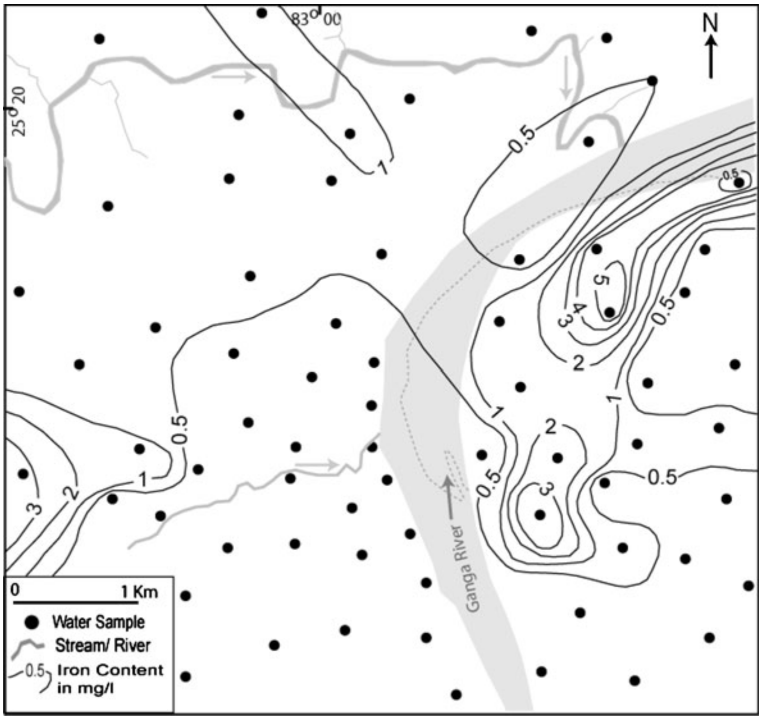
Fig. 3 Spatial distribution of nitrate concentration

parts of the study area such as Kakarmatha (90.4 mg/l), Shivdashpur (63.6 mg/l), Chandpur (62.4 mg/l), Manduadi (76 mg/l), Gurubagh (92 mg/l), Koharpur (55.1 mg/l), Cant Railway Station (66.7 mg/l), Kotwa (67.1 mg/l), and Rajghat (92 mg/l). However, in the remaining samples, the nitrate concentration was below the permissible limit of 45 mg/l (BIS 1991). In the study area, agricultural activities are mainly dependent on the groundwater resources. A very high nitrate concentration is observed along the Varuna River (Raju et al. 2009), which may be due to the seepage of irrigation waters from agricultural fields where chemical fertilizers are being used indiscriminately. The high nitrate values in the western segment are attributed to the overflowing domestic sewage water. Moreover, topographic depression and local water bodies of various dimensions in the study area are connected with domestic wastewater channels that are filled with nitrogen-enriched sewage water and contribute locally high content of nitrates to the groundwater. The fluoride concentration ranges from 0.3 to 1.3 mg/l with an average value of 0.7 mg/l. Concentration of fluoride was low in the major part of the study area, which indicates limited lithogenic input of fluoride ion in groundwater samples. The iron concentration generally varies from 0.1 to 6.9 mg/l with an average concentration of 0.9 mg/l (Table 1). The spatial distribution of iron concentration in groundwater is zoned and shown in Fig. 4. The high iron concentration is observed mainly in the eastern, i.e., concave side of Ganga River, and also in the extreme western parts of the study area. A very high concentration of iron in groundwater is found in eastern side villages of Bhojpur (6.9 mg/l), Bahadurpur (5.3 mg/l), Ratanpur (4.1 mg/l), Kutulupur (3.5 mg/l), Wajidpur (2.5 mg/l), Kateswar (1.4 mg/l), and Semra (1.4 mg/l). In the western part of Bhulanpur (3.1 mg/l) and the northern part of Kakarmatha (1.3 mg/l), a high iron concentration was also observed.

Hydrogeochemical facies and water types

The term “hydrogeochemical facies” is used to describe occurrence modes of groundwater in an aquifer that differs in their chemical composition.

Fig. 4 Spatial distribution of iron concentration



The facies are a function of lithology, solution kinetics, and flow patterns of the aquifer. Hydrochemical diagrams are aimed at facilitating interpretation of evolutionary trends, particularly in groundwater systems, when they are interpreted in conjunction with distribution maps and hydrochemical sections. Classification of geochemical facies and interpretation of chemical data of natural waters can be classified on the basis of dominant ions using the Chadha rectangular diagram (Chadha 1999). In the proposed diagram (Fig. 5), the differences in milliequivalent percentage between alkaline earths (Ca + Mg) and alkali metals (Na + K), expressed as percentage reacting values, are plotted on the *x*-axis, and the differences in milliequivalent percentage between weak acidic anions (CO_3 + HCO_3) and strong acidic anions (Cl + SO_4) are plotted on the *y*-axis. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions, would be plotted in one of the four possible subfields of the rectangular diagram. The rectangular field describes the overall character of the water. In order to define the primary character of the water, the rectangular field is divided into eight subfields, each of which represents a water type. Results of chemical analyses were plotted on the proposed diagram to test its applicability for geochemical classification of groundwater and to understand the hydrochemical processes shown in Fig. 5. The majority of groundwater samples (81%) in the study area fall under the subfield of alkaline earths and weak acidic anions that exceed both alkali metals and strong acidic anions (Ca^{2+}–Mg^{2+}–$HCO_3{}^-$ type); such waters may have temporary hardness. The 12% of the groundwater samples fall under the subfield of alkaline earths exceeding alkali metals and strong acidic anions exceeding weak acidic anions (Ca^{2+}–Mg^{2+}–Cl^- type), such waters have permanent hardness and do not deposit residual sodium carbonate (RSC) in irrigation use. The remaining 7% of the water samples concentrate in the category of Na^+–$HCO_3{}^-$ type; such waters release residual sodium carbonate while irrigating and cause foaming problems when used for domestic purposes.

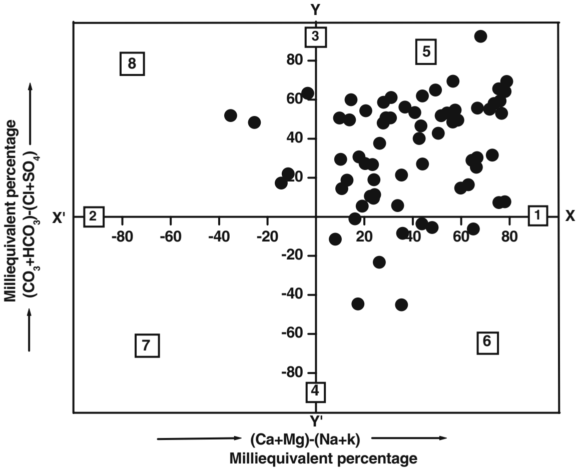


Fig. 5 Geochemical classification and hydrochemical parameters of groundwater (after Chadha 1999). *1* Alkaline earths exceed alkali metals; *2* alkali metals exceed alkaline earths; *3* weak acidic anions exceed strong acidic anions; *4* strong acidic anions exceed weak acidic anions; *5* Ca^{2+}–Mg^{2+}–HCO_3^- water type with temporary hardness; *6* Ca^{2+}–Mg^{2+}–Cl^- water type with permanent hardness; *7* Na^+–Cl^- water type with salinity problems both in irrigation and domestic uses; *8* Na^+–HCO_3^- water type causes foaming problems in domestic use

Gibbs (1970) has proposed a chemical diagram of mechanisms controlling chemistry of groundwater to understand the relationship of the chemical components of waters with their respective aquifer lithologies. Various researchers followed this type of chemical relationships of groundwater in different parts of India (Srinivasan 1992; Moses 1994; Raju 2006a). Three types of distinct fields are recognized in the Gibbs' diagram such as precipitation dominance, evaporation dominance, and rock dominance. Gibbs' ratio 1—Cl/(Cl + HCO_3) for anion and ratio 2—Na + K/(Na + K + Ca) for cation of groundwater samples of the study area were plotted separately against the respective values of total dissolved solids. Ratios 1 and 2 of groundwater samples range from 0.017 to 0.553 with an average of 0.189 and from 0.157 to 0.943 with an average of 0.534, respectively (Table 2). The chemistry of groundwater samples indicates that all samples have rock dominance, as per ratio 1. According to ratio 2, 90% of the samples are rock dominance, and the remaining 10% are evaporation dominance (Fig. 6). The rock dominance of most of the samples in ratios 1 and 2 is caused by the interaction between the chemistry of aquifer material and groundwater.

Table 2 Chemical indices derived from hydrogeochemical parameters

Locations (Fig. 1)	SAR	%Na	RSC	PI	CAI 1	CAI 2	Gibbs' ratio 1	Gibbs' ratio 2	MH	CR
1	0.36	11.10	—	46.93	0.29	0.05	0.094	0.220	45.42	1.33
2	0.83	20.74	—	54.34	−0.02	−0.01	0.130	0.301	29.07	2.01
3	0.51	14.10	—	46.95	−0.24	−0.03	0.083	0.580	85.66	1.62
4	0.94	38.41	—	35.95	0.37	0.16	0.274	0.332	50.05	7.38
5	0.42	13.16	—	47.88	0.34	0.08	0.125	0.317	59.02	1.46
6	1.01	24.74	—	56.99	0.03	0.01	0.165	0.332	21.96	2.27
7	0.41	12.09	—	44.40	0.33	0.07	0.127	0.300	62.18	1.43
8	1.83	26.00	—	41.13	0.12	0.05	0.279	0.618	74.94	15.13
9	0.73	17.74	—	45.32	−0.21	−0.03	0.122	0.619	84.27	3.21
10	1.35	28.29	—	56.75	−0.54	−0.12	0.131	0.701	80.20	2.68
11	0.87	21.70	—	52.98	−0.04	−0.01	0.142	0.650	82.21	1.98
12	1.7	28.10	—	46.32	−0.05	−0.02	0.251	0.800	88.72	9.57
13	1.49	28.64	—	54.03	−0.09	−0.03	0.187	0.650	74.90	3.04
14	0.53	16.91	—	42.78	0.27	0.08	0.177	0.439	69.20	4.22
15	1.27	32.94	—	47.96	−0.38	−0.10	0.142	0.477	60.64	1.56
16	0.47	12.28	—	42.67	0.04	0.01	0.090	0.306	61.73	1.35
17	1.39	28.00	—	54.01	0.06	0.02	0.214	0.509	56.44	3.88
18	1.34	38.20	0.094	66.15	−0.34	−0.13	0.208	0.797	81.62	3.20
19	0.64	16.70	—	45.89	0.30	0.10	0.185	0.259	31.58	2.51
20	1.74	32.30	—	55.49	−0.25	−0.09	0.204	0.622	66.03	4.98
21	0.45	10.13	—	46.29	0.18	0.12	0.506	0.565	56.97	5.70
22	1.95	38.00	—	55.54	−0.37	−0.15	0.237	0.936	95.14	11.14
23	1.39	37.97	—	58.82	−0.80	−0.22	0.176	0.698	62.99	4.20
24	1.71	41.90	—	59.04	−0.39	−0.17	0.265	0.790	76.03	8.66
25	1.35	44.90	1.117	65.80	−0.73	−0.24	0.184	0.888	85.74	4.75
26	1.58	31.99	—	48.91	−0.10	−0.06	0.359	0.560	55.42	3.27
27	3.67	55.35	1.403	79.06	−1.07	−0.42	0.212	0.931	89.14	4.69
28	2.32	43.59	0.094	63.98	−0.96	−0.28	0.183	0.753	67.97	6.06
29	1.32	29.58	—	59.05	−0.97	−0.16	0.114	0.502	51.12	1.77
30	1.98	36.78	—	61.17	−0.61	−0.18	0.181	0.588	52.27	2.96
31	2.31	37.05	—	52.08	−0.01	−0.01	0.393	0.698	70.34	7.46
32	1.62	37.79	—	57.77	−0.79	−0.21	0.186	0.724	69.14	5.30
33	0.89	18.53	—	41.85	0.40	0.17	0.247	0.447	66.90	4.45
34	2.64	45.20	1.3758	71.43	−2.19	−0.35	0.106	0.651	48.95	3.09
35	2.10	40.53	—	62.35	−1.22	−0.30	0.192	0.624	51.87	3.78
36	1.77	33.17	—	54.68	−0.10	−0.04	0.260	0.587	59.10	5.33
37	3.41	51.73	1.610	74.81	−16.18	−0.63	0.027	0.643	30.25	3.02
38	1.53	31.46	0.399	60.79	−1.41	−0.20	0.094	0.614	66.13	2.27
39	1.13	28.08	0.414	62.24	−0.83	−0.15	0.101	0.350	14.45	1.30
40	3.48	41.33	—	51.59	0.20	0.24	0.553	0.673	60.39	15.18
41	1.10	24.13	1.336	76.60	−0.65	−0.12	0.122	0.468	26.25	1.72
42	2.32	41.40	0.740	66.97	−0.32	−0.13	0.213	0.669	59.96	3.83
43	1.83	35.96	0.720	64.40	−1.18	−0.22	0.117	0.516	38.40	1.83
44	2.14	45.96	—	58.08	−0.19	−0.10	0.339	0.678	43.30	8.47
45	0.61	12.17	—	32.54	0.52	0.20	0.230	0.157	12.11	6.86
46	0.64	15.92	0.091	49.44	−4.99	−0.15	0.017	0.211	15.96	0.29
47	0.98	21.64	0.335	51.44	−0.52	−0.08	0.091	0.309	26.47	1.38
48	0.64	13.63	—	37.69	0.55	0.26	0.221	0.239	41.37	3.66
49	0.59	11.04	—	32.63	0.56	0.19	0.220	0.161	25.17	6.30
50	0.53	9.26	—	40.94	0.33	0.07	0.116	0.188	30.79	2.12
51	0.62	16.67	—	50.41	0.19	0.05	0.137	0.258	31.95	1.40
52	0.45	10.61	—	41.27	0.25	0.04	0.091	0.173	34.23	1.32

Table 2 (continued)

Locations (Fig. 1)	SAR	%Na	RSC	PI	CAI 1	CAI 2	Gibbs' ratio 1	Gibbs' ratio 2	MH	CR
53	1.43	34.66	0.922	71.80	−0.34	−0.10	0.155	0.397	6.71	1.56
54	0.32	42.81	2.814	64.21	−1.30	−0.31	0.125	0.809	79.45	3.08
55	2.09	34.49	1.501	59.26	−0.92	−0.20	0.118	0.481	34.50	2.53
56	2.18	43.07	0.986	73.42	−0.87	−0.28	0.159	0.469	0.76	1.80
57	0.89	21.30	—	54.01	0.04	0.01	0.141	0.310	30.77	1.69
58	0.93	24.14	—	57.36	−0.21	−0.06	0.150	0.303	15.58	1.21
59	1.14	20.10	—	36.05	0.45	0.26	0.282	0.415	55.61	8.12
60	2.67	42.49	—	65.21	−0.21	−0.14	0.293	0.623	43.89	4.81
61	5.25	57.05	2.716	73.06	−0.47	−0.31	0.285	0.801	60.80	8.52
62	6.49	67.55	6.261	89.60	−2.27	−0.60	0.141	0.904	74.62	4.54
63	2.40	39.72	1.966	65.68	−0.87	−0.22	0.136	0.639	56.92	2.95
64	2.51	39.83	0.360	61.02	−0.13	−0.07	0.245	0.604	48.62	4.85
65	2.14	38.76	—	63.27	−0.63	−0.18	0.195	0.534	36.63	5.61
66	2.06	36.07	0.044	60.62	−0.63	−0.21	0.166	0.625	60.95	2.44
67	5.10	62.67	4.286	86.53	−1.55	−0.51	0.166	0.942	88.26	3.21
68	1.02	25.00	0.188	60.61	−0.91	−0.14	0.089	0.380	36.41	1.12

Water–rock interaction and solute acquisition process

Weathering (disintegration and decomposition) of rock-forming minerals with minor input from atmospheric and anthropogenic sources contributes in the major and minor ionic chemistries of the aquatic system (Berner and Berner 1987; Raju et al. 2009). The water–rock interactions generally include chemical weathering of rock-forming minerals, dissolution–precipitation of secondary carbonates, and ion exchange between water and clay minerals. The abundance and distribution of elemental ions such as Ca, Mg, Na, K, HCO_3, SO_4, Cl, and Si in the water are dependent on erosion and chemical weathering of the rocks in the catchment/source area. Interaction between groundwater and surrounding minerals in the alluvium are believed to be the main process responsible for the observed chemical characteristics of groundwater in the study area. As the infiltrating water passes through the soil and weathered rock zones before reaching the groundwater table, it can dissolve the minerals present in the soils and the rocks, depending upon the pH–Eh conditions (Hem 1991). The dissolution of carbonate rocks

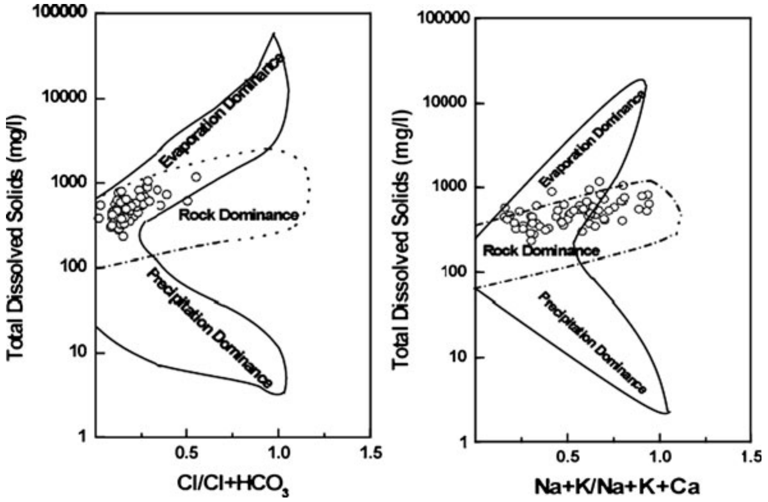


Fig. 6 Mechanism controlling chemistry of groundwater

proceeds more rapidly than silicate breakdown and is the likely mechanism of solute acquisition in water system. However, the solution products of silicate weathering are difficult to quantify because the degradation of silicates incongruently generates a variety of solid phases (mostly clays) along with the dissolved species. The relative proportions of the various ions in a solution depend upon their relative abundance in the host rock as well as on their solubility (Sarin et al. 1989).

The major reactions, contributing bulk of protons used for chemically weathered carbonates, silicates, and aluminosilicate minerals, are the dissolution of CO_2 and oxidation of sulfides. The proportion of HCO_3 and SO_4 in the water reflects the relative dominance of the two major sources of protons (carbonation and sulfide oxidation) during chemical weathering. The ternary anion diagram relating HCO_3, SO_4, and Cl shows that most of the groundwater samples contain a high amount of HCO_3 and plotted points cluster toward the alkalinity apex with secondary trends toward SO_4 (Fig. 7). The relative high ratio of $HCO_3/(HCO_3+SO_4)$ in most of the groundwater samples (>0.5) signified that carbonic acid weathering was the major proton producer in these waters (Pandey et al. 2001). The$HCO_3/(HCO_3+SO_4)$ ratio varies from 0.53 to 0.99 with an average value of 0.87, which indicates mostly carbonic acid weathering in the Varanasi groundwater. The presence of kankar carbonates in the alluvial sediments could have favored the carbonate weathering process in the study area. The dissolved bicarbonate (HCO_3) in the groundwater originates mainly from the biologically active layers of the soil where CO_2 is generated by root respiration and decay of humus that in turn combines with rainwater to form bicarbonates (Drever 1988). Bicarbonate may also be derived from the dissolution of carbonates and/or silicate minerals by the carbonic acid. In general, all the aquifers are chiefly composed of quartz, which is the more resistant mineral toward weathering. The feldspars and other mafic minerals have undergone chemical alteration to form clay minerals. The clays may have formed due to in situ weathering, and it is a result of interaction of the water with feldspars in the alluvial aquifer. Feldspars are converted to clay minerals such as kaolinite, smectite, etc.

$$CaCO_3 + H_2CO_3 - - - - Ca^{2+} + 2HCO_3^-$$

Limestone

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O - - - Al_2Si_2O_5\,(OH)_4 + 2Na^+ + 4H_4SiO_4 + 2HCO_3^-$$

Albite Kaolinite

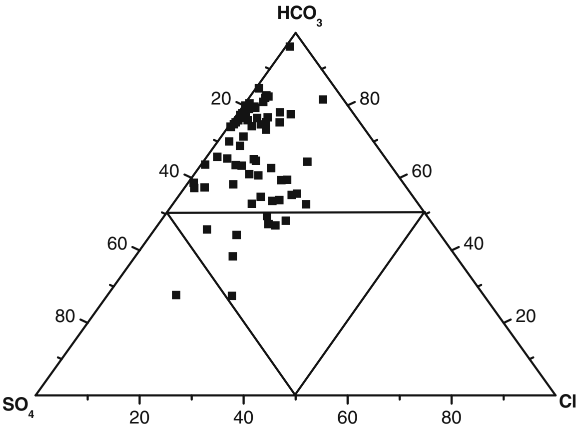


Fig. 7 The ternary anion diagram relating HCO_3, SO_4, and Cl

Rock weathering typically contributes to two major forms of sulfur in sedimentary rocks, pyrite (FeS_2) and gypsum ($CaSO_4$; Berner and Berner 1987). Few observed high values of sulfate in groundwaters of the study area may be attributed to oxidative weathering of pyrite by reaction sequence (Lowson et al. 1993). Pyrite (FeS_2) occurs as a secondary mineral in the alluvial sediments in the Gangetic plains.

$$2FeS_2 + 7O_2 + 2H_2O - - - - 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

Pyrite

Increased chloride concentration in groundwater may be due to the process of removal of other ions from the system either by adsorption or by precipitation. The high concentrations of chloride may result from pollution by domestic sewage wastes and leaching of saline residues in the soil (Appelo and Postma 1993), with a meager contribution from atmospheric or seawater sources as well. Lateral variations of chloride in an area may be attributed to the local wastewater recharge by anthropogenic sources such as domestic waste effluents and untreated industrial discharges.

Nitrate contamination in groundwater is one of the major issues in water quality studies (Schilling and Wolter 2007; Raju et al. 2009). Increased concentration of NO_3^- and Cl^- in groundwater contaminated by municipal wastewaters in some parts of the Varanasi urban area clearly indicates the urbanization consequence on the groundwater. However, the development of sanitary infrastructure for the disposal of municipal wastes is inadequate in swiftly expanded Varanasi City surroundings. This is a testimony to man-made pollution responsible for the inferior quality of groundwater in fast urbanizing areas (Raju et al. 1992; Raju and Reddy 2007). The main reason of nitrogen transformations associated with the soil–groundwater environment is domestic sewage, cesspools/septic tanks. Bulk ratio of nitrogen in wastewater at the septic tank is in the form of urea, organic nitrogen, and aqueous ammonium. Urea can be hydrolyzed under anaerobic conditions, and ammonium anion can be produced (Wilhelm et al. 1994). Ammonium anion can be immobilized geochemically by adsorption to the soil. Domestic sewage organic nitrogen is bound in carbon-containing compounds as proteins ($R\text{-}NH_2$). Decomposition of organic nitrogen ($R\text{-}NH_2$) in the sewage soil by a variety of microorganisms slowly transforms the organic nitrogen to ammonia (NH_3) by a process called "minerlization" (Viets 1974). Within the pH range of 6.8 to 7, ammonia exists mainly as the ammonium ion (NH_4^+). During the nitrification process, ammonium ion undergoes a transformation to nitrate in two steps. At the first stage, in the presence of oxygen, ammonia may be rapidly oxidized to nitrite (NO_2^-) by the autotrophic ammonia-oxidized bacteria (*Nitrosomonas*). In the second stage, the autotrophic nitrite-oxidized bacteria (*Nitrobactor*) oxidize nitrite to nitrate. Nitrite is a rather unstable nitrogen species, which will generally be reduced or oxidized. However, nitrate being an anion is quite soluble in water and is not significantly adsorbed by clay-rich soils. Usually, nitrification occurs mostly in the aerobic unsaturated zone, and it is thought generally that it is an oxic process. In some cases, ammonia oxidizers are able to oxidize ammonia under anoxic conditions (Wilhelm et al. 1994).

$$2NH_4^+ + 3O_2 ------ -2NO_2^- + 2H_2O + 4H^+$$

$$2NO_2^- + O_2 \quad ---------- 2NO_3^-$$

The negative charge on the clay particles retains ammonium ions (NH_4^+) and protects leaching of ammonium ions to groundwater. Negatively charged nitrate ions and water-filled pores of clay soils are devoid of oxygen. A group of soil bacteria (facultative anaerobes) use nitrates (instead of oxygen) for respiration, and they convert nitrates into nitrogen gas through a process called "denitrification." The high concentration of nitrate pollution in the localized areas of the study area reveals that the organic nitrogen is converted into the nitrate during the percolation of domestic sewage water directly from open sewer drainage or stagnant water pools (Raju et al. 1991; Reddy et al. 1992).

The fluoride is usually derived from weathering of fluoride-bearing rock-forming minerals such as muscovite, biotite, hornblende fluorite, fluoroapatite, etc. Low content of fluoride imply near absence of fluoride-bearing minerals in the Gangetic alluvium of the Varanasi area. Iron is generally derived from minerals, such as pyrite, limonite, goethite, etc. and occurs in the Gangetic alluvium. The oxide and sulfide iron species are usually the principal sources of iron in the groundwater. Hem (1991) has pointed out that the removal of iron from silicate minerals is a slow process normally, but near-surface weathering of iron-bearing silicates may produce an accumulation of ferric oxide or ferric hydroxide. The high iron concentrations in groundwater of the study area may be due to the organic content of municipal domestic waste and presence of iron minerals in the soils/weathered materials favorable for reduction of ferric iron into ferrous iron in the circulating groundwater (Hem 1991). Raju

(2006b) found that the iron contamination in the groundwater is caused by dissolution of ferruginous minerals in rocks and seepage of domestic sewage effluents in Tirumala-Tirupati environs, Andhra Pradesh. Eswari and Ramanibai (2000) have estimated the seasonal variation of iron in the waters of Chennai and suggested that the more iron concentration is due to anthropogenic activities and land run off. The organic content of the domestic sewage acts as a reducing agent and converts iron minerals into soluble form:

$$\mathrm{Fe}^{3+} + \text{organic matter} - - - - - \mathrm{Fe}^{2+} + \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O}$$

The cation diagram (Fig. 8) relating Ca, Mg, and Na + K shows that in the majority of the groundwater samples, alkaline earths (Ca + Mg) exceed alkalies (Na + K), while in some samples, contribution of alkalies (Na + K) exceeds alkaline earths (Ca + Mg). The (Ca + Mg)/(Na + K) ratio ranges from 0.47 to 8.44 with an average value of 3.1. Furthermore, the observed low ratio of (Ca + Mg)/(Na + K), i.e., 3.1, and relatively high contribution of alkalies (~25%) toward the total cations suggest that coupled reactions involving carbonate and silicate weathering controlled the solute acquisition process. High concentration of Ca and Mg is attributed to weathering of calcium carbonate and Ca–Mg silicates (amphiboles, pyroxenes, micas, and olivine). The calcareous nodules (kankar) are present mostly in the clay and fine sands of the Gangetic alluvial deposits in the study area. The sodium and the potassium in the aquatic system are derived from the atmospheric deposition, evaporite dissolution, and silicate weathering. The major possible source of Na in groundwaters is from sodic plagioclase because it occurs in all types of rocks and also Na–Ca silicate minerals weather most rapidly (Berner and Berner 1987). In the groundwater of Varanasi, K^+ is, however, not as abundant as Na^+ due to its fixation in the formation of clay minerals. Feldspars are more susceptible to weathering and alteration than quartz in silicate rocks.

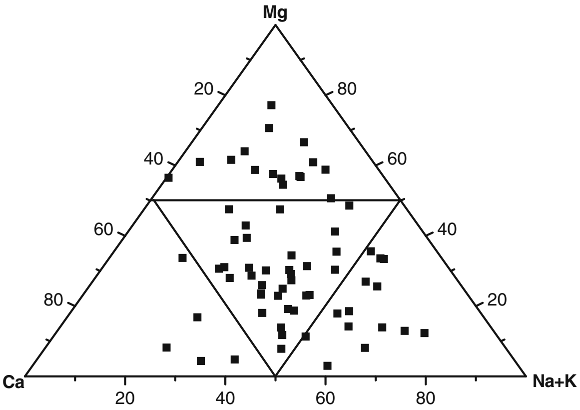


Fig. 8 The ternary cation diagram relating Ca, Mg, and Na + K

Groundwater quality assessment for domestic and irrigation use

The data obtained by chemical analyses were evaluated in terms of suitability for drinking and general domestic and irrigation uses.

Suitability for drinking and general domestic use

The range of hydrochemical parameters of groundwater of the Varanasi environs and their comparison with the prescribed specification of Indian standard (BIS 1991) and World Health Organization (WHO 1997) are summarized in Table 1, to evaluate the suitability of groundwater for drinking and domestic and public health uses. It is observed that most of the hydrochemical parameters of the groundwater samples in the study area exceed the desirable limits of the WHO and the Bureau of Indian Standards (BIS), although a number of samples are within the maximum permissible limits.

Based on the classification of TDS content (Fetter 1990), 97% of the groundwater samples come under the freshwater category (TDS < 1,000 mg/l) and 3% of the water samples under brackish category (TDS > 1,000 mg/l). Table 1 shows that 49% of the groundwater samples are exceeding the concentration of TDS more than the desirable limits (500 mg/l), while all samples are within the permissible limits of the WHO and the BIS. The higher concentration of total dissolved solids may cause a gastrointestinal irritation in human beings. The total hardness of the analyzed samples varies between 169 and 694 mg/l with an average value of 341 mg/l indicating hard to very hard types of waters (Sawyer and Mc Carthy 1967). The chemical data (Table 1) indicate that 53% of the total groundwater samples have total hardness beyond the safe limits of 300 mg/l for drinking water (BIS 1991). Hardness of the water results from the presence of divalent metallic cations of which calcium and magnesium are the most abundant in groundwater. Total hardness (TH) is calculated through the following equation (Todd 1980).

$$\mathrm{TH} = 2.5\,\mathrm{Ca} + 4.1\mathrm{Mg}$$
$$\left(\text{all ions are in milligramsperliter}\right)$$

These ions react with soap to form precipitates and with certain anions present in water to form scales. The property of hardness can prevent formation of lather with soap and also increases the boiling point of water, but it has no recognized adverse effect on human health. The high TH may cause encrustation on water supply distribution systems. Long-term consumption of very high hard water might lead to an increased incidence of urolithiasis, anencephaly, parental mortality, some types of cancer, and cardiovascular disorders (Agrawal and Jagetia 1997).

The desirable limit of calcium and magnesium is 75 and 30 mg/l, respectively. Twenty-nine percent of the calcium and 75% of the magnesium are exceeding desirable limits, and all are found within the permissible limits of the WHO and BIS standards (Table 1). Undesirable effect produced beyond the permissible limits of Ca and Mg is encrustation in water supply and has an adverse effect on domestic use. The recommended limit for sodium concentration in drinking water is 200 mg/l. Concentration of sodium in the groundwater samples of the study area indicates that 62% are exceeding the desirable limit (50 mg/l) and 4% exceeding the permissible limits (200 mg/l) set by the WHO (1997). A higher sodium intake may cause hypertension, congenial heart diseases, and kidney problems. Concentration of potassium reveals that 12% of the samples are exceeding both the desirable and permissible limits.

The analytical data show that $\mathrm{HCO_3}$ exceeds the desirable limit (300 mg/l) in about 82% of the samples and the permissible limit in about 4% of the groundwater samples in the study area. The bicarbonate ion has no known adverse health effects on human beings. The concentration of Cl in the groundwater indicates that 3% of the samples are exceeding the allowable safe limit. High concentration of Cl in drinking water causes the salty taste and has a laxative effect on people not habituated to it. The concentration of $\mathrm{SO_4}$ in all groundwater samples are within the desirable and permissible limits. Undesirable effects of high concentration of sulfate in drinking water are associated with respiratory problems (Maiti 1982). High sulfate content may have a laxative effect with excess of Mg and also causes corrosion of metals in the distribution system, particularly in waters having low alkalinity. About 15% and 18% of the groundwater samples have nitrate concentration higher than the recommended levels of 50 mg/l (WHO 1997) and 45 mg/l (BIS 1991), respectively (Table 1). High concentrations of nitrates can cause methemoglobinemia, gastric cancer, goiter, birth malformations, and hypertension (Majumdar and Gupta 2000). Ingestion of nitrate by infants can cause low oxygen level in blood (Nolan 2001) and ultimately may result to death (Shih et al. 1997). Fluoride is one among the substances for which there are both lower (<0.6 mg/l) and upper limits (>1.5 mg/l) of concentration in drinking water, with identified health effect (dental and skeletal fluorosis) and benefits for human beings (BIS 1991). All the groundwater samples of the study area are within the permissible limits of 1.5 mg/l (Table 1). Ray et al. (1983) have reported around 25% of dental fluorosis, but no case of skeletal fluorosis in Ledhupur and Rustampur villages in the Varanasi environs has been recorded. The results of chemical analysis of the groundwater samples of the study area show that most of the water samples (about 79%) have a higher iron concentration than the WHO drinking water guideline of 0.3 mg/l (Table 1). In potable water, iron more than the permissible limits is objectionable because it gives a bitter taste and excessive concentration of iron causes gastrointestinal upset, and moreover, it stains the cloth, teeth, gums, and utensils. Iron is an essential element in human nutrition and is contained in biologically significant proteins such as hemoglobin and cytochrome in the form of oxidation-reduction enzymes. Abnormally larger amount of iron adversely affects the human system and results into hemochromatosis, wherein tissues are damaged due to prolonged iron accumulation. Iron also promotes the growth of iron bacteria.

Suitability for irrigation use

The suitability of groundwater for irrigation is contingent on the effects of the mineral constituents in the water on both the plants and soil (Richards 1954). Salts may harm plant's growth physically by limiting the uptake of water through modification in the osmotic processes or chemically by metabolic reactions such as those caused by toxic constituents (Todd 1980). Effects of salts on soils cause changes in soil structure, permeability, and aeration, which indirectly affect plant growth. An important factor allied to the relation of crop growth to water quality is drainage. If a soil is open and well drained, crops may be grown on it with the application of generous amounts of saline water; on the other hand, a poorly drained area combined with application of good quality water may fail to produce as satisfactory a crop (Todd 1980). The important hydrochemical parameters of groundwater used to determine its suitability for irrigation are EC, salinity, percent sodium (%Na), sodium adsorption ratio (SAR), RSC, permeability index (PI), chloroalkaline indices (CAI), and magnesium ratio.

Electrical conductivity and percent sodium

EC and Na concentrations are important in classifying irrigation water. The EC values vary from 400 to 2,150 µS/cm (Table 1). High salt content (high EC) in irrigation water leads to formation of saline soil. Salinization, on the irrigated lands, is the major cause of loss of production, and it has adverse environmental impacts on irrigation. Saline conditions severely limit the choice of crops and adversely affect crop germination and yields. It is important that all evaluations regarding irrigation water quality are linked to the evaluation of the soils to be irrigated (Ayers and Wescot 1985). Sodium concentration is important in classifying irrigation water because sodium reacts with soil to reduce its permeability. In all natural waters, percent sodium is a parameter to evaluate its suitability for agricultural purposes (Wilcox 1948); sodium combining with carbonate forms alkaline soils, while sodium combining with chloride forms saline soils. Either type of sodium-enriched soil will support little or no plant growth (Todd 1980). The sodium percentage (%Na) in the study area ranges between 9% and 67.5% with an average of 38% (Table 2). A high sodium percentage causes deflocculation and impairment of the tilth and the permeability of soils (Karanth 1989). A maximum of 60% of the sodium is recommended for irrigation water for better crop yields (BIS 1991). The chemical quality of groundwater samples was studied by plotting analytical data (Wilcox 1948) relating EC and sodium percent (Fig. 9) that show that out of the 68 groundwater samples, 41% of the samples belong to excellent to good category followed by 53% of the samples belonging to good to permissible category, 3% belonging to permissible to doubtful, and 3% of the samples belonging to doubtful to unsuitable category for irrigation use (Table 3). The agricultural yields are generally low in lands irrigated with waters belonging to doubtful to unsuitable category. This is probably due to the presence of excess sodium salts, which

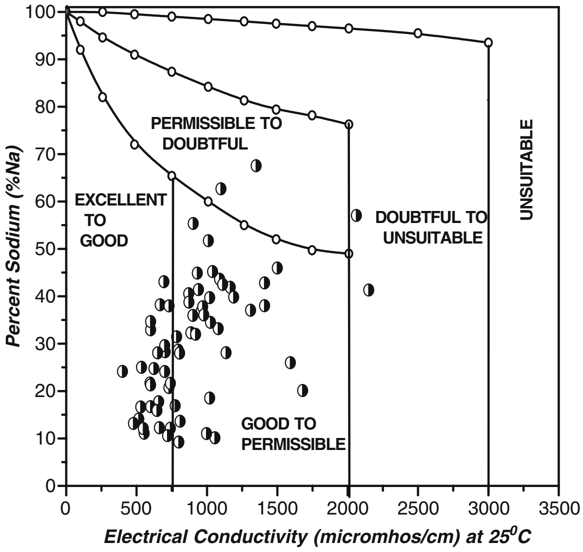


Fig. 9 Rating of groundwater samples on the basis of electrical conductivity and percent sodium (after Wilcox 1948)

Table 3 Geochemical classification of groundwater of the Varanasi area

Water type	Sample number	Total number of samples (%)
Wilcox classification (Fig. 9)		
Excellent to good	1–7, 9–11, 15, 16, 18, 19, 23, 29, 39, 41, 45–47, 51–53, 56–58, 68	28 (41%)
Good to permissible	8, 12–14, 17, 20–22, 24–28, 30–38, 42–44, 48–50, 54, 55, 59, 60, 63–66	36 (53%)
Permissible to doubtful	62, 67	2 (3%)
Doubtful to unsuitable	40, 61	2 (3%)
Unsuitable	—	—
US salinity laboratory classification (Fig. 10)		
C_2S_1	1–3, 5–7, 9–11, 15, 16, 18, 19, 23, 29, 39, 41, 45–47, 51–53, 56–58, 68	27 (40%)
C_3S_1	4, 8, 12–14, 17, 20–22, 24–28, 30–38, 40, 42–44, 48–50, 54, 55, 59, 60, 63–67	39 (57%)
C_3S_2	61, 62	2 (3%)

cause osmotic effects on soil–plant system. When the concentration of sodium is high in irrigation water, sodium ions tend to be adsorbed by clay particles, displacing Mg and Ca ions by base-exchange process. This exchange process of Na in water for Ca and Mg in soil reduces permeability and eventually results in soil with poor internal drainage. Hence, air and water circulation is restricted during wet conditions, and such soils are usually hard when dry (Collins and Jenkins 1996; Saleh et al. 1999).

Salinity hazard and alkali hazard

On the basis of EC values, Richards (1954) classified total concentration of soluble salts in irrigation water into four groups (Table 4). As per Richards' classification, 40% of the samples are good and 60% of the groundwater samples are medium in salinity. High-salinity problems are encountered where irrigation activity is in poor-drainage agricultural soils and also where water-logging allows the water table to rise close to the root zone of plants, causing accumulation of sodium salts in the soil solution through capillary rise following surface evaporation. The sodium or alkali hazard in the use of water for irrigation is determined by the absolute and relative concentration of cations. The relative activity of sodium ion in the exchange reaction with soil is expressed in terms of SAR. The SAR value in the study area ranges from 0.32 to 6.49 with an average of 1.66 (Table 2). The groundwater is of excellent quality since none of the samples exceeds the SAR value of 10 (Table 4). If high sodium content and low calcium content are present in waters used for irrigation purpose, the base-exchange complex may become saturated with sodium. This can destroy the soil structure due to the deflocculation (dispersion of clay particles) process. The plot of the analytical data on the US salinity diagram, in which the EC is taken as a salinity hazard and SAR as an alkalinity hazard (Fig. 10), shows that 40% (Table 3) of the groundwater samples

Table 4 Irrigation water quality classification (after Richards 1954)

Water class	Salinity hazard		Alkali hazard	
	EC (μS/cm)	Number of samples	SAR (epm)	Number of samples
Excellent	Up to 250	—	Up to 10	68
Good	250–750	27	10–18	—
Fair/medium	750–2,250	41	18–26	—
Poor/bad	2,250–5,000	—	> 26	—

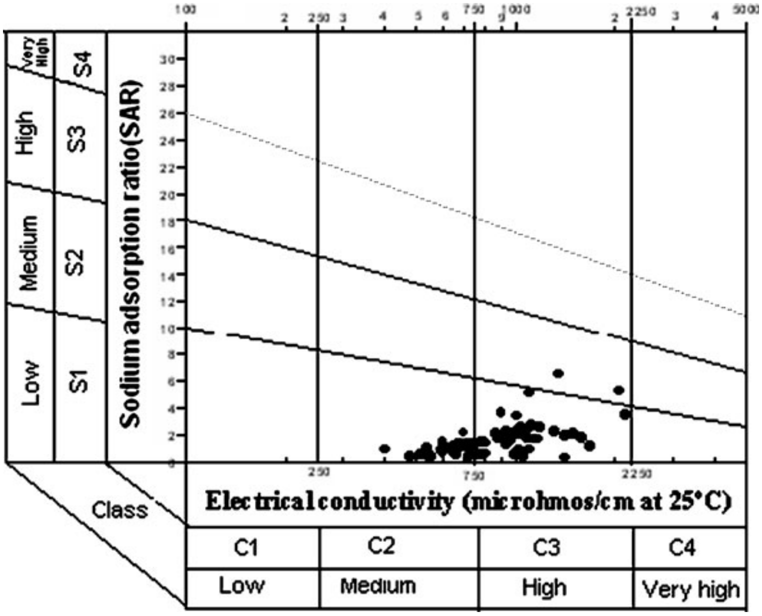


Fig. 10 Rating of groundwater samples in relation to salinity hazard and sodium hazard (after US Salinity Laboratory diagram 1954)

fall in the category of C_2S_1, indicating medium salinity and low alkali water, which can be used for irrigating most of the soils and crops with little danger of exchangeable sodium. However, 57% of the water samples fall in C_3S_1 class, which shows a high salinity hazard and low alkali hazards (Richards 1954). However, two samples (3%) fall in the C_3S_2 waters, indicating high salinity to a medium sodium type. This type of water may be used on coarse-fstextured or organic soils with good permeability (Karanth 1989). Therefore, water with high salinity cannot be used on soils with restricted drainage, and plants with good salt tolerance should be selected.

Residual sodium carbonate

Residual sodium carbonate (RSC) also influences the suitability of water for irrigation uses. RSC can be estimated by subtracting the quantity of alkaline earths (Ca + Mg) from the carbonates (CO_3 + HCO_3). When the sum of carbonates is in excess of calcium and magnesium, there may be a possibility of complete precipitation of Ca and Mg (Raghunath 1987). If the carbonates are less than alkaline earths, it indicates that the residual sodium carbonate is zero. The RSC values of the study area range from 0.044 to 6.261 with an average value of 1.464 (Table 2). A high value of RSC in water leads to an increase in the adsorption of sodium in soil (Eaton 1950). On the basis of RSC values, water can be classified as safe (<1.25 mEq/l), marginally suitable (1.25–2.5 mEq/l), and unsuitable (>2.5 mEq/l). It is observed that out of the 68 samples, 58 samples are safe, six are marginally suitable, and four samples are unsuitable for irrigation use. Waters having an RSC value greater than 5 mEq/l are considered harmful to the growth of plants. Only one sample exceeds the 5-mEq/l limit. This indicates that most of the water is suitable for irrigation uses in the study area.

Permeability index

Soil permeability is affected by long-term use of irrigation water with high salt content. Permeability is influenced by sodium, calcium, magnesium, chloride, and bicarbonate contents of the soil. Doneen (1964) has classified irrigation waters based on the PI, which indicates the suitability of groundwater for irrigation use. The calculation of PI is as follows:

$$\mathrm{PI} = \frac{\mathrm{Na} + \sqrt{\mathrm{HCO_3}}}{\mathrm{Ca} + \mathrm{Mg} + \mathrm{Na}} \times 100$$

(all ions are in equivalents per million)

The PI value of the groundwater samples ranges 32.54 to 89.60 with a mean of 56.26 (Table 2). The groundwater may be classified into classes 1, 2, and 3 based on the permeability indices. Classes 1 and 2 are suitable for irrigation, with 75% or more maximum permeability, and class 3 is unsuitable, with 25% maximum permeability. Based on the above classification, 97% of the samples fall in class 1 and 3% fall in class 2 in the Doneen's chart (Domenico and Schwartz 1990), implying that the groundwater in the study area is of good quality for irrigation uses.

Magnesium hazard

In general, calcium and magnesium will be in a state of equilibrium in groundwater. Szabolcs and Darab (1964) proposed a magnesium hazard (MH) value for irrigation water, and an MH ratio is calculated by the following equation:

$$\text{Magnesium ratio} = \frac{\mathrm{Mg}}{\mathrm{Ca} + \mathrm{Mg}} \times 100$$

(all ions are in equivalents per million)

The magnesium ratio values of the study area range from 0.76 to 95.14 with an average value of 52.98 (Table 2). The analyzed water samples indicate that 60% of the groundwater samples are exceeding the magnesium ratio of 50. A magnesium ratio of more than 50 is considered to be harmful and unsuitable for irrigation use. This would adversely affect the crop yield, as soils become more alkaline.

Chloroalkaline indices

Knowledge of the changes brought about in the chemical composition of the groundwater during underground travel is essential (Sastri 1994). Control on the dissolution of undesirable constituents in water is impossible during the subsurface runoff, but it is essential to know the various changes undergone by water during the travel (Johnson 1979). The chemical reactions in which ion exchange between the groundwater and the aquifer environment occurs during the periods of residence and movement may be understood through the study of chloroalkaline indices. The CAI 1 and 2 is calculated using the following formula (Schoeller 1977):

$$\mathrm{CAI\ 1} = \frac{\mathrm{Cl} - (\mathrm{Na} + \mathrm{K})}{\mathrm{Cl}}$$

(all ions are in equivalents per million)

$$\mathrm{CAI\ 2} = \frac{\mathrm{Cl} - (\mathrm{Na} + \mathrm{K})}{(\mathrm{SO_4} + \mathrm{CO_3} + \mathrm{HCO_3} + \mathrm{NO_3})}$$

The chloroalkaline index (CAI 1 and CAI 2) values of the study area range from −16.18 to 0.56 (mean, −0.85) and −0.63 to 0.26 (mean, −0.09), respectively (Table 2). The chloroalkaline indices may be positive or negative depending upon the exchange of sodium and potassium from rock with magnesium and calcium in water and vice versa. If CAI ratio is positive (direct exchange), there is exchange between sodium and potassium (Na + K) in water with calcium and magnesium (Ca + Mg) in rocks. If the CAI ratio is negative (reverse exchange), there is exchange between calcium and magnesium in water with sodium and potassium in rocks. CAI 1 and 2 of the samples in the study area indicate that 69% of the groundwater samples show a negative ratio depicting the type of base exchange and 31% of the groundwater samples indicate positive ratios.

Corrosivity ratio

Corrosivity ratio (CR) denotes susceptibility of groundwater to corrosion and is expressed as ratio of alkaline earths to saline salts in groundwater. The corrosivity ratio is defined by the formula:

$$\mathrm{CR} = \frac{(\mathrm{Cl}/35.5) + 2\left(\mathrm{SO_4}/96\right)}{2\left\{(\mathrm{CO_3} + \mathrm{HCO_3})/100\right\}}$$

(all ions are in parts per million)

The effects of corrosion are losses in the hydraulic capacity of pipes. Many researchers have used the ratio to evaluate corrosive tendency of groundwater on metallic pipes in different areas (Balasubramanian 1986; Sankar 1995; Aravindan et al. 2004). The corrosivity ratio of groundwater samples of the study area ranges from 0.29 to 15.18 with an average value of 4.17 (Table 2). About 99% of the groundwater samples collected have a corrosive ratio of more than 1, and 1% of the samples have corrosive ratio of less than 1. The groundwater samples have a CR of less than 1 (<1) to be a safe zone and more than 1 (>1) to be unsafe. Except one location in the eastern part of the study area, most of the samples were found to be in the unsafe zone. In the area where groundwater has CR values greater than 1, noncorrosive pipes, viz., polyvinyl chloride, should be used for water supply instead of metal pipes in the study region.

Conclusions

The rural–urban migration of population in the Varanasi City increases urban expansion that has led to environmental water quality problems. The groundwaters in the study area are slightly alkaline in nature. In general, the quality assessment of groundwater shows that water is suitable for domestic use with few exceptions that needs remedial measures. The relatively high ratio of $HCO_3/(HCO_3 + SO_4)$ in most of the groundwater signified that carbonic acid weathering is the major proton producer in the waters of the area. The overall hydrochemistry reflects rock weathering with inputs from anthropogenic impacts due to the fast urbanization. Hydrogeochemistry reveals that the order of cation abundance is $Na > Ca > Mg > K$ except in some groundwater samples where Ca replaces Na, and in anionic chemistry, the order is $HCO_3 > Cl > SO_4$. The Chadha diagram suggests that the alkaline earths and weak acidic anions exceed both the alkali metals and the strong acidic anions, respectively, and these waters have temporary hardness, and it can be removed by boiling. Gibbs' chemical diagram indicates that majority of the groundwater samples show rock dominance. The chemical data indicate that 53% of the total groundwater samples have total hardness beyond the safe limits. The groundwater usage for domestic purposes has been limited due to the excessive desirable limit of TDS, NO_3, Cl, Fe, and TH in the study area. Richards' classification on the basis of EC reveals that all the samples are of good to medium salinity hazard, and their SAR values indicate that all the waters are excellent. As per the Wilcox classification, the agricultural crop yields are generally low in lands irrigated in city station (no. 40) and Mannapur (no. 61) groundwaters. This is probably due to the presence of excess sodium salts that cause deflocculating and reduce the permeability of soils. The US salinity diagram shows that 3% of the groundwater samples fall in the C_3S_2, which indicates high salinity and medium sodium hazard rendering it usable only on coarse-textured or organic soils with good permeability. The permeability index indicates that the groundwater of the study area is of good quality for irrigation uses. About 60% of the groundwater samples with high magnesium ratio values are considered to be harmful and detrimental for crop yields. High salinity, %Na, RSC, and Mg hazard values at some locations limit the use of groundwater for agricultural activities. Hence, soils affected with the high salinity and alkalinity hazards require gypsum/lime treatment to improve permeability of the soils by base exchange.

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