

Hydrogeochemistry of groundwater and anthropogenic control over dolomitization reactions in alluvial sediments of the Deoria district: Ganga plain, India

Vikram Bhardwaj · Dhruv Sen Singh ·
A. K. Singh

Received: 17 September 2008 / Accepted: 9 February 2009 / Published online: 26 February 2009
© Springer-Verlag 2009

Abstract Groundwater is a critical resource in Deoria district, as it is the main source of drinking water and irrigation. The aquifer has deteriorated to a high degree, during the last two to three decades, in quality and quantity due to high population growth and environmental pollution. More than 90% of the population get their drinking water from subsurface waters. Fifteen wells were sampled in June 2006 to probe the hydrogeochemical components that influence the water quality. The results show that groundwater have EC, TDS, Na^+ , Mg^{2+} , HCO_3^- and TH higher than the WHO, 1997 maximum desirable limits. A hydrogeochemical numerical model for carbonate minerals was constructed using the PHREEQC package. The regression analysis shows that there are three groups of elements which are significantly and positively correlated. The main hydrochemical facies of the aquifer ($\text{Ca} + \text{Mg} - \text{HCO}_3$) represents 33.33% of the total wells. The geochemical modeling demonstrated that the reactions responsible for the hydrochemical evolution in the area fall into three categories: (1) dissolution of salts, (2) precipitation of dolomite, (3) ion exchange. Solubility of dolomite, calcite, aragonite and gypsum were assessed in terms of the saturation index. The thermodynamic prerequisites for dolomite supersaturation reactions are satisfied by subsurface waters, since they are supersaturated with respect to dolomite, undersaturated (or in equilibrium) with respect to calcite, and undersaturated with respect to

gypsum. The Ca^{2+} versus SO_4^{2-} and Mg^{2+} versus SO_4^{2-} trends are also compatible with homologous trends resulting from dolomite supersaturation.

Keywords Ganga plain · Deoria district · Groundwater · Hydrogeochemistry · Water quality

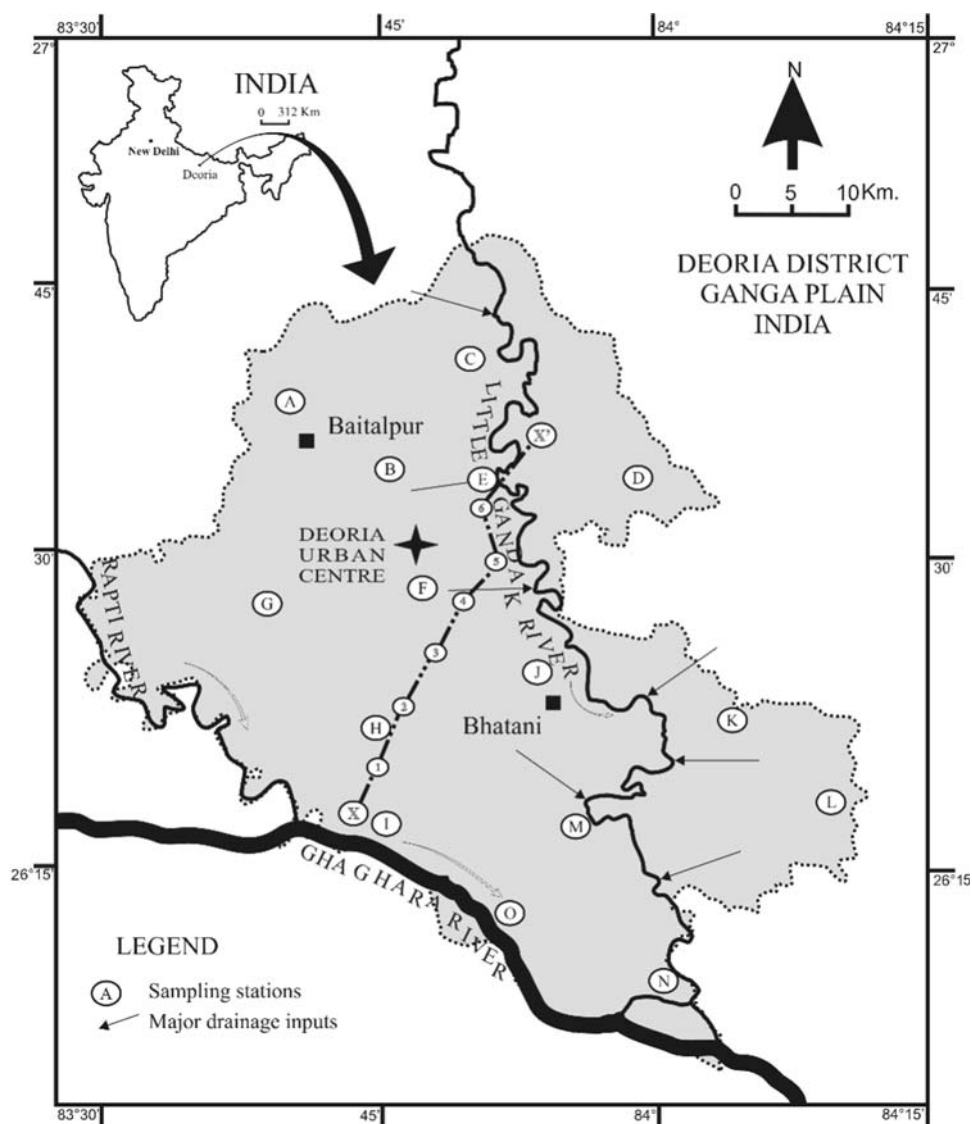
Introduction

Deoria district is located in the eastern part of the Ganga plain, at the both sides of the Little Gandak river (Fig. 1). It occupies an estimated area of approximately 2,489.41 km². The total population of the area is 27,30,376 inhabitants with population density of 1,062 persons per square kilometer according to 2001 census. Population growth rate of the area is about 23.85%. Groundwater is the sole source for regular water supply. The annual precipitation is about 1,128.11 mm. The residents have their own groundwater wells installed within the vicinity of the settlements. Groundwater studies in Deoria are very important due to the increasing demographic pressure. In such regions, groundwater is commonly, the only water resource. The increasing exploitation frequently causes deterioration of water.

In this area, urban and agricultural expansions have caused an ever-growing need for fresh water. In this region, water supply for most municipalities, domestic use water for urban developments and irrigation water for agricultural activities are almost exclusively provided through hand dug or drilled wells. In addition to obvious primary uses of water for domestic use (e.g., washing and bathing), the quantities required have been greatly increased by secondary demand, mainly for gardening, landscaping, etc. The main objectives of this paper are: (1) to assess the

V. Bhardwaj (✉) · D. S. Singh
Centre of Advanced Study in Geology,
University of Lucknow, Lucknow 226007, India
e-mail: vik_bhardwaj0710@rediffmail.com

A. K. Singh
Central Institute of Mining and Fuel Research,
Barwa Road, Dhanbad 826 001, India

Fig. 1 Location map

chemistry of groundwater, (2) to set qualitative and quantitative descriptions of aqueous geochemical processes, by using statistical and geochemical modeling techniques, (3) to report the occurrence of anthropogenic driven dolomite supersaturation in alluvial in the study area.

Site description

The study area is situated in Deoria district, Uttar Pradesh, India between $26^{\circ}06'–26^{\circ}44'N$ latitude and $83^{\circ}30'–84^{\circ}12'E$ longitude (Fig. 1). It is a part of Ganga plain, at an elevation between 65 a 106 m above mean sea level. Physiographically, this area is very fertile with a gentle slope towards southeast, which is in correspondence with the lineaments present under the alluvial cover of this region (Singh et al. 1996). The main river is the Little Gandak, which drains the entire district in crisscross way

from north to south. A number of tributaries joins this river on both the banks. Small lakes and abandoned river channels are abundant in the district. Climate is sub-humid and vegetation is characterized by deciduous trees and grassland. Maximum rain occurs in July. Average annual rainfall in the area is 1,128.11 mm and the annual potential evapotranspiration is about 1,955 mm. The area is hot in May and June, with mean maximum temperature of $39.2^{\circ}C$ and cool in December and January with mean minimum temperature of $9.5^{\circ}C$. Humidity is maximum in August (84%) and minimum in April (43%). The Little Gandak River with tributaries and small stretches of the Rapti and Ghaghara rivers control the drainage system of the district. The drainage pattern is subdendritic to dendritic. The length of the Little Gandak river is about 295 km. The slope gradient is 21.00 cm km^{-1} . The river originates near Baithulia in the terai region of Mahrajganj district. It is meandering with the sinuosity of about 2.05. Relief of the

river bank ranges from 0.1 to 7.0 m (Singh 1998). Channel width varies between 25 and 200 m and valley width between 0.1 and 0.5 km. This river joins the Ghaghara near Gothini in Siwan district of Bihar. The boundary of the district is delineated by Ghaghara river in south and by Rapti river in southwest.

The Section line X–X' shown in Fig. 1 runs in a SSW–NNE direction. The length of the section is about 40 km and the depth of the bore holes ranges from 70.10 to 103.63 m (Fig. 2). Lithologically, the study area is characterized by thick deposits of Quaternary alluvium consisting of clay, sand, kankar and gravel mixed in different proportions. Sedimentation on the interchannel areas takes place mainly by sheet flow (Kumar et al. 1995) and interfluvial deposits (Singh et al. 1999), whereas in the channel areas takes the form of channel bar deposits (Singh and Singh 2005). Geomorphologically, the interchannel areas are differentiated into broad low lying areas, minor ponds, lakes, minor creeks, abandoned channels and small ridges. Older alluvium (Bhangar) and newer alluvium (Khadar) are the two morphostratigraphic units in the classical literature of the Ganga Plain (Pascoe 1917). In this area, upland terrace surface, river valley terrace surface, and present day river channel made up of older alluvium and newer alluvium can be identified.

Clay mineralogy

The major clay minerals in the soils from the study area are illite, kaolinite, interstratified kaolinite-smectite, chlorite and vermiculite (Mohindra and Parkash 1990). Small amount of mixed layer illite–vermiculite–chlorite mineral also occur. Variation of clay minerals contents with depth in major horizons of pedons are shown in Fig. 3.

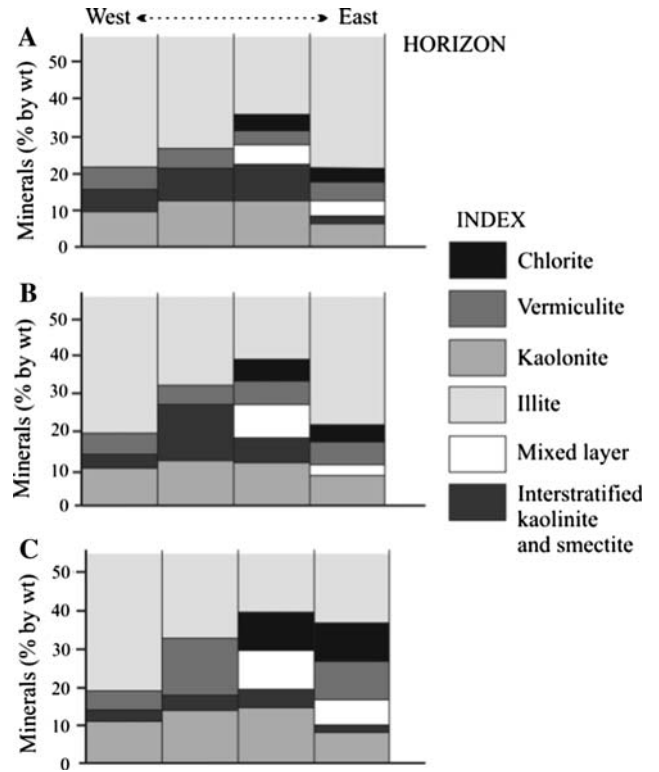


Fig. 3 Variation of clay minerals contents with depth in major horizons of pedons along east to west of the study area

Land use

Deoria district is occupied by approximately 2,158 villages surrounded by small farms and agricultural areas. Proportion of land use for agriculture is more than 80% (Fig. 4) in the area. Agriculture is associated with manure and fertilizers. The manures have nitrogen, potassium, sulphur, phosphorus, calcium and magnesium (Portela et al. 1993)

Fig. 2 Hydrogeological cross section in Deoria district

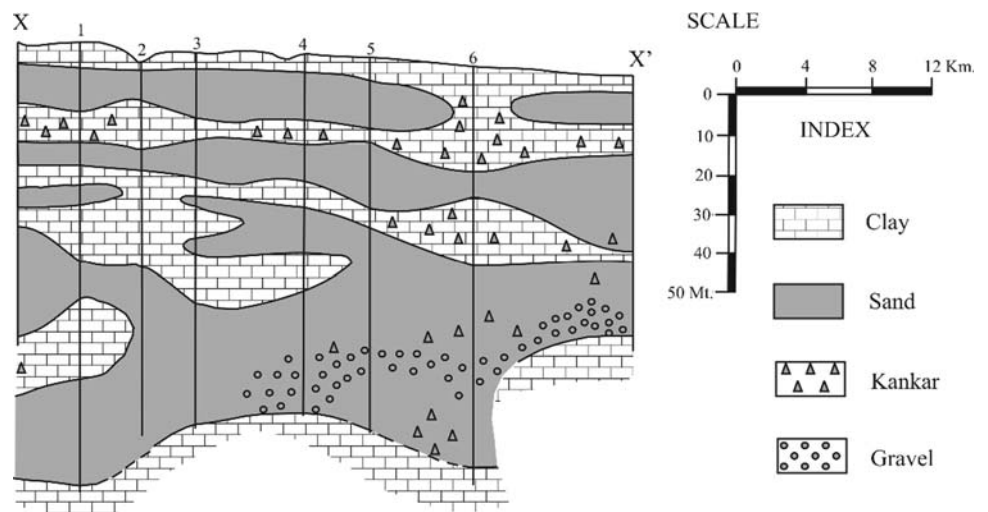
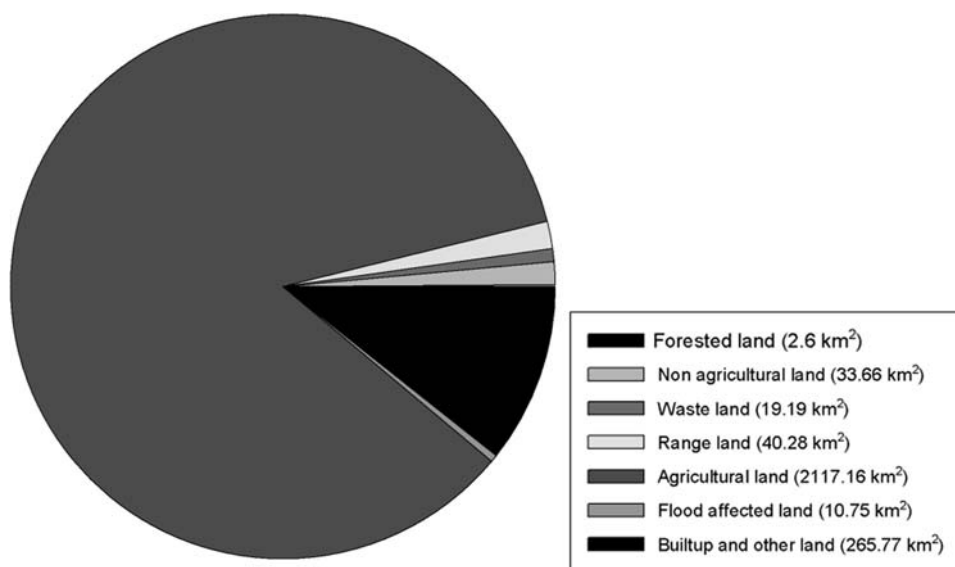


Fig. 4 Land use and land cover

and fertilizers have phosphorous, potassium, nitrogen, chloride, sulphur, calcium and magnesium. Continuous application of fertilizers and manures could also be the source of dissolved gypsum (Pacheco and Szocs 2006). Most villages have no sewage or proper drainage systems. These facts are responsible for the anthropogenic contribution to the chemistry of soil and groundwaters for decades.

Methodology

Water samples were collected from 15 wells within the Deoria district in June 2006 (Fig. 1). These wells are used for domestic and irrigation water supply in the area. All samples were filtered and split for subsequent analyses of cations and anions. The following parameters were analyzed both in the field and laboratory: EC, TDS, pH, F^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , HCO_3^- , Cl^- , and NO_3^- . Analyses were performed at the geochemical laboratory of the Department of Geology, University of Lucknow (Table 1). Conductivity, pH, total dissolved solids were determined in the field by Cyber Scan 510, Potassium and Sodium by Systronics Flame photometer 128, Nitrate by Perkin Elmer, UV/VIS spectrometer, Lambda 40, Ca^{2+} and Mg^{2+} by EDTA titration (APHA 1992), Cl^- by potentiometric method APHA 1998, F^- by SPADNS colorimetric method (APHA 1998), HCO_3^- estimated from total alkalinity (APHA 1998), SO_4^{2-} by turbidimetric method, APHA 1998, SiO_2 by molybdosilicate method (APHA 1998), total hardness (as $CaCO_3$) by EDTA titration method, APHA 1998. The reproducibility of the analytical procedures was checked by carrying out a duplicate analysis. Duplicate results did not differ by more than 5% of the mean.

Replicability of sampling was determined by collection of two samples at a location. All samples have ion balance average better than $\pm 13.46\%$.

Aqueous geochemical modeling

Inverse modeling is often used for interpreting geochemical processes that account for the hydrochemical evolution of groundwater (Plummer et al. 1983) and calculations were performed using PHREEQC (Parkhurst and Appelo 1999). We use the information from the lithology, general hydrochemical evolution patterns, and saturation indices (Table 1) to constrain the inverse models. PHREEQC was also used to calculate aqueous speciation and mineral saturation indices. Inverse modeling in PHREEQC uses the mass-balance approach to calculate all the stoichiometrically available reactions that can produce the observed chemical changes between end-member waters (Plummer and Back 1980). This mass-balance technique has been used to quantify reactions controlling water chemistry along flowpaths (Thomas et al. 1989) and quantify mixing of end-member components in a flow system (Kuells et al. 2000). Finally, the mineral reaction mode (dissolution or precipitation) is constrained by the saturation indices of each mineral (Table 1).

Thermodynamics and mass action constants

For precipitation of dolomite at the expense of calcite, solutions must simultaneously maintain some extent of oversaturation with respect to dolomite and undersaturation with respect to calcite. If the dissolution process is relatively rapid and the advective flux relatively slow, then groundwaters are maintained at near-equilibrium positions

Table 1 Values of ions in mg L⁻¹ (excluding physical data)

Sampling Locations	Parameters														Gypsum (SI)			
	ECa	TDSb	pH	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	F ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ⁻	THc	Aragonite (SI)		Calcite (SI)	Dolomite (SI)	IAP _{dot}
A	494.2	650	7.9	3.7	55.3	18.2	20.5	23.3	0.41	14	221	152	123	-0.17	-0.02	0.35	10 ^{-16.75}	-2.01
B	891.5	880	8.09	2.2	129.8	23.1	20.8	63.7	0.54	18	283	192	143	0.19	0.33	0.97	10 ^{-16.13}	-1.88
C	355.3	490	7.9	3.3	24.7	20.3	16.3	10.5	0.4	24	174	89	118	-0.19	-0.04	0.17	10 ^{-16.95}	-2.15
D	500	645	7.9	20.9	26.0	33.2	21.8	29.3	0.51	16	213	98	173	0.10	0.24	0.65	10 ^{-16.45}	-1.93
E	1380.5	1225	8.0	28.1	56.2	17.1	50.5	190.5	0.59	38	347	147	250	0.06	0.20	1.23	10 ^{-15.89}	-2.17
F	348.6	465	7.9	1.9	26.1	22.5	14.7	19.8	0.44	21	161	74	115	-0.17	-0.03	0.12	10 ^{-16.98}	-2.17
G	243	405	8.1	1.7	18.7	32.4	2.4	7.2	0.43	18	122	107	90	0.07	0.21	-0.36	10 ^{-17.45}	-1.84
H	434.3	615	7.9	3.1	41.2	22.6	17.6	16.3	0.44	14	189	144	130	-0.13	0.01	0.26	10 ^{-16.83}	-1.93
I	304	415	7.9	2.7	25.1	27.2	19.5	14.1	0.48	12	153	82	53.5	-0.11	0.04	0.28	10 ^{-16.82}	-2.06
J	526.8	690	8.0	10.0	42.5	22.5	25.3	59.6	0.52	26	189	141	160	-0.04	0.10	0.60	10 ^{-16.50}	-1.97
K	495.6	455	7.9	5.5	45.2	23.5	22.3	60.4	0.41	21	124	121	149	-0.28	-0.14	0.04	10 ^{-17.06}	-1.99
L	383	575	8.1	4.7	29.3	8.4	26.1	8.3	0.43	18	207	134	125	-0.34	-0.20	0.46	10 ^{-16.63}	-2.41
M	429.2	585	8.1	9.4	31.2	21.6	19.5	28.4	0.42	19	183	132	133	0.04	0.18	0.67	10 ^{-16.43}	-1.98
N	717.5	780	8.0	59.1	58.5	11.7	31.3	56.5	0.57	28	198	169	155	-0.35	-0.21	0.38	10 ^{-16.72}	-2.33
O	279.3	435	7.8	2.3	18.3	20.6	10.9	10.7	0.41	12	140	109	96.6	-0.37	-0.22	-0.38	10 ^{-17.47}	-2.03
Minimum	243.0	405.0	7.8	1.7	18.0	8.00	2.4	7.0	0.40	12.0	122.0	74.0	53.5	0.10	-0.22	-0.38	-	-2.33
Maximum	1380.5	1225	8.1	59.1	129.8	33	50.5	190.5	0.59	38.0	347.0	192.0	250.0	-0.37	0.33	1.23	-	-1.88
Mean	518.8	620.6	7.9	10.5	41.7	21.4	21.2	39.8	0.46	19.9	193.6	126.0	134.2	-	-	-	-	-
Median	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.13	0.01	0.35	10 ^{-16.74}	-2.01
Standard Deviation	291.7	217	0.1	15.4	27.8	6.5	10.4	46.5	0.06	6.9	59.1	33.2	43.9	-	-	-	-	-

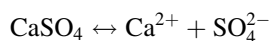
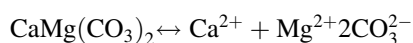
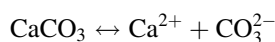
^a EC Conductivity (μS cm⁻¹ at 25°C)

^b TDS Total dissolved solids

^c TH total hardness (as CaCO₃)

Saturation index (SI) Log [ion activity product]/K_{sp}, where K_{sp} solubility product at given temperature. Phases and thermodynamic data are from PHREEQC and accompanying databases (Parkhurst and Appelo 1999). Saturation indices were calculated by the computer program PHREEQC (Version 2.14.2) (Parkhurst and Appelo 1999)

with respect to both minerals. Oversaturation with respect to dolomite is maintained by dissolution of a mineral at a rate greater than that of dolomite. Usually, this mineral is gypsum. In the present case acquisition of gypsum from fertilizers and manures in soil and groundwater are the major anthropogenic source, which may drive the system to additional geochemical processes and alter the weathering sequence. The dissolution reactions of calcite, dolomite and gypsum are:



and have laws of mass action given by:

$$K_{\text{cc}} = \{\text{Ca}^{2+}\}\{\text{CO}_3^{2-}\}$$

$$K_{\text{dol}} = \{\text{Ca}^{2+}\}\{\text{Mg}^{2+}\}\{\text{CO}_3^{2-}\}^2$$

$$K_{\text{gyb}} = \{\text{Ca}^{2+}\}\{\text{SO}_4^{2-}\}$$

where K_{cc} , K_{dol} and K_{gyb} are the solubility products of calcite, dolomite and gypsum, respectively, and $\{Y\}$ is the activity of ion Y (Pacheco and Szocs 2006). At temperatures of 25°C, the K_{cc} , K_{dol} and K_{gyb} values reported for perfectly ordered stoichiometric phases are $10^{-8.5}$, $10^{-17.0}$ and $10^{-4.6}$ (Appelo and Postma 1993). Usually, recent dolomite crystals are structurally imperfect, having equilibrium constants between 10^{-17} and $10^{-16.5}$, and may be Ca-rich (nonstoichiometric), in which case, the solubility product may be 10^{-16} (Blatt 1992), although the relation between crystal disordering and age is a matter of debate (Capo et al. 2000). There is no information on the chemistry and structure of the study area dolomites, but given the fact that local sediments are of Quaternary Age, it is assumed that dolomite is disordered, and hence that $K_{\text{dol}} = 10^{-16.5}$. Groundwater temperatures in the study area are on average 25°C.

Results and interpretations

Descriptive statistics

Numerical analysis of hydrogeochemical data has been attempted to determine the geochemical parameters of groundwater (Lawrence and Upchurch 1982). Correlation analysis is 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. Tables 1 and 2 show the data of chemical analysis and descriptive statistics. Data sets show that maximum values of the EC, TDS, Na^+ , Mg^{2+} , HCO_3^- and TH are higher than the WHO 1997 maximum desirable limits, $750 \mu\text{S cm}^{-1}$, 50 mg L^{-1} , 30 mg L^{-1} , 200 mg L^{-1} and 250 mg L^{-1} , respectively. The correlation matrix shows several significant values higher than 95% (shown bold marked in Table 2).

Regression analysis

The Spearman R correlation coefficients with a pre-established significance level of 0.05 (5%) or less are shown in Table 2 because the distributions were not normal.

Correlation matrix

The correlation matrix for groundwater samples are shown in Table 2. Good correlation was observed between Na^+ and Mg^{2+} , Mg^{2+} and Cl^- , Mg^{2+} and SO_4^{2-} , Na^+ and Cl^- , Na^+ and F^- , Na^+ and SO_4^{2-} , and Na^+ and K^+ , indicating that all of them might have the same origin (Chidambaram and Ramanathan 2000) (Table 2). Sodium showed good correlation with chloride (0.82), indicating anthropogenic input in groundwater. Chloride showed moderate correlation with HCO_3^- (0.52). EC and TDS (0.92) showed a good correlation in samples because conductivity increases as the concentration of all dissolved constituents/ions increases. EC showed good correlation with HCO_3^- (0.77), F^- (0.63), Na^+ (0.89), K^+ (0.67) and Cl^- (0.89), indicating that 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). There is a significant correlation of Na^+ with K^+ , Cl^- , Mg^{2+} , and SO_4^{2-} . The highest correlation value of Na^+ is reported to be with SO_4^{2-} , which is interpreted as a result of sulphate dissolution.

Hydrochemical facies

Two hydrochemical facies were reported in the studied wells as detected from the Piper diagrams (Fig. 5).

Facies (I) Na + K – Cl + SO₄

This facies represents 13.33% of the total water samples. Its source is believed to be mainly by sulphate dissolution, as Na^+ and SO_4^{2-} are the main ions that form this facies (Fig. 5).

Facies (II) Ca + Mg–HCO₃

This facies represents 33.33% of the total water samples (Fig. 5). It is interpreted as a result of dissolution of carbonate minerals (calcite, dolomite, and aragonite).

Table 2 Correlation coefficient of the chemical parameters

Parameters	EC	TDS	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	F ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ⁻	TH
EC	1											
Sign.	-											
TDS	0.914	1										
Sign.	0.000	-										
K ⁺	0.686	0.604	1									
Sign.	0.005	0.017	-									
Na ⁺	0.892	0.831	0.502	1								
Sign.	0.000	0.000	0.056	-								
Ca ²⁺	-0.175	-0.371	-0.357	-0.306	1							
Sign.	0.533	0.173	0.191	0.268	-							
Mg ²⁺	0.819	0.701	0.819	0.735	-0.368	1						
Sign.	0.000	0.004	0.000	0.002	0.177	-						
Cl ⁻	0.893	0.729	0.554	0.820	0.021	0.661	1					
Sign.	0.000	0.002	0.032	0.000	0.940	0.007	-					
F ⁻	0.627	0.625	0.348	0.502	0.056	0.559	0.567	1				
Sign.	0.012	0.013	0.203	0.056	0.844	0.030	0.027	-				
NO ₃ ⁻	0.510	0.442	0.516	0.407	-0.368	0.503	0.480	0.331	1			
Sign.	0.052	0.099	0.049	0.132	0.177	0.056	0.070	0.229	-			
HCO ₃ ⁻	0.765	0.903	0.486	0.687	-0.391	0.651	0.518	0.535	0.186	1		
Sign.	0.001	0.000	0.066	0.005	0.149	0.009	0.048	0.040	0.507	-		
SO ₄ ⁻	0.725	0.782	0.379	0.849	-0.411	0.576	0.536	0.391	0.205	0.674	1	
Sign.	0.002	0.001	0.164	0.000	0.128	0.025	0.040	0.149	0.464	0.006	-	
TH	0.914	0.796	0.814	0.697	-0.114	0.801	0.818	0.551	0.570	0.631	0.539	1
Sign.	0.000	0.000	0.000	0.004	0.685	0.000	0.000	0.033	0.027	0.012	0.038	-

Significant values of the correlation matrix higher than 95% are shown in bold

No pair up and no pair down

The no pair down facies represents none of the total wells, while the no pair up represents 53.33% of the total wells (Fig. 5). The high percentage of this type of water is attributed to the mixing process of different types of water.

Hydrogeochemical evaluation

The geochemical variations in the ionic concentrations of groundwater can easily be understood when they are plotted along a X–Y coordinate (Guler et al. 2002). The graph of Ca²⁺ + Mg²⁺ versus SO₄²⁻ + HCO₃⁻ will feature above 1:1 line if dissolutions of calcite, dolomite and gypsum are the dominant reactions in the system.

By considering the very strong correlation coefficient between Na⁺ and SO₄²⁻ (Table 2), it seems that some dissolution or anthropogenic addition of Na₂SO₄ to groundwater is enough to explain why points have moved upwards (Fig. 6a).

The source of Ca and Mg in the groundwater can be deduced from the (Ca²⁺ + Mg²⁺)/(HCO₃⁻) ratio.

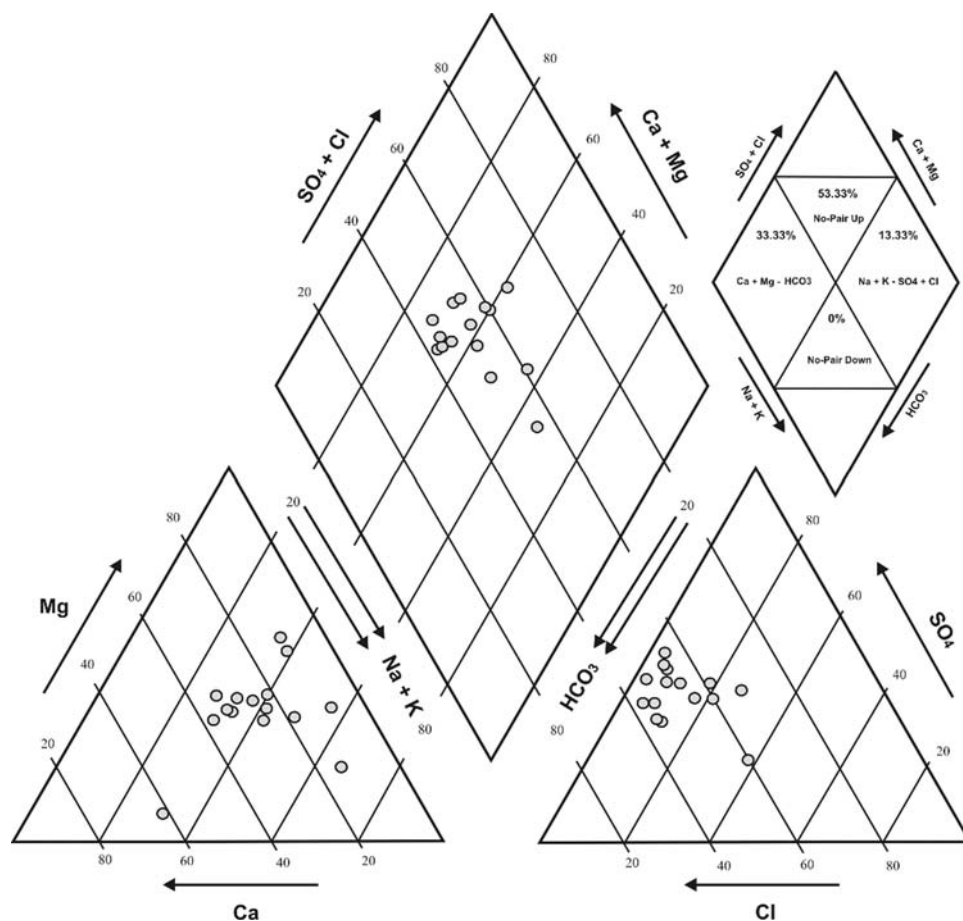
By looking at Fig. 6b it seems clear that Ca²⁺, Mg²⁺ and HCO₃⁻ result from weathering of minerals because the mole ratio is around 1.

The graph of TZ⁺ (total cation) versus Ca²⁺ + Mg²⁺ shows most of the samples far above the theoretical line (1:1) (Fig. 6c), indicating a variable contribution of alkalis to the major ions. The increase in alkalis with a simultaneous increase in Cl⁻ + SO₄²⁻ suggests a common source for these ions, as well as the presence of Na₂SO₄ and K₂SO₄ in the soils (Datta et al. 1996) (Fig. 6d).

Weathering and solute acquisition processes

The major ion chemistry of the aquatic system was mainly controlled by the contribution from anthropogenic sources and weathering of rock forming minerals. The dissolution of CO₂ and oxidation of sulphides are the two major sources of protons used to chemically weather carbonates, silicates and aluminosilicate minerals. The dissolution of carbonate rocks proceeds more rapidly than the silicate breakdown and was likely the mechanism of solute acquisition in the aquatic systems. However, the solution

Fig. 5 Piper diagram and hydrogeochemical facies shown on Piper diagram



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 solution depend on their relative abundance in the host rock as well as on their solubility (Sarin et al. 1989).

The abundance of various ions can be modeled in terms of anthropogenic contribution (SO_4^{2-} is also a major constituent of fertilizers) and weathering of various rock forming minerals (Singh and Hasnain 1998). The proportion of HCO_3^- and SO_4^{2-} in the water reflects the relative dominance of the two major sources of protons, i.e., carbonation and sulphide oxidation. The ternary anion diagram relating HCO_3^- , SO_4^{2-} and Cl^- shows that most of the samples of groundwater and surface water contain a high amount of HCO_3^- and plotted points cluster towards the alkalinity apex with secondary trends towards Cl^- (Fig. 6e). The relative high ratio of $\text{HCO}_3^-/(\text{HCO}_3^- + \text{SO}_4^{2-})$ in most of the subsurface waters (>0.5) signified that carbonic acid weathering was proton producer in these waters (Pandey et al. 2001). The bicarbonates are derived mainly from the soil zone CO_2 and weathering of parent minerals. The soil zone in the subsurface contains elevated CO_2 pressure (produced by decay of

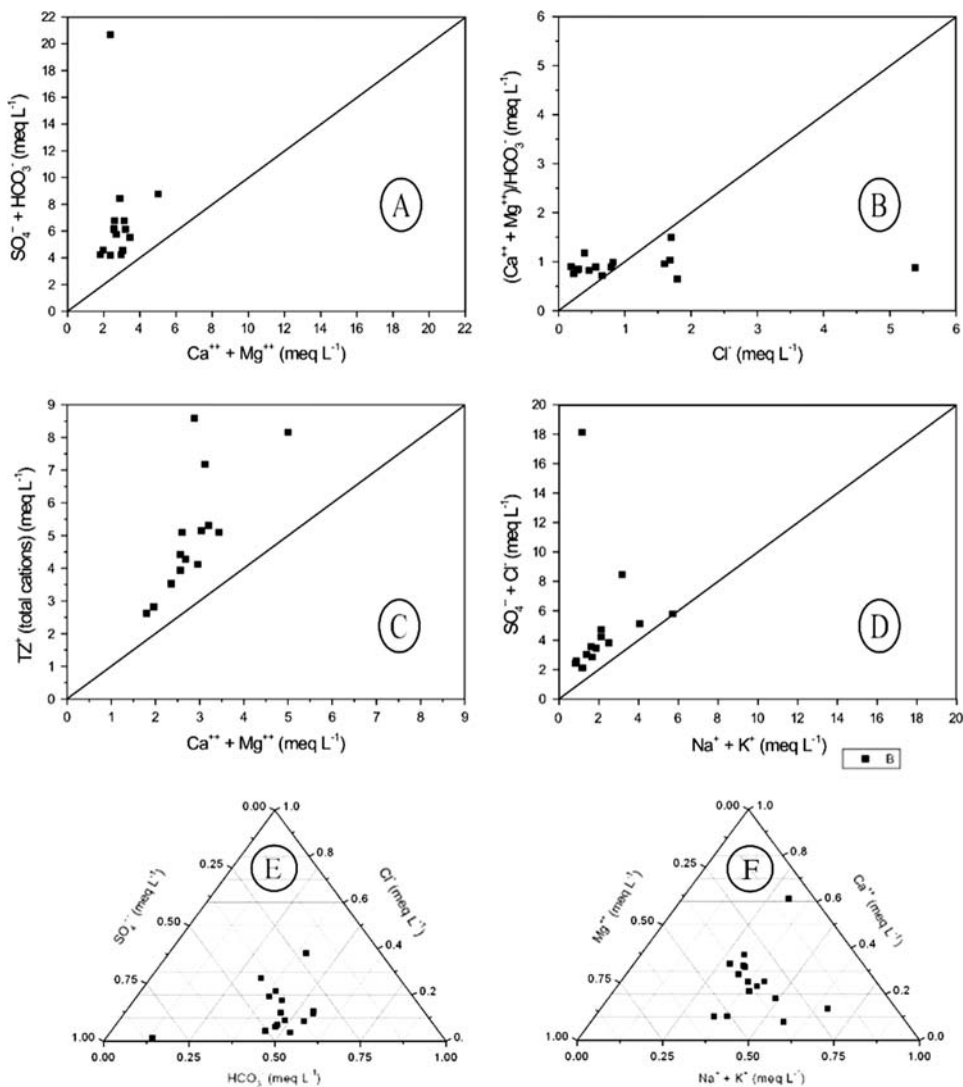
organic matter and root respiration), which in turn combines with rainwater to form bicarbonate (Drever 1988). Bicarbonate may also be derived from the dissolution of carbonates and/or silicate minerals. Sulphate in aquatic systems is derived from the anthropogenic sources because the area is associated with agriculture for more than 80% of its area and SO_4 is also a major constituent of fertilizers (Pacheco and Szocs 2006).

The cation diagram (Fig. 6f) relating Ca^{2+} , Mg^{2+} and $(\text{Na}^+ + \text{K}^+)$ shows that in the majority of samples, contribution of alkalis ($\text{Na}^+ + \text{K}^+$) exceeds alkaline earths ($\text{Ca}^{2+} + \text{Mg}^{2+}$). Further, the observed low ratio of $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{Na}^+ + \text{K}^+)$ and relatively high contribution of alkalis towards the total cations suggest that coupled reactions involving carbonate, silicate weathering and anthropogenic inputs, control the solute acquisition process.

Saturation index

The potential for a chemical reaction can be determined by calculating the chemical equilibrium of the water relative to the mineral phase. The equilibrium state of the water

Fig. 6 Graphs for different parameters



with respect to a mineral phase can be determined by calculating a saturation index (SI) using analytical data (Garrels and Mackenzie 1971; Stumm and Morgan 1981). The SI is defined as the logarithm of the ratio of ion activity product (IAP) to the mineral equilibrium constant at a given temperature and given as:

$$SI = \log 10 \frac{IAP}{K_{sp}}$$

(IAP = ion activity product, K_{sp} = solubility product at given temperature)

At the temperature of 25°C, the saturation indices (SI) relative to calcite, dolomite and gypsum are:

$$SI_{cc} = \log IAP_{cc} - \log K_{cc} = \log IAP_{cc} + 8.5$$

$$SI_{dol} = \log IAP_{dol} - \log K_{dol} = \log IAP_{dol} + 16.5$$

$$SI_{gyb} = \log IAP_{gyb} - \log K_{gyb} = \log IAP_{gyb} + 4.6$$

$$\log IAP_{cc} = \log \{Ca^{2+}\} + \log \{CO_3^{2-}\}$$

$$\log IAP_{dol} = \log \{Ca^{2+}\} + \log \{Mg^{2+}\} + 2 \log \{CO_3^{2-}\}$$

$$\log IAP_{gyb} = \log \{Ca^{2+}\} + \log \{SO_4^{2-}\}$$

The activities of Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} were determined from the measured concentrations. All calculations were done with the help of PHREEQC (Version 2.14.2) a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.

The saturation index is scaled logarithmically, indicating that saturation in natural waters may vary by orders of magnitude. For this expression a SI calcite value of 0 corresponds to calcite solubility in equilibrium state, while values of +1 and -1 correspond to 10 times and 1/10 times saturation, respectively. A positive SI specifies

that the water is supersaturated with respect to the particular mineral phase and therefore incapable of dissolving more of the mineral and that, under suitable physico-chemical conditions, the mineral phase may precipitate. A negative index (SI) indicates undersaturation condition and dissolution of the mineral phase, while a neutral SI indicates equilibrium state with the mineral phase. The precipitation of CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$ can be assessed in terms of the SI. The saturation indices of the carbonate minerals positively show supersaturation (precipitation) of dolomite. This may justify the presence of calcareous nodules (kankar) (Fig. 2), which contain a mixture of dolomite and calcite in the area. SI values of calcite and aragonite reveals a state of equilibrium and in the case of gypsum SI values indicate undersaturation of the mineral.

Geochemical patterns supporting dolomite supersaturation

the data sets show that all groundwater samples are supersaturated or close to equilibrium with respect to dolomite (SI limit > -0.5), unsaturated or close to equilibrium with respect to calcite (SI limit $< +0.5$) and undersaturates with respect to gypsum (Fig. 7). All samples also justify the thermodynamic prerequisites for dolomite supersaturation reactions to occur. The incidence of these reactions is also supported by the samples' $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]$ and $[\text{Mg}^{2+}]/[\text{SO}_4^{2-}]$ ratios, as explained below.

The state of equilibrium between groundwater and the minerals calcite and dolomite is described by the following reaction:

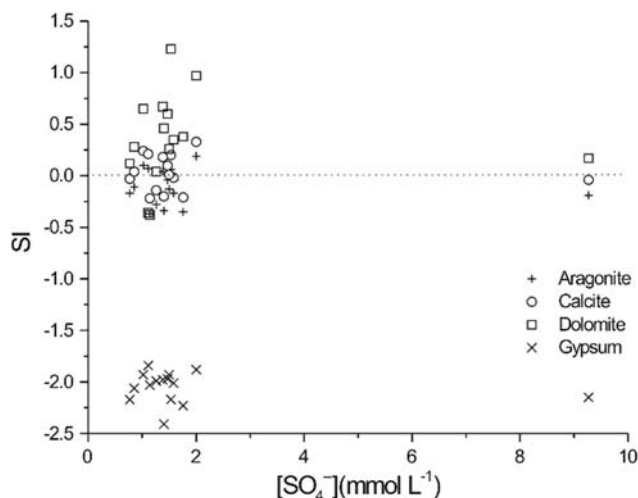
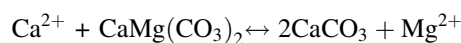


Fig. 7 Comparison of calcite, dolomite, gypsum and aragonite saturation indices as a function of total dissolved SO_4^{2-}



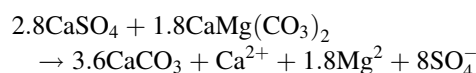
and forces the $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ ratio to:

$$\frac{[\text{Mg}^{2+}]}{[\text{Ca}^{2+}]} = \frac{K_{\text{dol}}}{K_{\text{cc}}^2} = \frac{10^{-16.5}}{(10^{-8.5})^2} = 3.16, \text{ at } 25^\circ\text{C}$$

When some oversaturation is observed with respect to dolomite (present case), the $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$ is instead forced to:

$$\frac{[\text{Mg}^{2+}]}{[\text{Ca}^{2+}]} = \frac{\text{IAP}_{\text{dol}}}{K_{\text{cc}}^2} = \frac{10^{-16.74}}{(10^{-8.5})^2} = 1.8$$

The dolomite supersaturation reaction under these circumstances is described by the reaction:



Which forces the $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]$ ratio to 0.36 and the $[\text{Mg}^{2+}]/[\text{SO}_4^{2-}]$ ratio to 0.71. These ratios, found in the study area, are closely followed by the actual ratios, $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}] = 0.38$ and $[\text{Mg}^{2+}]/[\text{SO}_4^{2-}] = 0.71$. In view of these results, it is suggested that dolomite supersaturation reactions are active in the Deoria sediments.

Conclusions

The city of Deoria depends entirely on water abstracted from the Little Gandak alluvial aquifer for its domestic and agricultural uses. Piper plots showed that one hydrochemical facies ($\text{Ca} + \text{Mg}-\text{HCO}_3$), represents 33.33% of the total wells in the city. Weathering of rock forming minerals and anthropogenic contribution from agricultural and domestic sources are the major controlling factors of water chemistry. High concentrations of TDS, Na^+ , Mg^{2+} , HCO_3^- and TH in sub-surface water samples are reported due to these diverse origins. Saturation indices of calcite, dolomite, aragonite and gypsum show positive values for dolomite, indicating a supersaturation of water with respect to this phase and justifying the presence of calcareous nodules (kankar) in the alluvial sediments. This is also deduced from geochemical trends ($[\text{Ca}^{2+}]/[\text{SO}_4^{2-}]$ and $[\text{Mg}^{2+}]/[\text{SO}_4^{2-}]$ ratios).

Acknowledgments The financial assistance from Department of Science and Technology, Government of India, New Delhi is highly acknowledged (Project No—SR/54/ES-21/Ganga Plain/P₃). We thank the Head, Centre of Advanced Study in Geology, University of Lucknow for providing the working facilities. Thanks are also expressed to the Central Ground Water Board and Ground Water Directorate for providing the necessary data and USGS for providing PHREEQC software.

References

- American Public Health Association (1992) Standard methods for the examination of water and wastewater, 19th edn. APHA, Washington, DC
- American Public Health Association (1998) Standard methods for the examination of water and wastewater, 20th edn. APHA, Washington, DC
- Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. AA Balkema, Rotterdam
- Balasubramanian A, Sharma KK, Sastri JCV (1985) Geoelectrical and hydrogeochemical evaluation of coastal aquifer of Tambraparni basin, Tamilnadu. *Geophysics Res B* 23:203–209
- Blatt H (1992) Sedimentary petrology, 2nd edn. W.H. Freeman and Company, New York
- Capo RC, Whipkey CE, Blachere J, Chadwick OA (2000) Pedogenic origin of dolomite in a basaltic weathering profile, Kohala, Peninsula, Hawaii. *Geology* 28:271–274
- Chidambaram S, Ramanathan AL (2000) Ph.D. Thesis, Annamalai University, Tamil Nadu, India
- Datta PS, Bhattacharya SK, Tyagi SK (1996) 18O studies on recharge of phreatic aquifers and groundwater flow paths of mixing in Delhi area. *J Hydrol* 176:25–36
- Drever JI (1988) The geochemistry of natural waters. Prentice Hall, Englewood Cliffs
- Garrels RM, Mackenzie FT (1971) Gregor's denudation of the continents. *Nature* 231:382–383
- Guler C, Thyne GD, McCray JE, Turner AK (2002) Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeol J* 10:455–474
- Kuells C, Adar EM, Udluft P (2000) Resolving patterns of ground water flow by inverse hydrochemical modeling in a semiarid Kalahari basin. *Tracers. Model Hydrogeol* 262:447–451
- Kumar S, Singh IB, Singh M, Singh DS (1995) Depositional pattern in upland surface of Central Ganga Plain near Lucknow. *J Geol Soc India* 46:545–555
- Lawrence FW, Upchurch SB (1982) Identification of recharge areas using geochemical factor analysis. *Ground Water* 20: 680–687
- Mohindra R, Parkash B (1990) Clay mineralogy of the soils of Gandak megafan and adjoining area, Middle Gangetic Plain, India. *Proc 9th int Sci geol Bull* 43(2-3):193–203
- Pacheco FAL, Szocs T (2006) “Dedolomitization Reactions” driven by anthropogenic activity on loessy Sediments, SW Hungary. *Appl Geochem* 21:614–631
- Pandey SK, Singh AK, Hasnain SI (2001) Hydrochemical characteristics of meltwater draining from Pindari glacier, Kumon Himalaya. *J Geol Soc India* 57:519–527
- Parkhurst DL, Appelo CAJ (1999). User's guide to PHREEQC (Version 2.14.2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS water resource investigation report. 99–4259
- Pascoe EH (1917) A manual of geology of India and Burma. Gov. India Publ, Delhi
- Plummer LN, Back WW (1980) The mass balance approach-application to interpreting the chemical evolution of hydrological systems. *Am J Sci* 280:130–142
- Plummer LN, Parkhurst DL, Thorstenson DC (1983) Development of reaction models for ground-water systems. *Geochim Cosmochim Acta* 47:665–686
- Portela EAC, Lopes H, Cardoso C (1993) A estrumacão no sistema de agricultura de montanha do Barroso, v. 2 – Estrumes e seu valor fertilizante. Technical Report (estudos camar 6), Departamento de Economia e Sociologia, Tra's-os-Montes e Alto Douro University, Vila Real, 39 pp
- Sarin MM, Krishnaswamy S, Dilli K, Somayajulu BLK, Moore WS (1989) Major ion chemistry of the Ganga–Brahmaputra river system: weathering processes and fluxes to the Bay of Bengal. *Geochim Cosmochim Acta* 53:997–1009
- Singh DS (1998) Sedimentology of Gandak Megafan, Ganga Plain. PhD Thesis, University of Lucknow, India
- Singh AK, Hasnain SI (1998) Major ion chemistry and control of weathering in a high altitude basin, Alaknanda, Garhwal Himalaya, India. *Hydrol Sci J* 43:825–845
- Singh DS, Singh IB (2005) Facies architecture of the Gandak Megafan, Ganga Plain, India. Special Publication of Palaeontol Soc India 2:125–140
- Singh IB, Ansari AA, Chandel RS, Misra A (1996) Neotectonic control on drainage system in Gangetic plain, Uttar Pradesh. *J Geol Soc India* 45:599–609
- Singh IB, Srivastava P, Shukla U, Sharma S, Sharma M, Singh DS, Rajagopalan G (1999) Upland interfluvial (Doab) deposition: Alternative model to muddy overbank deposits. *Facies* 40:197–210
- Stumm W, Morgan JJ (1981) Aquatic chemistry. Wiley Interscience, New York
- Subba Rao N (2002) Geochemistry of groundwater in parts of Guntur district, Andhra Pradesh. *India Environ Geol* 41:552–562
- Thomas JM, Welch AH, Preissler AM (1989) Geochemical evolution of ground water in Smith Creek Valley—a hydrologically closed basin in central Nevada. *USA Appl Geochem* 4:493–510