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Hydrochemistry and evaluation of groundwater suitability for irrigation and drinking purposes in the Markandeya River basin, Belgaum District, Karnataka State, India

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Abstract Markandeya River basin stretches geographically from 15°56′ to 16°08′ N latitude and 74°37′ to 74°58′ E longitude, positioned in the midst of Belgaum district, in the northern part of Karnataka. Since the quantity and quality of water available for irrigation in India is variable from place to place, groundwater quality in the Markandeya River basin was evaluated for its suitability for drinking and irrigation purposes by collecting 47 open and bore-well samples during the post-monsoon period of 2008. The quality assessment was made by estimating pH, electrical conductivity, total dissolved solids, hardness, and alkalinity besides major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) and anions (HCO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, F^-, and NO_3^-). Based on these analyses, irrigation quality parameters like, sodium absorption ratio, %Na, residual sodium carbonate, residual sodium bicarbonate, chlorinity index, soluble sodium percentage, non-carbonate hardness, potential salinity, permeability index, Kelley's ratio, magnesium hazard/ratio, index of base exchange, and exchangeable sodium ratio were calculated. According to Gibbs' ratio, majority of water samples fall in the rock dominance field. The groundwater samples were categorized as normal chloride (95.75%), normal sulfate (95.75%), and normal bicarbonate (61.70%) water types based on Cl, SO_4, and HCO_3 concentrations. Based on the permeability index, majority of the samples belongs to classes 1 and 2, suggesting the suitability of groundwater for irrigation. The negative index of base exchange indicates the existence of chloro-alkaline disequilibrium (indirect base exchange reaction) in majority of the samples (68.08%) from the study area.

Keywords Markandeya river basin · Soluble sodium percentage (SSP) · Permeability index (PI) · Kelly index (KI) · Potential salinity (PS)

Introduction

Fresh water is limited, but demand is increasing day by day. Where surface water is not available, sufficient, convenient, or feasible for consumption, but groundwater potential is suitable in quantity or quality, groundwater consumption has great importance. As for contamination, it cannot be polluted easily comparing with surface water because it is protected naturally, less affected by drought even when close to point of use, and does not require much treatment, so it is more

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reliable. Agriculture is a dominant sector in the economic development of India, as it is the source of sustenance for the majority of the population, and contributes 46% of the gross national product (Singh 1983). About one billion people are directly dependent upon groundwater resources in Asia alone (Foster 1995), and the dependence on groundwater has increased tremendously in recent years in many parts of India, especially in the arid and semi-arid regions, due to the vagaries of monsoon and the scarcity of surface water. Even though the quantity and quality of water available for irrigation is variable from place to place in India, many groundwater exploitation schemes in developing countries like India are designed without due attention to quality issues. Rapidly shrinking surface water resources due to over-exploitation and resultant contamination with several chemical and biological agents all over the globe have shifted tremendous pressure on the groundwater resources, contributing to the complexity of its quality assessment. Furthermore, continuously reduced annual recharge of the groundwater aquifers over the decades has lowered the groundwater table, influencing the redox chemistry of the aquifer and solid–water interfaces, causing mobilization of several chemical constituents of the aquifer matrices. Usually, water quality gets modified in the course of movement of water through the hydrological cycle that depends on the natural and anthropogenic processes which can alter these systems by contaminating them or modifying the hydrological cycle. The composition of groundwater in a region can be changed through the operation of the processes such as evaporation and transpiration (evapo-transpiration), wet and dry depositions of atmospheric salts, selective uptake by vegetation, oxidation/reduction, cation exchange, dissociation of minerals (soil/rock–water interactions), precipitation of secondary minerals, mixing of waters, leaching of fertilizers and manure, pollution of lake/sea, and biological process (Appelo and Postma 1993).

Quality of surface water, weathered mantle, underlying soil characteristics, and atmosphere are responsible for contribution of dissolved solids to water and in determining the composition and quality of the groundwater in a region. The type and extent of chemical contamination of the groundwater is largely dependent on the geochemistry of the soil through which the water flows prior to reaching the aquifers (Zuane 1990). Since it is impossible to control the dissolution of undesirable constituents in the waters after they enter the ground (Johnson 1979; Sastri 1994), groundwater quality data give important clues to the geologic history of rocks (lithology) of the area and indications of groundwater recharge, movement, and storage (Walton 1970) and the residence time of water in contact with rock material. It was observed that the criteria used in the classification of waters for a particular purpose considering the individual concentration do not find its suitability for other purposes, and better results can be obtained only by considering the combined chemistry of all the ions rather than individual or paired ionic characters (Handa 1964, 1965; Hem 1985). Hence, in order to assess the fate and the impact of the chemical discharge onto the soil, it is important to understand the hydrogeochemistry of the chemical–soil–groundwater interactions (Miller 1985) and to determine the origin of chemical composition of groundwater (Zaporozec 1972).

A number of studies on groundwater quality with respect to drinking and irrigation purposes have been carried out in the different parts of India (Durvey et al. 1997; Agrawal and Jagetia 1997; Niranjan Babu et al. 1997; Subba Rao et al. 1999; Majumdar and Gupta 2000; Dasgupta and Purohit 2001; Khurshid et al. 2002; Sujatha and Reddy 2003; Sreedevi 2004; Pulle et al. 2005; Hussain et al. 2005; Sunitha et al. 2005; Subba Rao 2006). So far, the geochemistry and the suitability of the groundwater for drinking and agricultural purposes in the Markandeya River Basin study area has not been studied in great detail. Since groundwater is intensively used for irrigation and drinking purposes, an effort is made in the current paper to discern the hydrogeochemistry of groundwater and to classify the water in order to evaluate its suitability for municipal and irrigational/agricultural use.

Study area

The River Markandeya is one of the major tributaries of River Ghataprabha in the northern Karnataka that subsequently joins the River Krishna. River Markandeya originates in Bailur in Western Ghats and flows for a length of 66 km toward the east before joining Ghataprabha near Gokak. A dam has been constructed across River Markandeya (Latitude 16°2′0″ and longitude 74°38′30″) to establish a reservoir at the Shirur village in Gokak taluk. The present study area, the Markandeya River basin, stretches geographically from 15°56′ to 16°08′ N latitude and 74°37′ to 74°58′ E longitude (Fig. 1), positioned in the midst of the Belgaum district in the northern part of the Karnataka state. The study area is covered in the survey of India toposheets 47 L/12, 47 L/16, 48 I/9, and 48 I/I3, with a catchment area of 432 km^2. The command area is around 191.05 km^2 (19,105 ha), covering part of Gokak (95.83 km^2), Saundatti (80.37 km^2), Hukkeri (8.90 km^2), and Belgaum taluks (5.95 km^2) of Belgaum District. The reservoir water has been directed via the Markandeya Left Bank Canal (MLBC, 15 km) and the Markandeya Right Bank Canal (MRBC 71 km) to irrigate an area of around 8.9 km^2 (890 ha) and 182.15 km^2 (18,215 ha), respectively, and to provide enhanced irrigation facilities and an improved drinking water system to the villages of four taluks of Belgaum District.

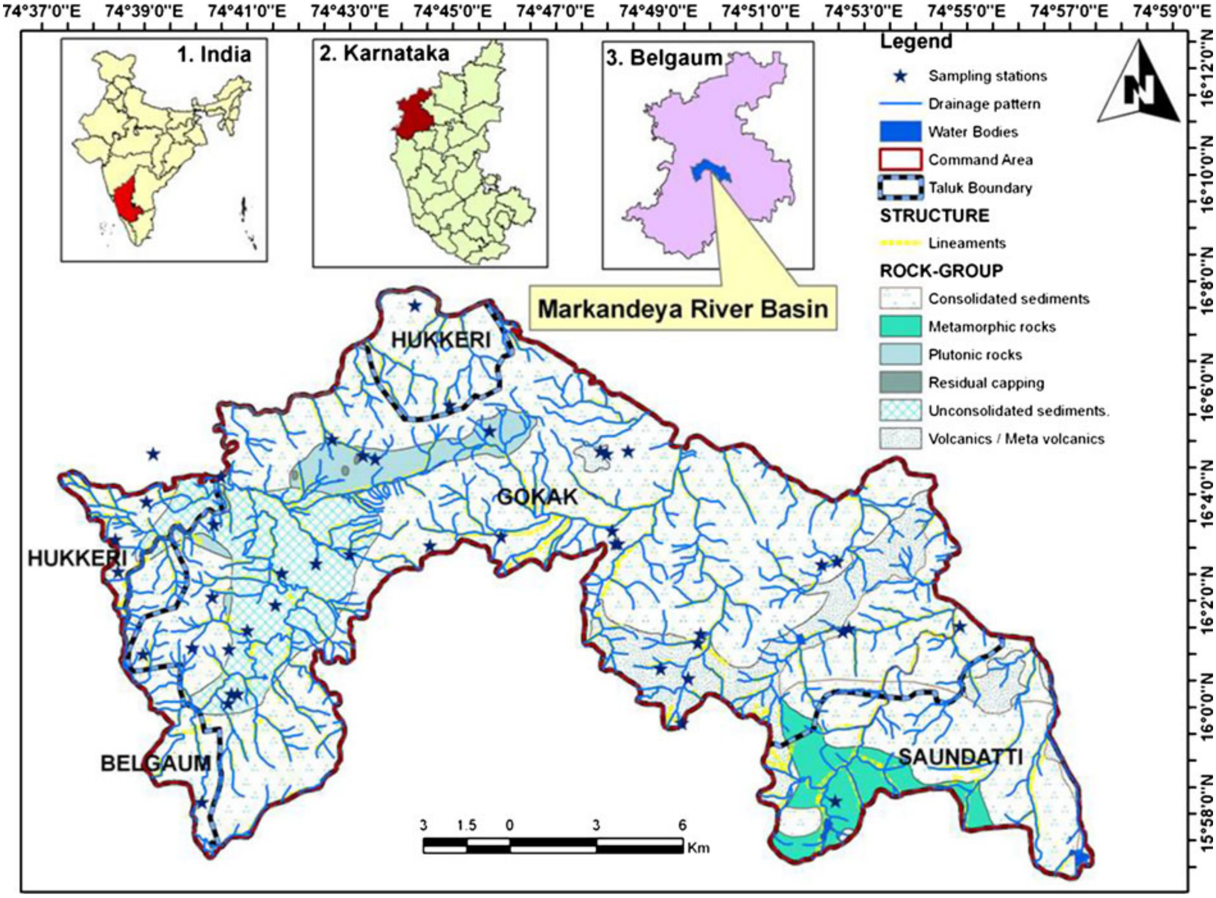


Fig. 1 Location map of the Markandeya command area showing drainage pattern, lithology, and lineaments along with the sampling stations

Physiography and climate

The command area comes under the northern dry zone of the tenfold agro-climatic zone of Karnataka and has a semi-arid subtropical climate. The climate condition on the whole is healthy, agreeable, and characterized by general dryness, except during the monsoon season. The summer season is between March and May and is dry, dusty, and very hot, with a maximum temperature reaching up to 42°C. December to February is the cold season when minimum temperature falls to 18°C. Generally, humidity varies from less than 20% during summer to 85% during the monsoon period. June to September is the period during which humidity is normally higher. Rainfall is unevenly distributed and unpredictable, and crop failures are of common occurrence. Heavy precipitation can be observed both from the southwest and northeast monsoons during the months of June, July, August, September, and October. Most of the rainfall is received during the southwest monsoon period, with August being the wettest month. The average annual rainfall is 503 mm, may vary between 480 m and 640 mm. On average, there are about 50 rainy days in a year. The winds are generally light with slight increase in the force observed during the late summer and monsoon seasons. Two distinct cropping seasons, namely, kharif and rabi, can be seen in the study area, with crops grown mainly under rain-fed conditions. Crops grown during the kharif season includes kharif jowar, hybrid jowar, bajara, tobacco, horsegram, cow pea, tur, ground nut, sunflower, til, blackgram, beans, soya, and French beans. Similarly, rabi jowar, hybrid jowar, hybrid maize, bengal gram, linseed, sunflower, and safflower are grown during the rabi season.

Geology and hydrogeology

The Krishna River basin covers a major portion of Belgaum District and is characterized by various geological formations belonging mainly to the Upper Proteozoic followed by the Archean and Lower Proteozoic periods (Fig. 1). The consolidated and unconsolidated sediments rock types cover a major portion of the district with small patches of metamorphic, plutonic, volcanic, or meta-volcanic rocks. The lineaments and the joints with orientation toward the NNE–SSW are prominent in this area, responsible for partial controlling of the groundwater flow in the region. Belgaum taluk comprises varying slopes such as gentle, moderate, nearly level, very gentle, strong, and very steep, with slope value varying from 0–35%.

The topology of the regions is generally flat with a nearly level slope in the SSW part of the study area. The geomorphology of Belgaum District is generally plateau hilly zone with patches of alluvial, coastal, hilly, lateritic, pediment, and pediplain here and there. The soil of Belgaum taluk consists of clayey, clayey mixed, clayey skeletal, and loamy layers. The occurrence, storage, and depth of the water table is dependent on the rate of weathering and topographical factors like lithology, thickness, and rock formations like weathered and fractured granite, gneisses. As the study area is dependent mainly on rain-fed irrigation, the chief source of groundwater is infiltration and recharge of rainwater. Considering the climatic water balance, soil characteristics account for nearly 70%, allowing only 20% rainfall being added again to the groundwater pool. Percolation and recharges in the groundwater account for 10% discharge of water through wells. The depth of the water table varied between 10 and 370 ft in bore wells from the ground level.

The present study aimed at understanding the prevailing water quality of groundwater in the Markandeya River basin collected during the post-monsoon season of the year 2008. An attempt has been made to describe the hydrochemistry and the suitability of groundwater for drinking and irrigation purposes. Also, concentration/contour maps were constructed to delineate spatial variation in the physico-chemical and irrigational quality parameters.

Methodology

A total of 47 groundwater samples (Fig. 1) were collected in the command area of the Markandeya River basin during the post-monsoon in November 2008. The water samples were collected after 10 min of pumping and transferred into pre-cleaned polyethylene bottles. Electrical conductivity, pH, temperature, redox potential (Eh), and total dissolved solids (TDS) for the collected samples were measured in the field immediately after sampling. To prevent changes in chemical equilibrium and adsorption on the inner surface of the bottles, the samples were acidified with 1:1 extra pure HNO_3 without disturbing the sample volume, and the final acidity of the samples during storage was around pH $\leq$ 2.0. The sample bottles were labeled, sealed, and transported to the laboratory under standard preservation methods. The major anionic and cationic concentrations were determined in the laboratory using the standard analytical procedures (Table 1) as recommended by the American Public Health Association (2005). The accuracy of the chemical analyses was checked by taking the relationship between the total cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and the total anions (PO_4^{3-}, NO_3^{-} , SO_4^{2-},

Table 1 Physico-chemical and irrigation quality parameters with BIS standards

Sl no.	Category of parameters	Characteristics	Analytical method	Unit	BIS Max. Permissible limit (1998)
1	General	pH	Electrode	–	6.5–8.5
2		Redox potential (Eh)	Electrode	mV	NA
3		EC	Conductivity–TDS meter	μS/cm	3,000
4		TDS	Conductivity–TDS meter	mg/L	2,000
5		Total alkalinity (as $CaCO_3$)	Titrimetric	mg/L	600
6		Temperature	Electrode	°C	NA
7		Total hardness (as $CaCO_3$)	EDTA titrimetric	mg/L	600
8		Calcium hardness (as $CaCO_3$)	EDTA titrimetric	mg/L	200
9		Color	Colorimetric	Hazens	25
10		Turbidity	Colorimetric	NTU	10
11	Major cations	Calcium (as Ca^{2+})	EDTA titrimetric	mg/L	200
12		Magnesium (as Mg^{2+})	EDTA titrimetric	mg/L	100
13		Sodium (as Na^{+})	Flame photometric	mg/L	200
14		Potassium (as K^{2+})		mg/L	10
15	Major anions	Bicarbonates (as HCO_3^{-})	Titrimetric	mg/L	NA
16		Carbonates (as CO_3^{2-})	Titrimetric	mg/L	NA
17		Chlorides	Argentometric	mg/L	1,000
18		Nitrates (as NO_3^{-})	ISE (ion selective electrode)	mg/L	45
19		Fluoride (as F^{-})		mg/L	1.5
20		Phosphates (as PO_4^{3-})	Stannous chloride	mg/L	0.3
21		Sulfates (as SO_4^{2-})	Barium chloride	mg/L	400
23	Irrigation water quality	Boron (B)	Curcumin method	mg/L or μg/L	–
24		Hardness (as $CaCO_3$)	By calculation using equations	mg/L	<75
25		Salinity		‰	NA
26		SAR		–	<10 or 10–18
27		RSC		meq/L	<1.25
28		RSBC		meq/L	<5 mg/L
29		%Na		%	<20 or 20–40
30		PI		%	Class 1 or 2
31		KI		–	<1.0
32		PS		–	NA
33		MH		%	Below 50%
34		MR (Mg/Ca)		–	<1.5
35		CAI-1 and CAI-2		–	+ve or −ve values
36		SSP		–	NA

NA not available, ESR — NA

CO_3^{2-}, HCO_3^-, and Cl^-) for each set of complete analyses of water sample using the ion charge balance equation or the ion balance error computation (Mathhess 1982; Domenico and Schwartz 1990) as follows:

$$E = \frac{\sum \text{citation} - \sum \text{anions}}{\sum \text{citation} + \sum \text{anions}} \times 100, \qquad (1)$$

where E is the error percent/reaction error and Σ cations and Σ anions are the sum of the total cations and total anions expressed in milliequivalents per liter. The reaction (cationic and anionic balance) error (E) of all the groundwater samples was less than the accepted limit of ±10%, an added proof of the precision of the data. In addition, E greater than 10% was eliminated from the subsequent analyses.

Based on the physico-chemical analyses, irrigation quality parameters like boron, sodium absorption ratio (SAR), %Na, residual sodium carbonate (RSC), residual sodium bicarbonate (RSBC), soluble sodium percentage (SSP), non-carbonate hardness, potential salinity, permeability index, Kelley's ratio, magnesium hazard (MH)/ratio, and index of base exchange were calculated. The correlation of the analytical data has been attempted by plotting different graphical representation such as those of Piper (1994), Back and Hanshaw (1965), Wilcox (1995), Eaton (1950), Gibbs (1970), Todd (1959), Handa (1969), and Richards (1954) for the classification of water and to study the suitability of groundwater for utilitarian purposes by ascertaining various factors on which the chemical characteristics of water depend. The suitability of the water from the groundwater sources for drinking, domestic, and irrigation purposes was evaluated by comparing the values of different water quality parameters with those of the Bureau of Indian standards (BIS 1998) and World Health Organization (1984) guideline values for drinking water. In addition to this, visually communicating iso-concentration/contour maps were constructed using the Surfur-7.0 and ArcGIS-9.0 softwares to delineate spatial variation of physico-chemical and irrigation quality parameters in the study area.

Results and discussion

General parameters

The analytical results for all the physico-chemical parameters for the groundwater samples of post-monsoon season from the study area are presented in Table 2. The values of pH in the groundwater samples collected from the study area varied from 6.35 to 8.45 (Fig. 2a), indicating a slightly acidic to slightly basic nature. All the samples showed a pH value within the permissible limit of 6.5–8.5 (BIS 1998), except for one sample (sample No. RM19), which showed a pH value of 6.35, crossing the permissible limit.

Redox potential and temperature were measured at all water points during the monitoring survey. It was found that the redox potential (Eh) varied from −76.6 to 48.9 mV and temperature was in the range of 23.7°C to 30.8°C (Table 2). The color and turbidity of drinking water are some of the physical parameters of water quality. Color is a common constituent of many natural waters, and it is caused by many natural water and metallic substances such as iron and manganese compounds, humus materials, peat, tannins, algae, weeds, and protozoa. Industrial effluents also contribute color to water supply. In the study area, the color values varied from 0 to 1 hazens compared to the maximum permissible level of color of 25 hazens (Table 2). The suspended sediments in the water give a muddy or turbid appearance. It may have been caused by erosion and iron deposition in the tube well pipe itself, which is the most common source of high level of suspended solids in water. The presence of suspended materials such as clay, silt, colloidal organic matter, and other inorganic impurities contributes to turbidity. Turbidity values ranged from 0.05 to 0.1 nephelometric turbidity units (NTU) compared to the maximum permissible level of turbidity of 10 NTU. All the groundwater samples showed color and turbidity values within the safe limit as suggested by the BIS (1998).

In the study area, the electrical conductivity (EC) of groundwater varies widely and ranges between 160.4 and 9003 μS/cm (Fig. 2b), and 6.4% of the samples (i.e., sample nos. RM10, RM26, and RM40) showed the conductivity value

Table 2 Analytical results of groundwater samples in the Markandeya Command Area (post-monsoon, 2008)

Sample ID	Temperature (°C)	pH	EC	TDS	Redox potential (Eh)	Salinity (‰)	Total hardness	Calcium hardness	Total alkalinity	Major cations				Major anions					
										Ca	Mg	Na	K	F	Cl	HCO_3	NO_3	SO_4	PO_4
RM1	26.5	7.28	1190	714	−6.4	0.59	370.0	140.0	340.0	56.0	56.1	68.7	110.5	0.7	120.0	414.8	30	82.5	0.509
RM2	30.3	7.12	1396	836	2.9	0.70	430.0	180.0	410.0	72.0	61.0	75.4	89.7	0.3	150.0	500.2	40	96.09	0.223
RM3	27.7	7.06	1308	793	6.6	0.66	530.0	170.0	540.0	68.0	87.8	75.9	54.8	0.5	179.9	658.8	35	63.59	0.403
RM4	29.0	7.14	1090	658	1.6	0.54	500.0	230.0	460.0	92.0	65.9	64.5	11.9	0.4	169.9	561.2	25	48.75	0.382
RM5	30.6	7.51	2103	1264	−20.3	1.08	780.0	410.0	625.0	164.0	90.3	92.6	54.1	0.3	279.9	762.5	42	142.2	0.191
RM6	27.4	7.32	620	373	−8.9	0.30	260.0	100.0	260.0	40.0	39.0	59.9	16.1	0.7	80.0	317.2	24	17.03	0.106
RM7	27.8	7.54	2104	1262	−22.1	1.08	580.0	260.0	595.0	104.0	78.1	139.3	93.5	0.6	219.9	725.9	36	264.9	0.212
RM8	30.2	7.70	1457	873	−31.8	0.73	120.0	40.0	98.4	16.0	19.5	61.9	2.9	0.9	100.0	120.0	39	16.56	0.223
RM9	30.8	7.95	1858	1118	−46.5	0.95	740.0	270.0	630.0	108.0	114.7	122.1	8.9	0.9	259.9	768.6	34	169.0	0.360
RM10	26.9	7.38	3712	2250	−12.8	1.97	1000.0	320.0	569.7	128.0	165.9	77.3	3.6	1.0	335.0	695.0	50	345.0	0.339
RM11	25.4	7.52	711	428	−21.1	0.35	270.0	140.0	245.0	56.0	31.7	71.9	6.4	0.4	90.0	298.9	19	48.91	0.456
RM12	27.8	7.45	2233	1349	−16.8	1.15	490.0	100.0	430.0	40.0	95.2	170.5	124.4	0.7	209.9	524.6	26	239.4	0.233
RM13	29.8	7.40	685	411	−13.9	0.33	250.0	130.0	270.0	52.0	29.3	68.8	36.6	0.8	70.0	329.4	31	29.06	0.127
RM14	30.0	6.87	1613	978	17.7	0.81	530.0	300.0	550.0	120.0	56.1	88.3	96.6	0.4	169.9	671.0	40	119.9	0.180
RM15	27.0	7.42	1374	828	−14.9	0.69	470.0	180.0	465.0	72.0	70.8	94.3	43.0	0.4	140.0	567.3	38	81.72	0.170
RM16	27.4	7.22	1127	678	−2.8	0.56	350.0	190.0	325.0	76.0	39.0	109.6	8.5	0.4	110.0	396.5	31	48.44	0.127
RM17	27.4	7.31	1054	633	−8.6	0.52	280.0	130.0	270.0	52.0	36.6	101.5	6.1	0.3	100.0	329.4	26	55.94	0.138
RM18	27.9	7.09	719	433	4.5	0.35	270.0	150.0	285.0	60.0	29.3	66.2	41.3	0.5	90.0	347.7	20	55.63	0.117
RM19	28.4	6.35	307	184.5	48.9	0.15	130.0	70.0	120.0	28.0	14.6	25.6	12.3	0.2	50.0	146.4	21	10.94	0.074
RM20	25.9	8.04	2808	1700	−52.1	1.46	450.0	210.0	508.2	84.0	58.6	125.3	106.6	0.7	240.0	620.0	36	172.0	0.543
RM21	30.3	6.76	648	392	24.5	0.31	240.0	120.0	225.0	48.0	29.3	54.7	32.3	0.5	70.0	274.5	21	29.06	0.318
RM22	27.2	6.81	708	427	21.3	0.34	290.0	170.0	310.0	68.0	29.3	49.2	28.5	0.4	100.0	378.2	27	26.25	0.148
RM23	24.9	7.49	774	468	−19.3	0.38	250.0	120.0	265.0	48.0	31.7	88.3	40.4	1.0	60.0	323.3	18	65.16	0.223
RM24	27.0	7.46	467	281	−7.4	0.22	220.0	130.0	192.6	52.0	22.0	25.0	41.0	0.5	120.0	235.0	20	16.41	0.170
RM25	27.9	7.90	657	394	−43.4	0.32	395.7	190.0	242.4	76.0	50.2	67.6	35.6	1.0	135.0	295.7	23	28.75	0.201
RM26	29.4	7.27	3944	2380	−6.1	2.10	1250.0	900.0	750.0	360	85.4	170.5	14.7	0.9	589.8	915	44	103.6	0.074
RM27	24.6	7.35	1358	820	−10.9	0.68	450.0	120.0	385.0	48.0	80.5	103.8	9.5	0.8	120.0	469.7	27	37.19	0.244
RM28	27.8	8.45	214.8	129.4	−76.4	0.10	130.0	60.0	120.0	24.0	17.1	14.6	8.5	0.3	40.0	146.4	14	7.97	0.583
RM29	28.7	7.61	1207	730	−26.1	0.60	430.0	140.0	445.0	56.0	70.8	105.1	8.5	2.0	70.0	542.9	31	95.0	0.138
RM30	27.6	7.44	1229	740	−16.1	0.61	420.0	150.0	405.0	60.0	65.9	88.9	10.9	1.0	100.0	494.1	28	72.34	0.191
RM31	26.1	7.26	2771	1667	−5.6	1.44	850.0	330.0	675.0	132.0	126.9	171.7	1.4	0.9	309.9	823.5	38	256.7	0.159
RM32	28.4	7.88	1684	1015	−42.3	0.86	400.0	130.0	385.0	52.0	65.9	129.5	76.7	1.0	189.9	469.7	32	159.4	0.191
RM33	29.8	6.98	902	544	11.5	0.44	310.0	130.0	295.0	52.0	43.9	86.2	7.8	0.5	120.0	359.9	30	51.56	0.148
RM34	29.9	7.38	1685	1012	−12.6	0.85	400.0	190.0	415.0	76.0	51.2	110.1	120.6	0.4	199.9	506.3	35	121.6	0.647
RM35	27.1	7.41	984	592	−14.4	0.49	370.0	150.0	385.0	60.0	53.7	61.4	0.4	0.7	80.0	469.7	21	64.38	0.265
RM36	28.0	7.61	973	588	−26.3	0.48	400.0	120.0	415.0	48.0	68.3	90.5	2.1	2.0	70.0	506.3	23	56.56	0.201
RM37	27.5	7.33	1319	797	−9.6	0.66	410.0	210.0	425.0	84.0	48.8	109.3	58.9	2.0	120.0	518.5	29	115.5	0.297
RM38	26.6	7.30	1039	625	−7.5	0.51	400.0	200.0	375.0	80.0	48.8	85.5	22.3	1.0	90.0	457.5	26	77.97	0.674
RM39	26.1	7.52	2830	1711	−21.1	1.47	1230.0	590.0	725.0	236.0	156.2	118.1	4.4	0.5	319.9	884.5	37	173.6	0.095
RM40	24.8	7.54	9003	5410	−22.5	5.03	2530.0	890.0	855.0	356.0	400.2	66.5	35.7	0.8	1359.6	1043.1	75	387.2	0.678
RM41	23.7	7.48	1353	814	−18.6	0.68	450.0	150.0	385.0	60.0	73.2	108.6	21.8	0.7	179.9	469.7	34	118.8	0.265
RM42	28.6	7.64	1142	686	−28.0	0.57	370.0	130.0	354.1	52.0	58.6	76.8	0.2	0.7	140.0	432.0	22	86.9	0.244
RM43	29.3	7.89	1972	1183	−43.3	1.01	680.0	270.0	620.0	108.0	100.0	125.4	10.4	1.0	160.0	756.4	33	120.9	0.254
RM44	26.6	8.43	182.5	110.3	−74.9	0.09	130.0	60.0	115.2	24.0	17.1	16.5	1.4	0.3	40.0	140.5	20	17.5	0.138
RM45	24.8	7.81	493	294	−38.4	0.24	250.0	120.0	225.0	48.0	31.7	31.7	1.3	2.0	50.0	274.5	18	15.0	0.276
RM46	25.8	7.74	1004	603	−33.8	0.50	320.0	80.0	335.0	32.0	58.6	108.9	0.3	1.0	60.0	408.7	29	39.69	0.466
RM47	27.4	8.45	160.4	96.4	−76.6	0.07	110.0	50.0	95.0	20.0	14.6	14.0	0.9	0.3	40.0	115.9	10	10.47	0.435

All the values are in milligrams per liter except conductivity (μS/cm), redox potential (mV), salinity (‰), temperature (°C), and pH

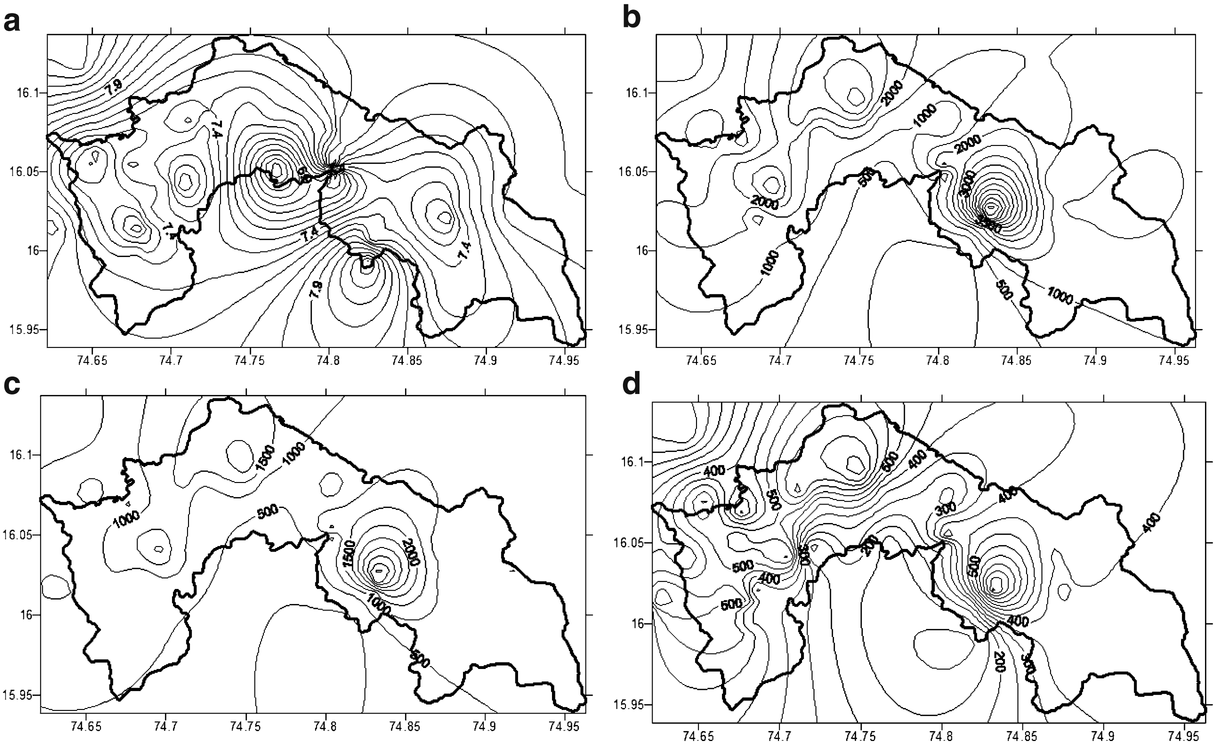


Fig. 2 Iso-concentration maps showing spatial variation in **a** pH, **b** conductivity, **c** total dissolved solids, and **d** total alkalinity in the study area

crossing the permissible limit of 3,000 μS/cm (BIS 1998). The salinity values varied from 0.07‰ to 5.03‰ in the groundwater samples (Table 2). The TDS values varied between 96.4 and 5410 mg/L (Fig. 2c), and 6.4% of the samples (i.e., sample nos. RM10, RM26, and RM40) showed TDS value above the permissible limit of 2,000 mg/L (BIS 1998). The total alkalinity (as $CaCO_3$) values were found to vary from 95.0 to 855.0 mg/L (Fig. 2d) in the post-monsoon samples, and 14.9% of the samples crossed the permissible limit of 600 mg/L (BIS 1998).

Water hardness is caused primarily by the presence of cations such as calcium and magnesium and anions such as carbonate, bicarbonate, chloride, and sulfate in water. The total hardness (as $CaCO_3$) values range between 110 and 2,530 mg/L (Fig. 3a) in the post-monsoon samples in the study area; 17% of the samples were having hardness values above the permissible limit of 600 mg/L (BIS 1998). It was found that 70.2% of the groundwater samples have a total hardness more than the total alkalinity, which indicates that the groundwater is characterized by non-carbonated hardness (Chow 1964), while 29.8% of the samples showed total alkalinity values higher than the total hardness values.

The calcium hardness (as $CaCO_3$) values range between 40 and 900 mg/L (Fig. 3b) in the groundwater samples; only 72.3% of the samples were having calcium hardness values within the permissible limit of 200 mg/L (BIS 1998), while the remaining 27.7% of the samples were having higher calcium hardness values.

Anion chemistry

Among the alkaline earths, the concentration of calcium (Fig. 4a) and magnesium (Fig. 4b) were in the range of 16 to 360 and 14.6 to 400.2 mg/L, respectively. Among 47 samples, 6.4% and 10.6% were having higher calcium and magnesium

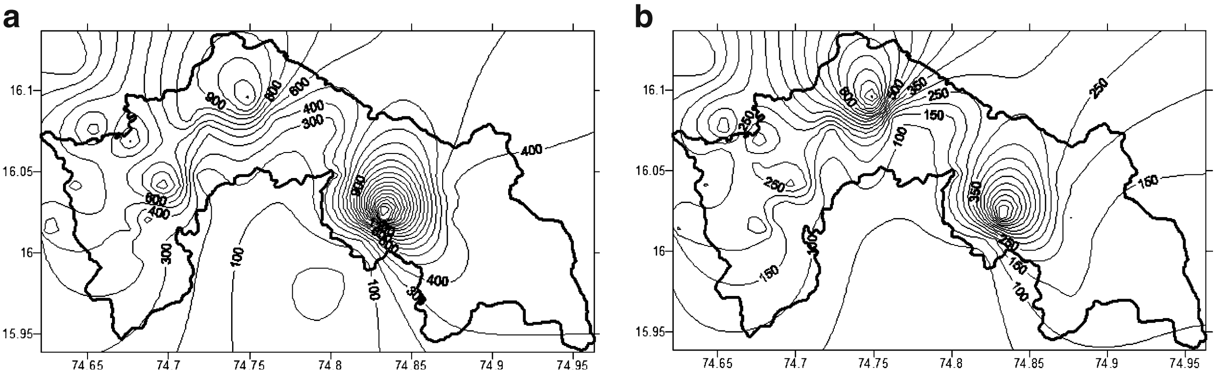


Fig. 3 Iso-concentration maps showing spatial variation in **a** total hardness and **b** calcium hardness in the study area

content in comparison to their BIS permissible limit of 200 and 100 mg/L, respectively. Among the alkalies, the concentration of sodium (Fig. 4c) and potassium (Fig. 4d) ranged from 14 to 171.7 and 0.2 to 124.4 mg/L, respectively. Among the 47 samples, 59.6% were having high potassium content above the permissible limit of 10 mg/L (BIS 1998), while all the samples showed a sodium concentration within the permissible limit of 200 mg/L.

Cation chemistry

Bicarbonate is the predominant anion in the post-monsoon season samples, ranging from 115.9 to 1,043.1 mg/L (Fig. 5a), except for one sample

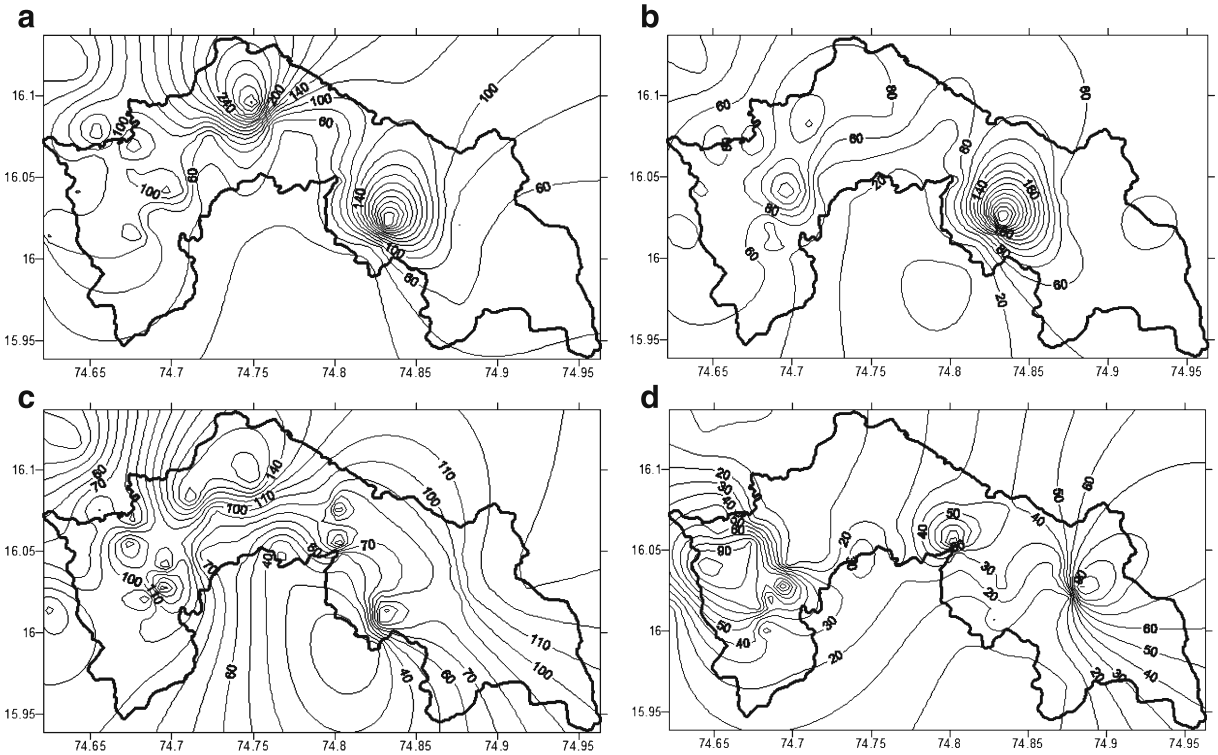


Fig. 4 Iso-concentration maps showing spatial variation in **a** calcium, **b** magnesium, **c** sodium, and **d** potassium in the study area

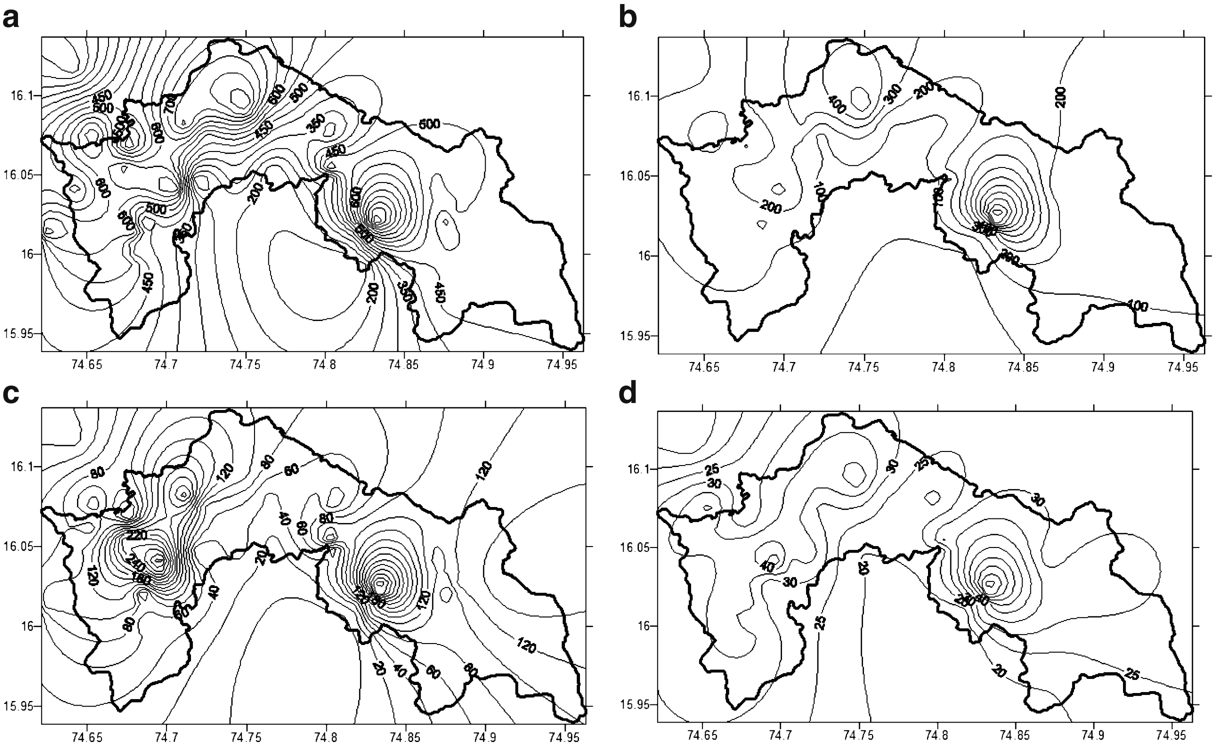


Fig. 5 Iso-concentration maps showing spatial variation in **a** bicarbonates, **b** chlorides, **c** sulfates, and **d** nitrates in the study area

(i.e., sample No. RM40) in which chloride concentration was higher than that of bicarbonate. In the area of investigation, the chlorides are in the range of 40 to 1,360 mg/L (Fig. 5b) during post-monsoon, and it was found that all the samples were having chloride values within the permissible limit of 1,000 mg/L (BIS 1998), except for one sample (sample No. RM40, 1,360 mg/L). The sulfate content in the groundwater during the post-monsoon season varies from 7.97 to 387.2 mg/L (Fig. 5c), well within the permissible limit of 400 mg/L (BIS 1998). The nitrate concentration in the region ranges from 10 to 75 mg/L (Fig. 5d). Among the 47 samples, 4.3% (sample Nos. RM10 and RM40) showed a nitrate concentration above the permissible limit of 45 mg/L (BIS 1998).

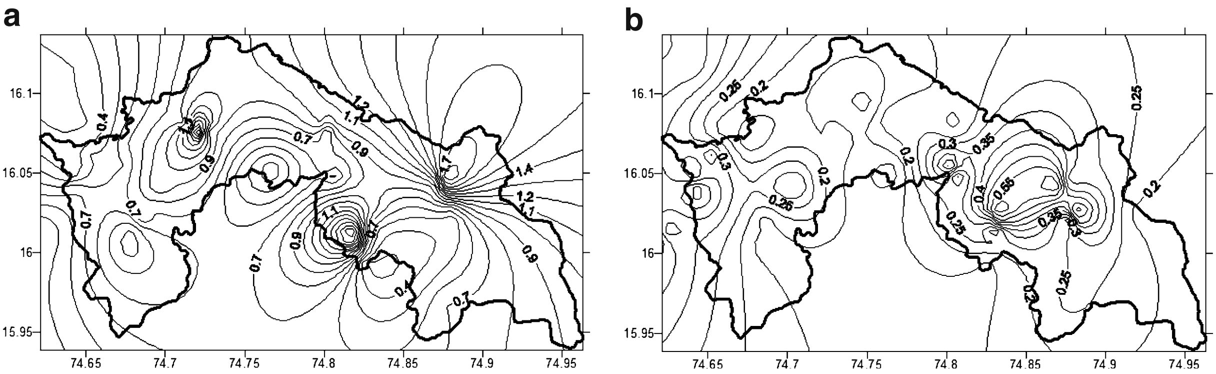


Fig. 6 Iso-concentration maps showing spatial variation in **a** fluorides and **b** phosphates in the study area

The fluoride concentration varied from 0.2 to 2.0 mg/L (Fig. 6a) in the Markandeya River basin. The presence of low concentration of fluoride in majority of the wells in the study area is of minor concern, as all the samples are found to have a fluoride concentration within the permissible limit of 1.5 mg/L (WHO 1984), except four samples (8.5%; sample Nos. RM29, RM36, RM37, and RM45). In addition to this, phosphate concentration was found to vary from 0.074 to 0.678 mg/L (Fig. 6b), and 29.8% of the samples (14 samples) showed a phosphate concentration exceeding the permissible limit of 0.3 mg/L (BIS 1998).

Hydrochemical facies

To know the hydrogeochemical regime of the study area, the analytical values obtained from the groundwater samples are plotted on Piper (1994) trilinear diagram. These plots include two triangles, one for plotting cations and the other for plotting anions. The cations and anion fields are combined to show a single point in a diamond-shaped field from which inference is drawn on the basis of the hydrogeochemical facies concept. These trilinear diagrams are useful in bringing out chemical relationships among groundwater samples in more definite terms than other possible plotting methods. Facies are recognizable parts of different characters belonging to any genetically related system. Hydrochemical facies are distinct zones that possess cation and anion concentration categories, and this concept helps to understand and identify the water composition in different classes. To define composition class, Back and Hanshaw (1965) suggested subdivisions of the trilinear diagram to define composition class, based on which the interpretation of distinct facies from the 0% to 10% and 90% to 100% domains on the diamond-shaped cation-to-anion graph is more helpful than using equal 25% increments. The Piper trilinear graphical representation of the chemical data of the representative samples from the study area for the post-monsoon period reveals the analogies, dissimilarities, and different types of waters in the study area, which are identified and listed in Table 3. It clearly explains the variations or domination of cation and anion concentrations during the post-monsoon season.

The diamond-shaped field of Piper diagram can be further classified into (1) Ca^{2+}–Mg^{2+}–Cl^-–SO_4^{2-}, (2) Na^+–K^+–Cl^-–SO_4^{2-}, (3) Na^+–K^+–HCO_3^-, and (4) Ca^{2+}–Mg^{2+}–HCO_3^-. Majority of the samples belong to the Ca^{2+}–Mg^{2+}–HCO_3^- type followed by the Ca^{2+}–Mg^{2+}–Cl^-–SO_4^{2-} and Na^+–K^+–Cl^-–SO_4^{2-} types in the study area (Fig. 7). The Ca–Mg type of water predominated during the post-monsoon in November 2008, accounting for 63.83% of the samples. Similarly, for anion concentration, the HCO_3^- type of water predominated during the post-monsoon season, with 97.87% of the samples (Table 3). There is no significant change in the hydrochemical facies noticed during the study period (post-monsoon), which indicates that most of the major ions are natural in origin. The reason is that groundwater passing through igneous rocks dissolves only small quantities of mineral matters

Table 3 Characterization of the groundwater of the Markandeya River basin based on the Piper trilinear diagram

Subdivision of the diamond	Characteristics of corresponding subdivisions of diamond-shaped fields	Number and percentage of samples in the category	
		No. of samples	Percentage
1	Alkaline earth (Ca+Mg) exceed alkalies (Na+K)	30	63.83
2	Alkalies exceeds alkaline earths	17	36.17
3	Weak acids ($CO_3 + HCO_3$) exceed strong acids ($SO_4 + Cl$)	46	97.87
4	Strong acids exceeds weak acids	01	2.13
5	Magnesium bicarbonate type	42	89.36
6	Calcium-chloride type	01	2.13
7	Sodium–chloride type	02	4.255
8	Sodium–bicarbonate type	00	–
9	Mixed type (no cation–anion exceed 50%)	02	4.255

Fig. 7 Piper trilinear diagram (post-monsoon 2008)

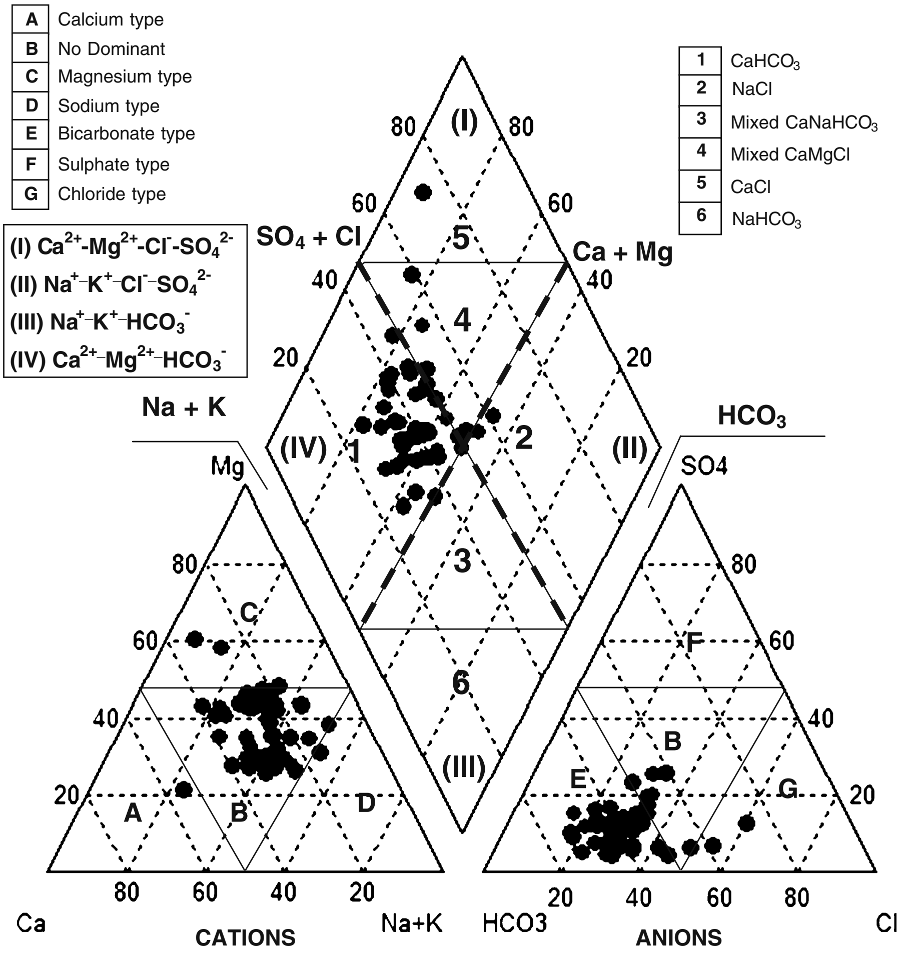


Table 4 Variation in hydrochemical facies in Markandeya River Basin

Hydrochemical facies	Sample no.	Percent
Mg–Na–Ca–HCO_3–Cl	RM6, RM7, RM15, RM30, RM31, RM42, RM43	14.89
Mg–Ca–Na–HCO_3–Cl	RM2, RM9, RM21, RM25, RM35, RM38, RM45	14.89
Mg–Ca–HCO_3–Cl	RM3, RM4, RM28, RM39, RM44, RM47	12.76
Na–Ca–Mg–HCO_3–Cl	RM11, RM13, RM16, RM37	8.51
Na–Mg–Ca–HCO_3–Cl	RM17, RM20, RM33, RM34	8.51
Ca–Mg–Na–HCO_3–Cl	RM14, RM19, RM22	6.39
Mg–Na–Ca–HCO_3	RM29, RM36	4.25
Ca–Mg–HCO_3–Cl	RM24, RM5	4.25
Mg–Na–HCO_3–Cl	RM27, RM41	4.25
Mg–Ca–HCO_3–Cl–SO_4	RM10	2.13
Mg–Na–HCO_3–Cl–SO_4	RM12	2.13
Ca–Na–Mg–HCO_3–Cl	RM18	2.13
Mg–Na–K–Ca–HCO_3	RM1	2.13
Na–Mg–Ca–HCO_3	RM23	2.13
Ca–Na–Mg–Cl–HCO_3	RM26	2.13
Na–Mg–HCO_3–Cl–SO_4	RM32	2.13
Mg–Ca–Cl–HCO_3	RM40	2.13
Mg–Na–HCO_3	RM46	2.13
Na–Mg–Cl–HCO_3	RM8	2.13

Table 5 Irrigation water quality parameters of groundwater samples from the Markandeya command area (Post-monsoon, 2008)

Sample ID	%Na	SAR	RSBC	RSC	B (μg/L)	PI	KI	PS	MR	MH	Index of base exchange		SSP	ESR
											CAI-1	CAI-2		
RM1	22.596	1.552	4.00	3.91	0.54	53.82	0.403	4.24	1.65	62.28	−0.717	−0.27	28.74	0.403
RM2	23.120	1.580	4.61	5.04	1.71	51.66	0.381	5.23	1.40	58.27	−0.317	−0.12	27.58	0.381
RM3	21.549	1.433	7.40	7.37	0.95	47.33	0.311	5.74	2.13	68.04	0.073	0.03	23.72	0.311
RM4	21.379	1.254	4.61	5.31	0.20	45.55	0.280	5.30	1.18	54.15	0.351	0.16	21.89	0.280
RM5	19.157	1.441	4.31	5.20	0.68	38.51	0.258	9.38	0.91	47.58	0.315	0.15	20.51	0.258
RM6	31.688	1.615	3.20	3.45	0.25	62.56	0.501	2.43	1.61	61.65	−0.337	−0.13	33.36	0.501
RM7	30.196	2.514	6.71	8.20	0.40	53.80	0.522	8.96	1.24	55.32	−0.362	−0.12	34.28	0.522
RM8	52.084	2.456	1.17	0.87	0.98	80.37	1.121	2.99	2.01	66.77	0.019	0.02	52.84	1.121
RM9	26.078	1.950	7.21	6.15	1.04	44.00	0.358	9.09	1.75	63.65	0.245	0.11	26.37	0.358
RM10	14.313	1.062	5.00	−1.06	1.60	28.79	0.168	13.04	2.14	68.12	0.635	0.31	14.37	0.168
RM11	35.972	1.903	2.10	2.76	0.03	62.61	0.579	3.05	0.93	48.27	−0.296	−0.12	36.66	0.579
RM12	36.307	3.345	6.60	4.49	BDL	60.01	0.755	8.41	3.92	79.69	−0.789	−0.33	43.01	0.755
RM13	33.495	1.891	2.80	3.99	BDL	66.47	0.598	2.28	0.93	48.16	−0.989	−0.30	37.41	0.598
RM14	22.705	1.668	5.01	7.71	BDL	49.55	0.362	6.04	0.77	43.52	−0.317	−0.11	26.59	0.362
RM15	28.056	1.890	5.71	6.07	BDL	52.90	0.436	4.80	1.62	61.85	−0.317	−0.11	30.34	0.436
RM16	39.773	2.548	2.71	3.82	BDL	62.17	0.681	3.61	0.85	45.83	−0.606	−0.23	40.51	0.681
RM17	43.380	2.637	2.80	3.39	BDL	67.24	0.787	3.40	1.16	53.71	−0.620	−0.25	44.06	0.787
RM18	30.827	1.751	2.70	4.09	BDL	63.58	0.533	3.12	0.81	44.60	−0.550	−0.19	34.76	0.533
RM19	27.653	0.977	1.00	1.40	0.54	71.73	0.429	1.52	0.86	46.22	−0.012	−0.01	30.00	0.429
RM20	31.706	2.567	5.97	7.91	2.43	59.73	0.605	8.56	1.15	53.49	−0.207	−0.10	37.68	0.605
RM21	29.698	1.535	2.10	2.69	1.59	62.64	0.495	2.28	1.01	50.16	−0.623	−0.23	33.11	0.495
RM22	24.674	1.256	2.81	4.52	1.84	58.28	0.369	3.09	0.71	41.53	−0.017	−0.01	26.94	0.369
RM23	38.884	2.428	2.90	3.82	1.15	69.46	0.768	2.37	1.09	52.12	−1.879	−0.46	43.43	0.768
RM24	16.624	0.733	1.26	2.01	1.29	55.53	0.247	3.56	0.70	41.09	0.369	0.28	19.80	0.247
RM25	24.974	1.477	1.05	0.15	0.72	47.33	0.371	4.11	1.09	52.13	−0.011	−0.01	27.07	0.371
RM26	22.621	2.098	−2.97	−0.01	1.91	34.83	0.297	17.72	0.39	28.11	0.532	0.50	22.88	0.297
RM27	32.773	2.126	5.30	3.80	1.31	53.87	0.501	3.77	2.76	73.44	−0.405	−0.15	33.36	0.501
RM28	18.370	0.556	1.20	1.39	1.79	67.42	0.244	1.21	1.17	54.01	0.245	0.10	19.60	0.244
RM29	34.094	2.202	6.10	6.20	1.98	57.27	0.530	2.96	2.08	67.58	−1.425	−0.25	34.66	0.530
RM30	30.783	1.885	5.10	5.07	0.81	54.65	0.459	3.57	1.81	64.42	−0.469	−0.13	31.48	0.459

Table 5 (continued)

Sample ID	%Na	SAR	RSBC	RSC	B (μg/L)	PI	KI	PS	MR	MH	Index of base exchange		SSP	ESR
											CAI-1	CAI-2		
RM31	30.443	2.559	6.91	5.45	2.61	45.49	0.439	11.41	1.58	61.31	0.142	0.06	30.49	0.439
RM32	36.082	2.813	5.10	4.80	1.28	61.60	0.703	7.02	2.09	67.63	−0.417	−0.19	41.27	0.703
RM33	36.919	2.128	3.30	3.62	2.89	62.06	0.604	3.92	1.39	58.19	−0.166	−0.08	37.66	0.604
RM34	30.160	2.394	4.51	5.82	1.38	59.95	0.598	6.90	1.11	52.62	−0.396	−0.20	37.43	0.598
RM35	26.460	1.387	4.70	5.41	0.61	54.01	0.360	2.93	1.48	59.60	−0.188	−0.05	26.49	0.360
RM36	32.790	1.966	5.90	5.81	1.35	57.04	0.491	2.56	2.35	70.11	−1.020	−0.20	32.94	0.491
RM37	32.861	2.347	4.31	5.95	1.96	59.17	0.579	4.59	0.96	48.92	−0.849	−0.25	36.68	0.579
RM38	30.243	1.858	3.51	4.48	2.02	55.07	0.464	3.35	1.01	50.14	−0.689	−0.18	31.71	0.464
RM39	17.193	1.464	2.72	−0.48	2.93	30.05	0.209	10.83	1.09	52.18	0.418	0.20	17.26	0.209
RM40	5.308	0.574	−0.67	−22.21	3.58	13.12	0.057	42.38	1.85	64.95	0.901	1.31	5.40	0.057
RM41	33.038	2.225	4.70	3.81	4.36	54.57	0.524	6.31	2.01	66.79	−0.040	−0.02	34.38	0.524
RM42	31.040	1.735	4.49	4.38	1.29	55.80	0.450	4.85	1.86	65.01	0.153	0.07	31.05	0.450
RM43	28.206	2.090	7.01	7.03	1.74	47.06	0.401	5.77	1.53	60.42	−0.267	−0.08	28.60	0.401
RM44	21.372	0.629	1.11	1.23	1.62	67.28	0.276	1.31	1.17	54.01	0.332	0.13	21.60	0.276
RM45	21.492	0.872	2.10	2.49	1.99	54.84	0.276	1.57	1.09	52.12	−0.001	0.00	21.60	0.276
RM46	42.434	2.644	5.10	4.74	2.26	65.67	0.738	2.11	3.02	75.12	−1.803	−0.38	42.46	0.738
RM47	21.508	0.581	0.90	0.96	0.54	70.77	0.277	1.24	1.20	54.62	0.440	0.22	21.68	0.277

%Na Percent sodium, *SAR* Sodium absorption ratio, *RSBC* Residual sodium bicarbonate, *RSC* Residual sodium carbonate, *B* Boron, *PI* Permeability index, *KI* Kelly index, *PS* Potential salinity, *MR* Magnesium ratio, *MH* Magnesium hazard, *CAI* Chloro alkaline indices, *SSP* Soluble sodium percentage, *ESR* Exchangeable sodium ratio, *BDL* Below Detectable limit

because of the relative insolubility of the rock composition.

The variation in hydrochemical facies in the samples collected from the Markandeya River basin is given in Table 4.

Based on Cl, SO_4, and HCO_3 concentrations, the groundwater sources were categorized as normal chloride (<15 meq/L), normal sulfate (<6 meq/L), and normal bicarbonate (2–7 meq/L) water types (Soltan 1998). Among the 47 groundwater samples, about 95.75% and 95.75% were respectively categorized as normal chloride and normal sulfate, whereas 61.70% were of normal bicarbonate type.

Groundwater quality analysis for irrigation

Water quality, soil types, and cropping practices play an important role for a suitable irrigation practice. Excessive amounts of dissolved ions in irrigation water affect plants and agricultural soil physically and chemically, thus reducing productivity. The physical effects of these ions is to lower the osmotic pressure in the plant structural cells, thus preventing water from reaching the branches and leaves. The chemical effects disrupt plant metabolism. Water quality problems in irrigation include indices for salinity, chlorinity, sodicity (Mills 2003), and alkalinity. The important chemical constituents that affect the suitability of water for irrigation (Table 5), which can be utilized to verify the suitability, are as follows:

- Salinity index or salinity hazard or total concentration of soluble/dissolved salt as computed by measured EC values.
- Sodicity index or sodium hazard or relative proportion of sodium to other principal cations as expressed by SAR.
- Sodium hazard expressed as percent sodium of total cations (%Na).
- Bicarbonate hazard or bicarbonate (HCO_3) concentration as related to the concentration of calcium plus magnesium such as RSC and RSBC.
- Boron hazard (concentration of boron or other elements) that may be toxic.
- Chlorinity index (measured chloride ion concentration in water).
- Magnesium hazard/ratio, Kelly index (KI), permeability index (PI), potential salinity (PS), SSP, and index of base exchange, and exchangeable sodium ratio (ESR).

Salinity index

Based on the analysis, the groundwater samples have been classified (Handa 1969) and are given in Table 6. It is found that all the samples collected during the post-monsoon season of the year 2008 are categorized under low to high extensive salinity classes. The majority of the samples (59.58%) belong to the high salinity category, indicating that the water is of permissible quality.

The salinity index of the groundwater samples was computed using the measured electrical conductivity values. Water exhibiting low to moderate salinity (classes 1 and 2) are not considered very harmful to soils or crops, whereas those exhibiting high salinity (class 3) are suitable for irrigating the medium and high salt-tolerant crops. High salinity water (class 4) is suitable for irrigating high salt-tolerant crops, whereas water

Table 6 Classification of waters based on of EC (Handa 1969)

EC (μS/cm)	Water salinity	Range (no. of samples)	Percent
0–250	Low (excellent quality)	160.4–214.8 (3 samples)	6.38
251–750	Medium (good quality)	307–719 (10 samples)	21.28
751–2,250	High (permissible quality)	774–2,233 (28 samples)	59.58
2,251–6,000	Very high	2,771–3,944 (5 samples)	10.64
6,001–10,000	Extensively high	9,003 (1 sample)	2.12
10,001–20,000	Brines weak concentration	–	–
20,001–50,000	Brines moderate concentration	–	–
50,001–100,000	Brines high concentration	–	–
>100,000	Brines extremely high concentration	–	–

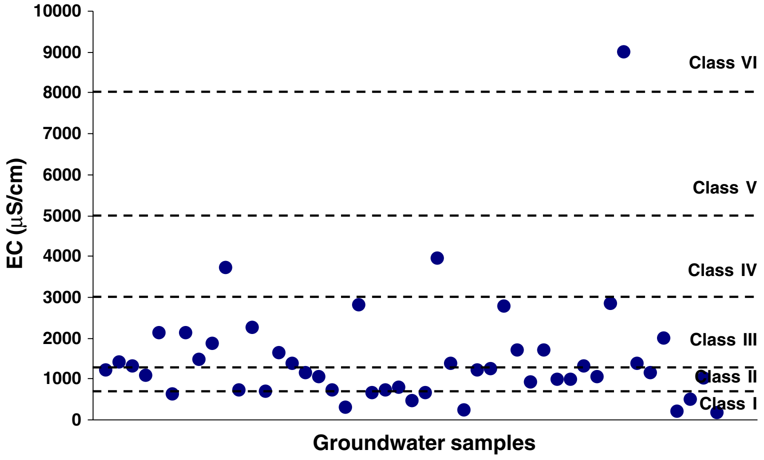


Fig. 8 Salinity index for the groundwater samples of the study region

of salinity class 5 or above are generally unsuitable for irrigation. Majority of the groundwater samples (93.6%) in the study region are categorized as classes 1–3 and thus may be considered as suitable for irritation (Fig. 8). However, about 6.4% of the water samples are found to exhibit very high to extremely high salinity (classes 4–6) and may not be suitable for irrigation (Fig. 8).

Chlorinity index

Low salt tolerance crops are usually chloride sensitive. The chlorinity index of the groundwater sources was calculated using the measured chloride ion concentration in water. Majority of the groundwater samples (~95.75%) are found to be suitable (classes 1 and 2) for irrigation (Fig 9).

Total hardness

In determining the suitability of groundwater for domestic and industrial purposes, hardness is an important criterion, as it is involved in making the water hard. Water hardness has no known adverse effects; however, it causes more consumption of detergents at the time of cleaning, and some evidence indicates its role in heart disease (Schroeder 1960). The total hardness (TH) in ppm (Todd 1980; Hem 1985; Ragunath 1987) was determined by following Eq. 2:

$$\mathrm{TH} = 2.497\,\mathrm{Ca}^{2+} + 4.115\,\mathrm{Mg}^{2+}. \qquad (2)$$

Hence, classification of the groundwater of the study area based on hardness (Sawyer and McCarthy 1967) has been carried out and is presented in Table 7. Accordingly, 32 samples

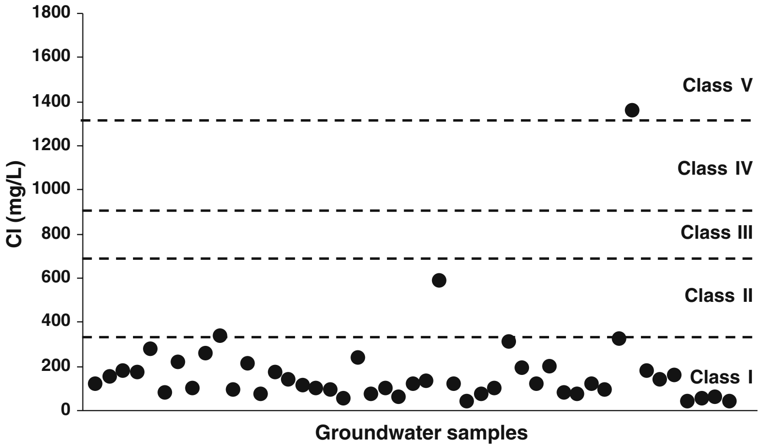


Fig. 9 Chlorinity index for the groundwater samples of the study region

Table 7 Sawyer and McCarty's classification for groundwater based on hardness

TH as $CaCO_3$ (mg/L)	Water classes	Range (no. of samples)	Percent
<75	Soft	–	–
75–150	Moderately hard	110–130 (5 samples)	10.64
150–300	Hard	220–290 (10 samples)	21.28
>300	Very hard	310–2,530 (32 samples)	68.08

(68.08%) collected during the post-monsoon season of the year 2008 fall under the very hard class.

SAR or sodicity index

Another important factor for water quality is the sodium concentration to express reactions with the soil and know reduction in its permeability. High sodium-depositing waters are generally not suitable for irrigating the soils, as higher deposition of sodium may deteriorate the soil characteristics. Therefore, SAR is considered a better measure of sodium (alkali) hazard in irrigation, as SAR of water is directly related to the adsorption of sodium by soil and is a valuable criterion for determining the suitability of the water for irrigation. Excessive sodium content relative to calcium and magnesium reduces soil permeability and thus inhibits the supply of water needed for the crops. The SAR measures the relative proportion of sodium ions to those of calcium and magnesium in a water sample. The SAR is used to predict the sodium hazard of high carbonate waters, especially if they contain no residual alkali. The excess sodium or limited calcium and magnesium content are evaluated by SAR (Kalra and Maynard 1991), which is computed as

$$\mathrm{SAR}\frac{\mathrm{Na}^{+}}{\sqrt{\left(\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}\right)/2}}, \qquad (3)$$

where all cationic concentrations are expressed in equivalents per million or milliequivalents per liter.

The classification of groundwater samples from the study area with respect to SAR (Todd 1959) is represented in Table 8. During post-monsoon, the SAR value of all the samples are found to be less than 10 and are classified as excellent for irrigation (i.e., S1 category). The sodicity index was calculated using the SAR, with water up to class 2 are generally considered suitable for irrigation, and was used for the classification of the groundwater samples. Based on the sodicity index, all the samples belong to class 0 (Fig. 10), except for one sample with a SAR value of 3.345 that belongs to class 1. Spatial variation of SAR is shown in Fig. 11a.

Salinity hazard

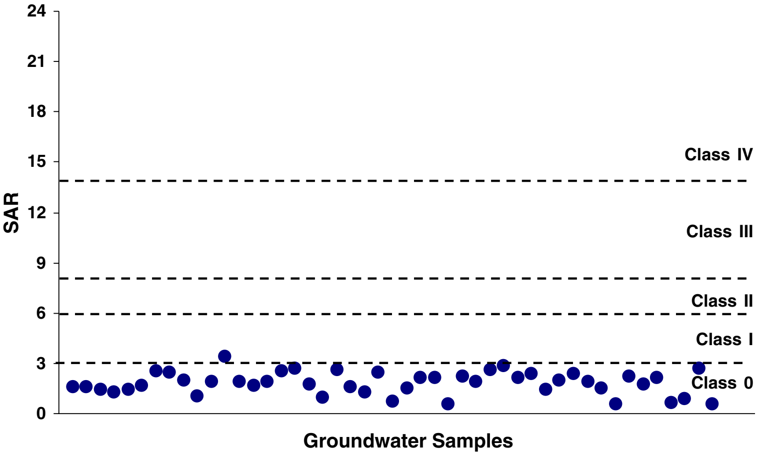
For the purpose of diagnosis and classification, the total concentration of soluble salts (salinity hazard) in irrigation water can be expressed in terms of specific conductance. Classification of groundwater based on salinity hazard is presented in Table 9. It is found from the salinity hazard classes that only six samples during the post-monsoon season was found to be unsuitable for irrigation purposes as they belong to the high salinity (C4 and C5) categories.

Groundwater samples that fall in the low salinity hazard class (C1) can be used for irrigation of most crops and majority of soils. However, some leaching is required, but this occurs under normal irrigation practices except in soils of extremely low permeability. Groundwater samples that fall in the medium salinity hazard class (C2) can be

Table 8 Classification of waters based on SAR values (Todd 1959; Richards 1954) and sodium hazard classes based on USSL classification

SAR values	Sodium hazard class	Remark on quality	Post-monsoon samples
<10	S1	Excellent	0.556–3.345 (all samples)
10–18	S2	Good	–
19–26	S3	Doubtful/fair poor	–
>26	S4 and S5	Unsuitable	–

Fig. 10 Sodicity index for the groundwater samples of the study region



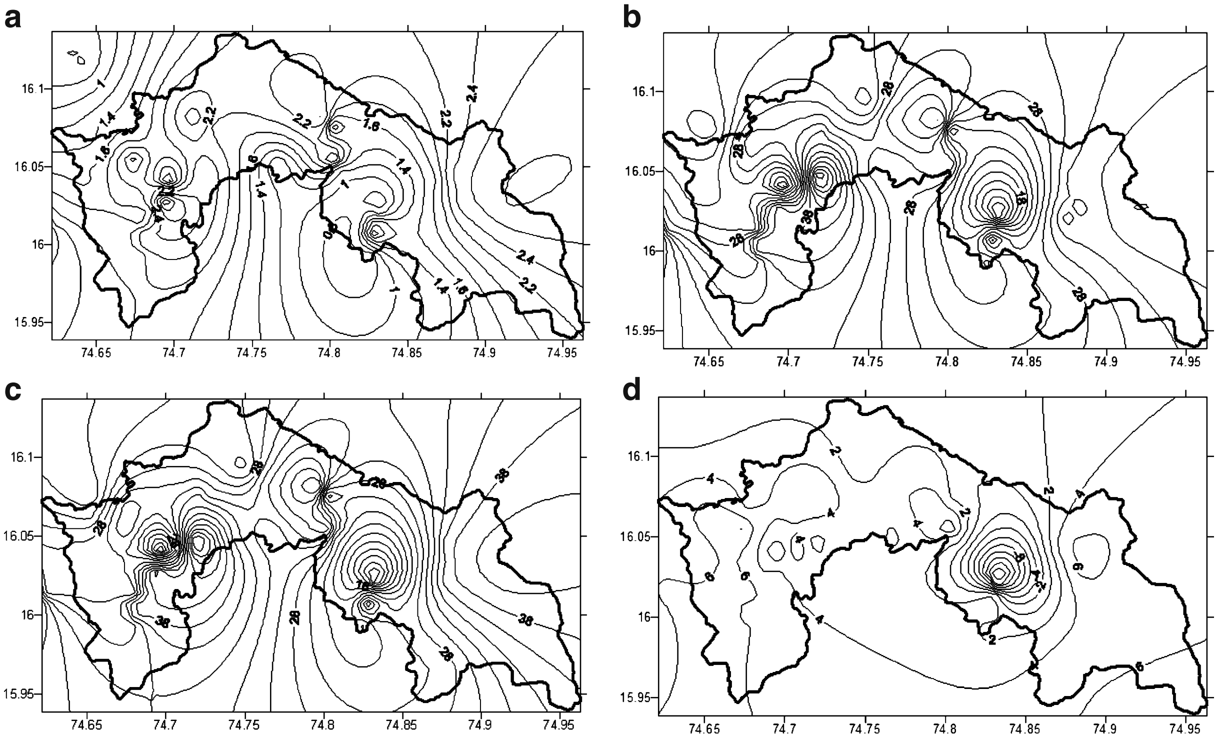


Fig. 11 Iso-concentration maps showing spatial variation in **a** SAR, **b** percent sodium, **c** soluble sodium percentage, and **d** residual sodium carbonate in the study area

Table 9 Salinity hazard classes

Salinity hazard class	EC (μS/cm)	Remark on quality	Range (no. of samples)
C1	100–250	Excellent	160.4–214.8 (3 samples)
C2	250–750	Good	307–719 (10 samples)
C3	750–2,250	Doubtful	774–2,233 (28 samples)
C4 and C5	>2,250	Unsuitable	2,771–9,003 (6 samples)

used if a moderate amount of leaching occurs. High salinity/low sodium water (C4 and C5) can be suitable for plants having good salt tolerance but restricts its suitability for irrigation, especially in soils with restricted drainage (Karanth 1989; Mohan et al. 2000). High salinity water (C3, C4, and C5) cannot be used in soils with restricted drainage. Even with adequate drainage, special management for salinity control is required, and crops with good salt tolerance should be selected. Such areas need special attention as far as irrigation is concerned. A more detailed analysis for the suitability of water for irrigation can be made by plotting the sodium absorption ratio and

Fig. 12 US salinity hazard diagram (after Richards 1954; post-monsoon)

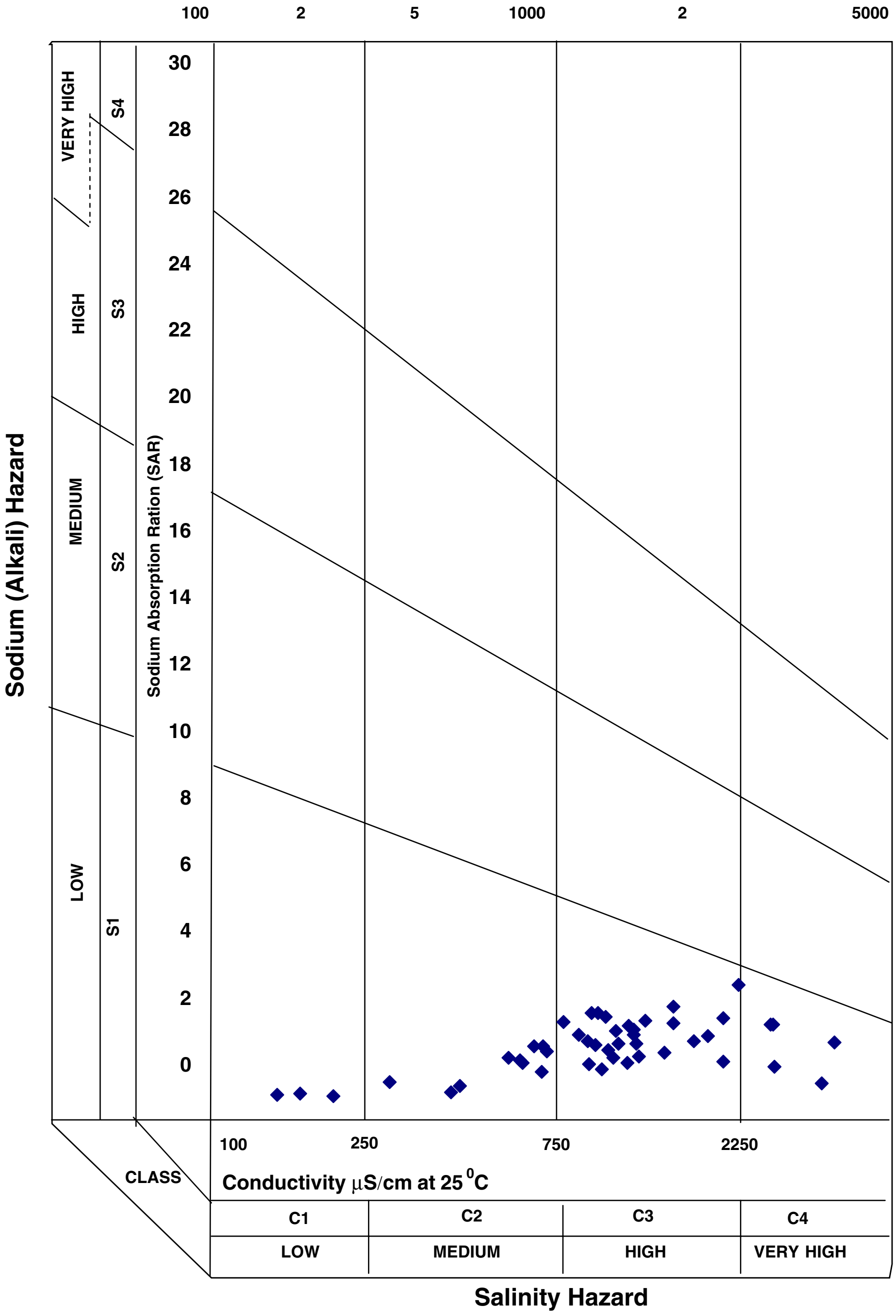


Table 10 Sodium percent water class (Wilcox 1955)

Sodium (%)	Water class	Range (no. of samples)
<20	Excellent	5.308–19.157 (6 samples)
20–40	Good	21.372–39.773 (38 samples)
40–60	Permissible	42.434–52.084 (3 samples)
60–80	Doubtful	–
>80	Unsuitable	–

electrical conductivity (Fig. 12) data on the US Salinity Laboratory (USSL) diagram (Richards 1954). Accordingly, 28 samples fall in the category of C3S1 (59.57%), indicating a high salinity/low sodium type. Of the remaining 19 samples, six samples belong to C4 and C5S1, indicating very a high salinity/low sodium type (12.77%), while ten and three samples belong to the C2S1 (21.28%) and C1S1 (6.38 %) groups, illustrating medium salinity/low sodium and low salinity/low sodium types, respectively.

Percent sodium

Methods of Wilcox (1995) and Richards (1954) have been used to classify and understand the basic character of the chemical composition of groundwater, since the suitability of the groundwater for irrigation depends on the mineralization of water and its effect on plants and soil. Percent sodium can be determined using the following formula:

$$\%\mathrm{Na} = \frac{\left(\mathrm{Na}^{+} + \mathrm{K}^{+}\right) \times 100}{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+}\right)}, \quad (4)$$

where the quantities of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} are expressed in milliequivalents per liter or equivalents per million.

When the concentration of sodium is high in irrigation water, sodium ions tend to be absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process of Na^{+} in water for Ca^{2+} and Mg^{2+} in soil reduces the permeability and eventually results in soil with poor internal drainage. Hence, air and water circulation is restricted during wet conditions, and such soils become usually hard when dry (Saleh et al. 1999).

The classification of groundwater samples with respect to percent sodium (Fig. 11b) is shown in Table 10 and it was found that 44 samples (93.6%) belong to the excellent to good category. Based on Eaton's (1950) classification, all the samples belong to the safe category (Table 11).

Wilcox (1948) classified groundwater for irrigation purposes by correlating percent sodium (i.e., sodium in irrigation waters) and electrical conductivity. A perusal of Wilcox's (1995) diagram (Fig. 13) shows that out of 47 samples, 26 (55.32%) belong to the good to permissible; 13 (27.66%), excellent to good; 6 (12.77%), doubtful to unsuitable; and 2 (4.25%), unsuitable categories.

Soluble sodium percentage

Water quality for agricultural purposes in the Markandeya River basin shows variation between excellent and good based on Todd's classification of SSP values, which is defined as

$$\mathrm{SSP} = \left(\frac{(\mathrm{Na}^{+})}{(\mathrm{Na}^{+} + \mathrm{Ca}^{+2}\mathrm{Mg}^{+2})}\right) \times 100, \quad (5)$$

where all concentrations are in milliequivalents per liter. The SSP values ranged from 5.4 to 52.84 for the post-monsoon season of the year 2008 (Fig. 11c).

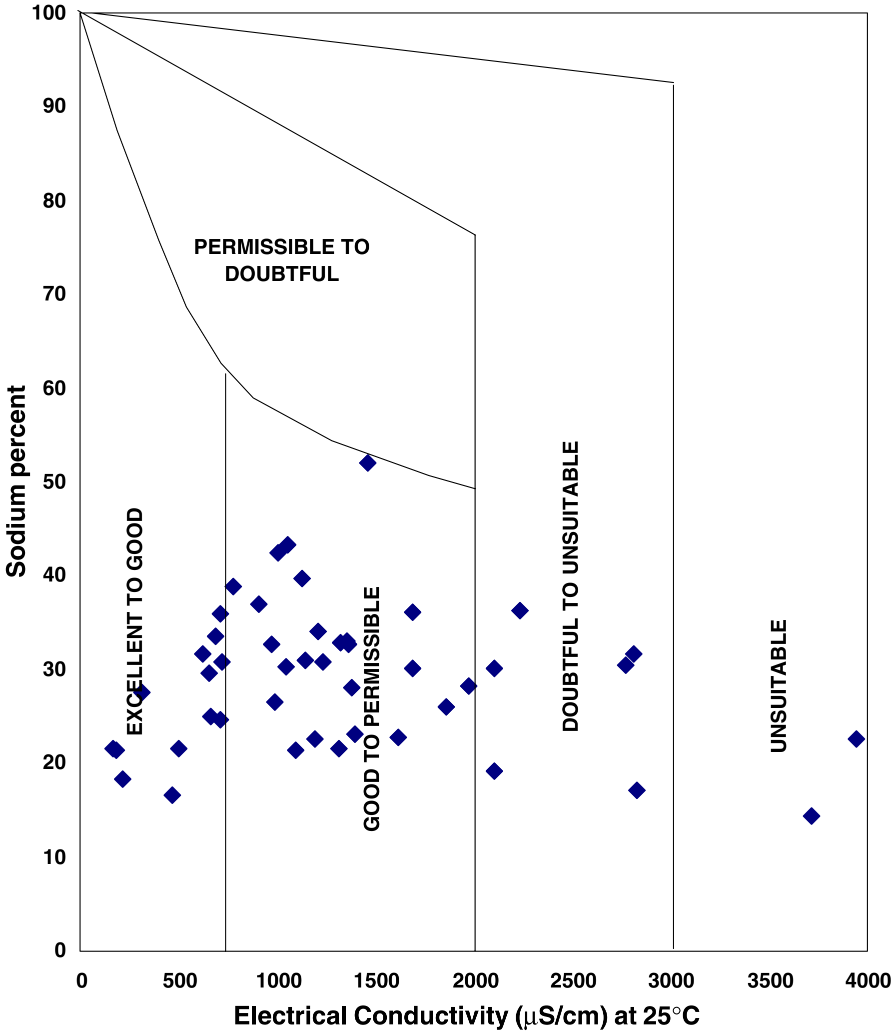
Residual sodium carbonate

In addition to the SAR and % Na, the excess sum of carbonate and bicarbonate in groundwater over the sum of calcium and magnesium also influences the suitability of groundwater for irrigation because in waters having high concentration of bicarbonate, there is tendency for calcium and magnesium to precipitate as the water in the soil becomes more concentrated. An excess quantity

Table 11 Sodium percent water class (Eaton 1950)

Sodium (%)	Water class	Range (no. of samples)
>60	Unsafe	–
<60	Safe	5.308–52.084 (all samples)

Fig. 13 Percent sodium vs. EC plot (after Wilcox 1995; post-monsoon)



of sodium bicarbonate and carbonate is considered to be detrimental to the physical properties of soils, as it causes dissolution of organic matter in the soil, which in turn leaves a black stain on the soil surface on drying. As a result, the relative proportion of sodium in the water is increased in the form of sodium carbonate, and this excess, denoted by RSC, is calculated as follows (Eaton 1950; Ragunath 1987):

$$\mathrm{RSC} = \left(\mathrm{CO_3}^{2-} + \mathrm{HCO_3}^{-}\right) - \left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right), \quad (6)$$

where all ionic concentrations are expressed in equivalents per million or milliequivalents per liter.

According to the US Department of Agriculture, water having more than 2.50 epm of RSC is not suitable for irrigation purposes. The groundwater in the study area is classified on the basis of RSC (Fig. 11d), and the results are presented in Table 12 for the post-monsoon seasons.

Based on the RSC values, 35 samples (74.47%) showed RSC values more than 2.50 epm, considered to unsuitable for irrigation. The positive RSC values in 43 samples indicated that dissolved

Table 12 Groundwater quality based on RSC (after Richards 1954)

RSC (epm)	Remark on quality	Range (no. of samples)
<1.25	Good	−22.21–1.23 (8 samples)
1.25–2.50	Doubtful	1.4–2.49 (4 samples)
>2.50	Unsuitable	2.69–8.2 (35 samples)

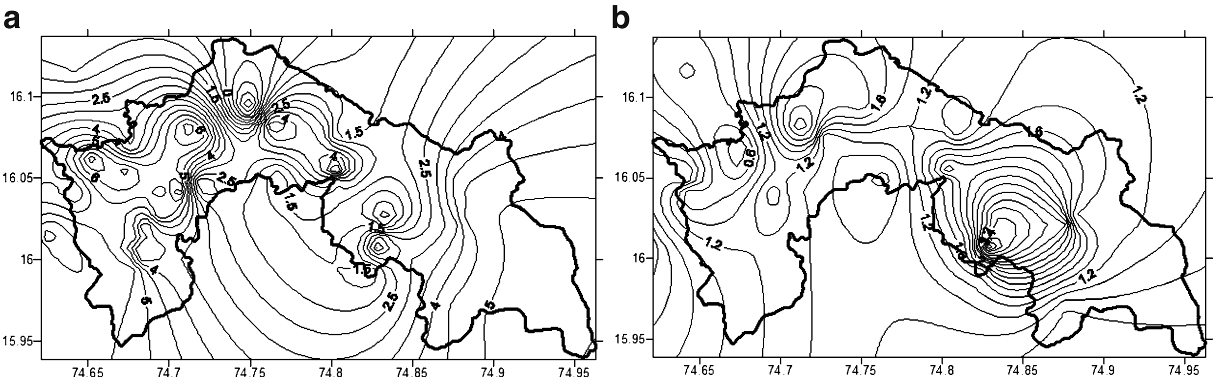


Fig. 14 Iso-concentration maps showing spatial variation in **a** RSBC and **b** boron (μg/L) in the study area

Ca^{2+} and Mg^{2+} ion contents was less than the CO_3^{2-} and HCO_3^- contents. The remaining eight samples (17.02%) were having a RSC value below 1.25 epm, and only four samples (8.51%) belong to the doubtful category.

Residual sodium bicarbonate

Gupta and Gupta (1987) defined RSBC as given in Eq. 7:

$$\mathrm{RSBC} = \left(HCO_3^- - Ca^{2+}\right) \qquad (7)$$

The samples' RSBC values varied from −2.97 to 7.4 meq/L (Fig. 14a) in post-monsoon. All the samples collected during post-monsoon were found to be satisfactory (<5 mg/L) according to the criteria set by Gupta and Gupta (1987).

Boron

The curcumin method employed in the present study is applicable to groundwater samples containing boron in the range of 0.1 to 1.0 mg/L; samples with higher concentration above this value must be diluted to determine the boron content. Boron concentration (Fig. 14b) in the groundwater of the area during November 2008 ranges between 0.03 and 4.36 μg/L (i.e., 0.00003–0.00436 mg/L) with an average value of 1.785 μg/L (i.e., 0.001785 mg/L). The proposed limits of boron concentration in irrigation water and the total number of groundwater samples of the study area representing the boron classes (McCarthy and Ellery 1994) are presented in (Table 13). All the samples were found to be excellent for tolerant and semi-tolerant crops based on boron concentration.

Permeability index

The PI values also indicate suitability of groundwater for irrigation, as the soil permeability is affected by long-term use of irrigation water, influenced by the Na^+, Ca^{2+}, Mg^{2+}, and HCO_3^- contents of the soil. Doneen (1964) and Ragunath (1987) evolved a criterion for assessing

Table 13 Permissible limits of boron in irrigation water for several types of crops

Boron class	Semi-sensitive crops		Semi-tolerant and tolerant crops	
	Range(mg/l)	Total no. of wells	Range	Total no. of wells
		November 2008		November 2008
Excellent	<0.33	0.00003–0.00436 (47 samples)	<0.67	0.00003–0.00436 (47 samples)
Good	0.33–0.67	Nil	0.67–1.33	Nil
Permissible	0.67–1	Nil	1.33–2.0	Nil
Doubtful	1–1.25	Nil	2.0–2.5	Nil
Unsuitable	>1.25	Nil	>2.5	Nil

the suitability of water for irrigation based on PI, and waters can be classified as classes 1, 2, and 3. The PI can be written as follows:

$$\mathrm{PI} = \frac{\left(\mathrm{Na}^{+} + \sqrt{\mathrm{HCO}_3}\right) \times 100}{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+}\right)}, \tag{8}$$

where the concentrations are reported in milliequivalents per liter.

The permeability index of the Markandeya River basin ranges from 13.12% to 80.37% (Fig. 16a) during the post-monsoon in November 2008, with an average value of about 55.26%. Accordingly, all the 47 samples are categorized under classes 1 and 2 of Doneen's chart (Domenico and Schwartz 1990; Fig. 15). WHO (1989) uses a criterion for assessing the suitability of water for irrigation based on the permeability index. According to the permeability index values, 95.76% of the samples fall under class 2 (PI ranged from 25% to 75%) and 2.12% belong to class 1 (PI > 7.5%) in the post-monsoon in November 2008.

Potential salinity

(Doneen 1961, 1964) pointed out that the suitability of water for irrigation is not dependent on the concentration of soluble salts. (Doneen 1962) is of the opinion that low solubility salts precipitate in the soil and accumulate with each successive irrigation, whereas the concentration of highly soluble salts increases the salinity of the soil. "Potential salinity is defined as the chloride concentration plus half of the sulfate concentration."

$$\text{Potential salinity} = \mathrm{Cl} - + \frac{1}{2}\mathrm{SO}_4^{2-} \tag{9}$$

The PS value is more pronounced in the estuarine region than in the fresh region samples and is expressed in milliequivalents per liter. The huge amount of potential salinity in the estuarine region is due to the presence of chlorides, which are derived from sea source. The potential salinity of the water samples varied from

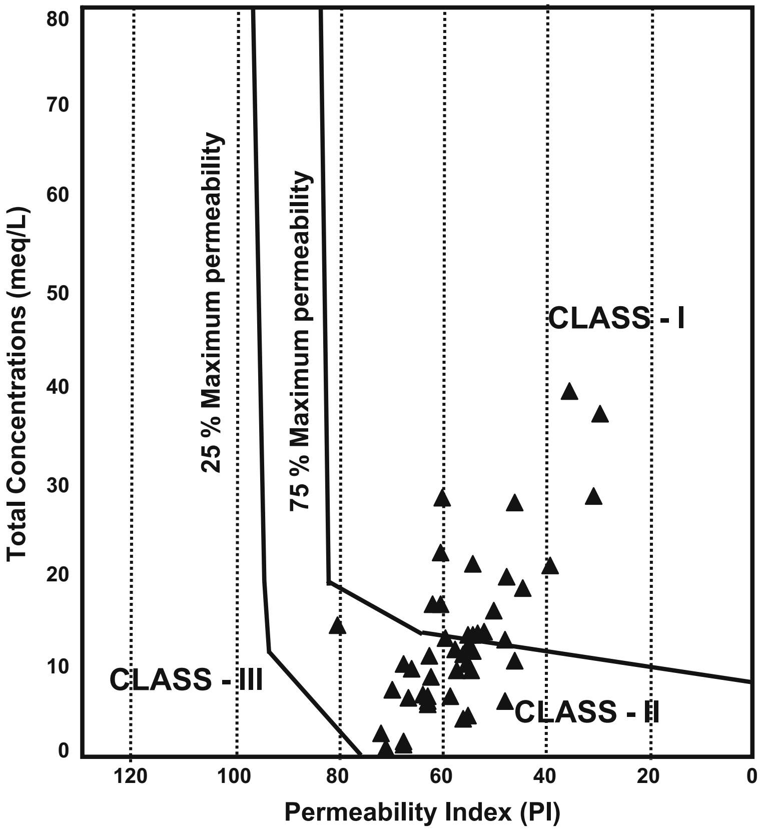


Fig. 15 Doneen (1964) classification of irrigation water based on the permeability index

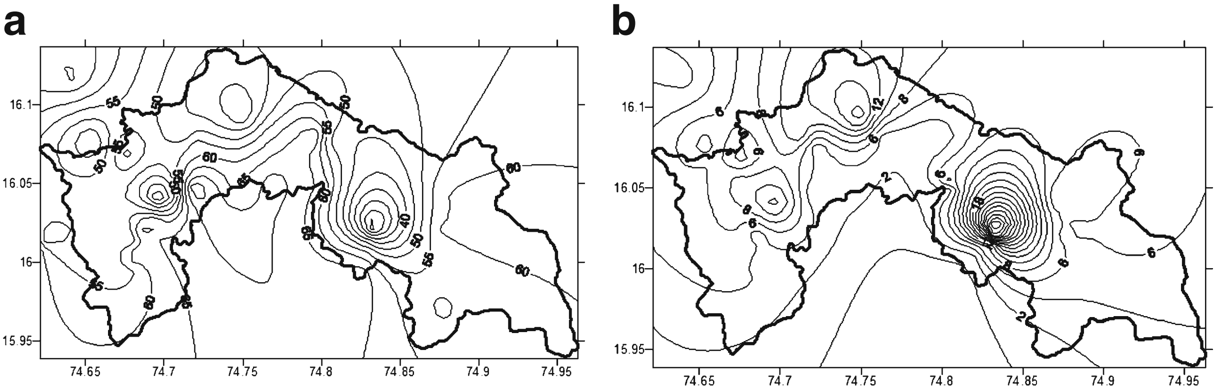


Fig. 16 Iso-concentration maps showing spatial variation in **a** permeability index and **b** potential salinity in the study area

1.21 to 42.38 meq/L during the post-monsoon in November 2008 (Fig. 16b).

Ion exchange processes

Control on the dissolution of undesirable constituents in water is impossible during the subsurface runoff, but it is essential to know the various changes in chemical composition undergone by groundwater during its trend/travel in the subsurface (Johnson 1979; Sastri 1994). The chloro-alkaline indices CAI-1 and CAI-2 are suggested by (Schoeller 1965, 1967, 1977), which indicate ion exchange between the groundwater and its host environment during residence or travel. If Na^+ and K^+ ions in water are exchanged with Mg^{2+} and Ca^{2+} ions and the index values are positive, this indicates a direct base (cation–anion) exchange reaction. In contrast, if the exchange is in the reverse order, then the exchange is indirect and the indices are found to be negative, indicating chloro-alkaline disequilibrium. These reactions are known as cation–anion exchange reaction. The chloro-alkaline indices used in the evaluation of base exchange are calculated using the formulae

$$\begin{aligned}&\text{Chloro alkaline index 1}\\&\quad=\left(\mathrm{Cl}^- - \left(\mathrm{Na}^+ + \mathrm{K}^{+}\right)\right)/\mathrm{Cl}^-\\&\text{Chloro alkaline index 2}\\&\quad=\left(\mathrm{Cl}^- - \left(\mathrm{Na}^+ + \mathrm{K}^{+}\right)\right)/\\&\quad\left(\mathrm{SO}_4^{2-}+\mathrm{HCO}_3^-+\mathrm{CO}_3^{2-}+\mathrm{NO}_3^-\right)\end{aligned} \quad . \qquad (10)$$

The chloro-alkaline indices (Fig. 17a and b) are calculated for post-monsoon waters of the areas, and it has been observed that 68.08% of the

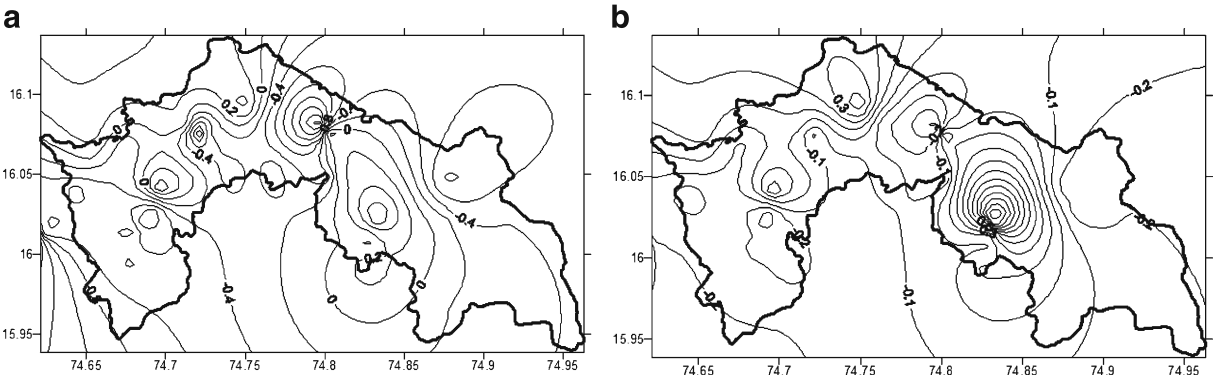


Fig. 17 Iso-concentration maps showing spatial variation in **a** chloro-alkaline indices 1 and **b** 2 in the study area

post-monsoon samples of the Markandeya River basin showed negative ratios with an indirect base exchange reaction. In contrast, 31.92% of the samples showed positive chloro-alkaline indices, illustrating that they had direct base exchange reaction. During this process, the host rocks are the primary sources of dissolved solids in the water.

The Schoeller index values of the groundwater samples of the study area (Table 5) reveal a base exchange reaction (chloro-alkaline disequilibrium) existing in majority of the samples from the area (32 samples), except at 11 sites where the values are positive, indicating a cation–anion exchange (chloro-alkaline equilibrium). Groundwater with a base exchange reaction in which the alkaline earths have been exchanged for Na^+ ions ($HCO_3^- > Ca^{2+} + Mg^{2+}$) may be referred to as base exchange-softened water, and those in which the Na^+ ions have been exchanged for the alkaline earths ($Ca^{2+} + Mg^{2+} > HCO_3^-$) may be referred to as base exchange-hardened water (Handa 1969). In the study area, all the collected water samples have higher $HCO3^-$ concentration than alkaline earths, thereby indicating base exchange-softened water.

Kelly's index

Sodium measured against Ca^{2+} and Mg^{2+} is used to calculate Kelley's ratio (Kelly 1940, 1951; Paliwal 1967). However, nowadays, SAR is a better measure for sodium, and this particular ration is not in common use, but this study also presents a review of all the quality criteria of classification to evaluate the obtained dataset. A Kelly's index of more than 1 indicates an excess level of sodium in waters. Hence, waters with a Kelly's index less than 1 are suitable for irrigation, while those with a ratio more than 1 are unsuitable. Kelly's index (Fig. 18a) in the present study varied from 0.057 to 1.121, and all the water samples are suitable for irrigation according to Kelly's index, except for one sample (RM8) with a KI value of 1.121.

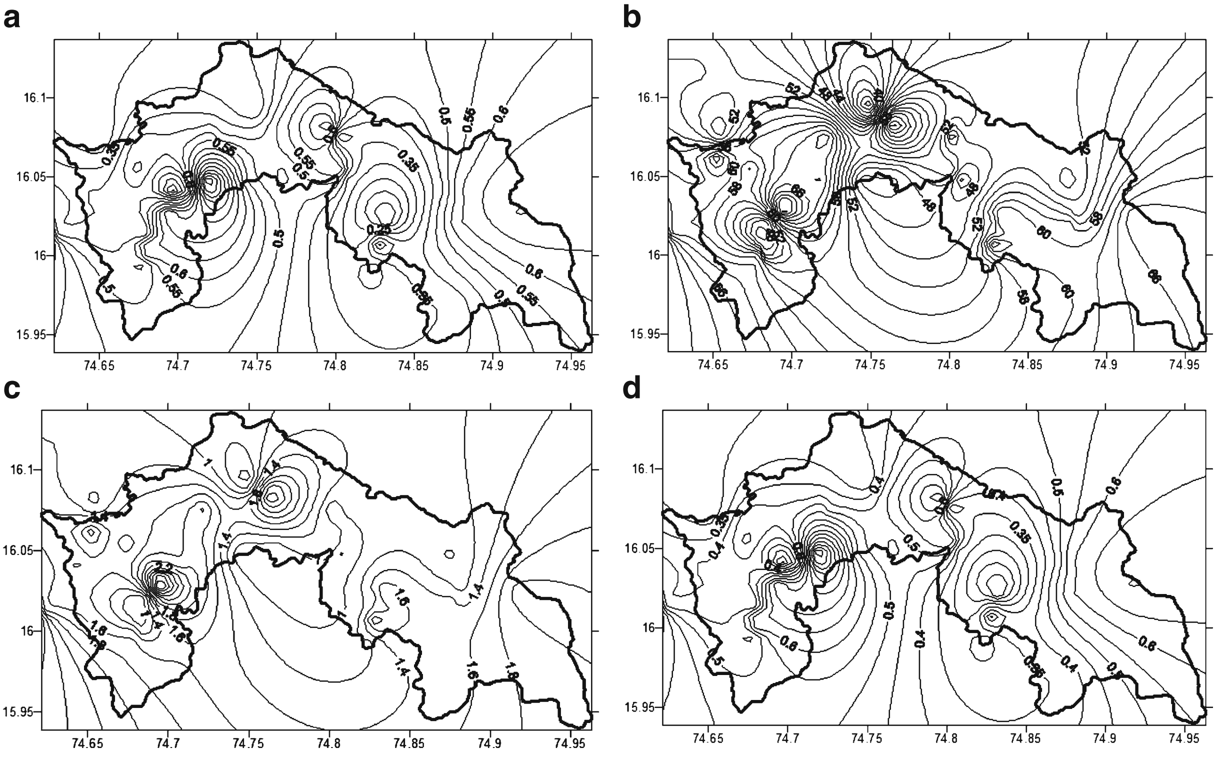


Fig. 18 Iso-concentration maps showing spatial variation in **a** the Kelly index, **b** magnesium hazard, **c** magnesium ratio, and **d** exchangeable sodium ratio in the study area

Magnesium hazard

Generally, calcium and magnesium maintain a state of equilibrium in most waters. Calcium and magnesium do not behave equally in the soil system, and magnesium deteriorates soil structure particularly when waters are sodium dominated and highly saline. A high level of Mg is usually due to the presence of exchangeable Na in irrigated soils. In equilibrium, more Mg^{2+} present in water will adversely affect the soil quality, rendering it alkaline, resulting in decreased and adversely affected crop yields. Paliwal (1972) introduced an important ratio called index of magnesium hazard. Magnesium hazard value of more than 50% would adversely affect the crop yield as the soils become more alkaline.

$$\text{Magnesium ratio} = \frac{(\mathrm{Mg}^{2+}) \times 100}{(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})} \tag{11}$$

In the Markandeya River basin, the MH values were reported to be in the range of 28.11% to 79.69% (Fig. 18b). Of the 47 samples, 23.4% of the samples showed a magnesium ratio below 50%, suggesting their suitability, while only 76.6% fall in the unsuitable category with MH more than 50%, indicating their adverse effect on crop yield.

Magnesium ratio

Based on the Mg/Ca ratio (Fig. 18c), we can classify waters as suitable or unsuitable for irrigation, and majority of the samples belong to the safe to moderate category (Table 14).

Exchangeable sodium ratio

ESR can be defined as

$$\mathrm{ESR} = \frac{\mathrm{Na}^{+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}. \tag{12}$$

Table 14 Permissible limits of residual Mg/Ca ratio in irrigation water

Class	Remarks	Range (no. of samples)
<1.5	Safe	0.39–1.48 (28 samples)
1.5–3.0	Moderate	1.53–2.76 (27 samples)
>3.0	Unsafe	3.02–3.92 (2 samples)

The ESR values calculated to determine the suitability of water sample for agricultural purposes, varied from 0.057 to 1.121 (Fig. 18d).

Mechanisms controlling groundwater chemistry

Lastly, to know the groundwater chemistry and the relationship of the chemical components of water to their respective aquifers such as chemistry of the rock types, chemistry of precipitated water, and rate of evaporation, Gibbs (1970) has suggested a diagram in which ratio of dominant anions and cations are plotted against the value of TDS. Gibbs diagrams, representing the ratio 1 for cations [(Na+K)/(Na+K+Ca)] and ratio 2 for anions [Cl/(Cl+ HCO_3)] as a function of TDS are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation, rock, and evaporation dominance (Gibbs 1970).

The chemical data of groundwater samples are plotted in the Gibbs diagram (Figs. 19 and 20). Majority of the water samples suggest that the chemical weathering of rock-forming minerals are

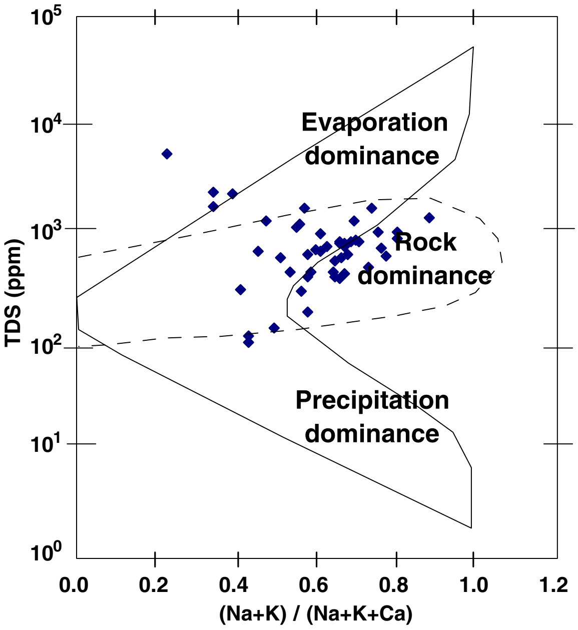


Fig. 19 Gibbs variation diagram (TDS vs. [(Na+K)/(Na+K+Ca)])

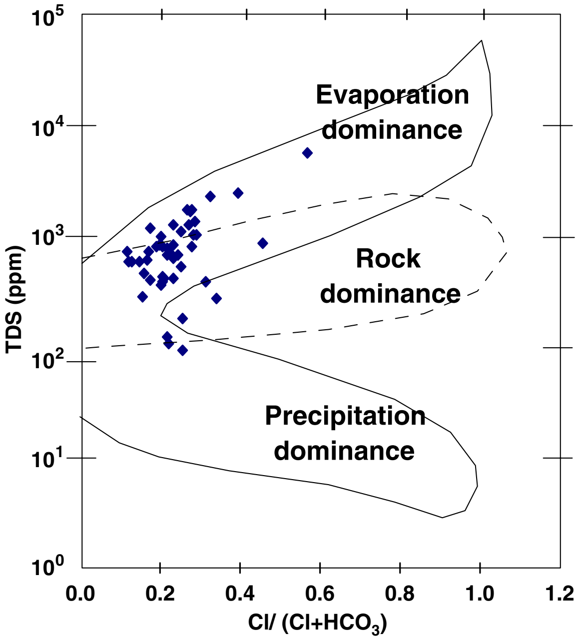


Fig. 20 Gibbs variation diagram (TDS vs. [Cl/(Cl + HCO_3)])

influencing the groundwater quality by dissolution of rock through which water is circulating. Only a few samples represent evaporation and precipitation dominance. Most of the samples falling in the precipitation, and evaporation dominance are collected from dug wells in the areas of semi-arid climatic condition (the northwestern part of the study area). Evaporation increases salinity by increasing Na^+ and Cl^- with relation to increase of TDS, and anthropogenic activities (agricultural fertilizers and irrigation return flows) also influence the evaporation by increasing Na^+ and Cl^- and thus TDS.

Conclusions

The groundwater sources in the Markandaya River basin, Belgaum District, were evaluated for their chemical composition and suitability for drinking, irrigation, and industrial uses. The groundwater in the region is classified in the moderately to very hard category based on hardness. It is evident from the higher values of physico-chemical results like hardness, alkalinity, bicarbonates, and potassium that most of the groundwater samples analyzed in the present investigation might be under natural and anthropogenic influences through infiltration and percolation during monsoon.

The suitability of groundwater for irrigation was evaluated based on the irrigation quality parameters like boron, SAR, %Na, RSC, RSBC, SSP, non-carbonate hardness, potential salinity, permeability index, Kelley's ratio, magnesium hazard/ratio, and index of base exchange. Among these parameters, SAR, boron, KI, MH, MR, and %Na imply that the water samples fall in excellent, suitable, unsuitable, safe to unsafe, and excellent to permissible, respectively, for irrigation. RSC values specify that water samples belong to good to unsuitable classes. Permeability index recommends that the water samples from the Markandeya River basin, belonging to classes 1 and 2, are suitable for irrigation. Water that is not suitable based on the above classification may be suitable in well-drained soils. The negative index of base exchange indicate that there does exist a chloro-alkaline disequilibrium, i.e., ion exchange between the groundwater and its host environment during residence or travel.

Based on the attempt made to study the hydrochemistry of groundwater, it was found that the HCO_3 type of water predominated anions, while the Ca–Mg type dominates cations during the post-monsoon in November 2008. The type of water that predominates in the study area belong to the Ca^{2+}–Mg^{2+}–HCO_3^- type followed by the Ca^{2+}–Mg^{2+}–Cl^-–SO_4^{2-} and Na^+–K^+–Cl^-–SO_4^{2-}. It was also noticed that alkaline earth elements exceeded alkalies concentration, and weak acids exceeded the strong acid element. Based on the Cl, SO_4, and HCO_3 concentrations, the groundwater sources were categorized as normal chloride (95.75%), normal sulfate (95.75%), and normal bicarbonate water type (61.70%).

From US salinity hazard diagram, it is evident that about 59.57% of the samples are grouped within the C3S1 classes in the post-monsoon season, indicating high salinity and low sodium type and there is a need for better drainage to overcome the salinity problem. From the Wilcox plot, it is observed that most of the samples from the study area fall in the excellent to unsuitable classes for irrigation purpose. Furthermore, the Gibbs plot indicates that the chemistry of the groundwater of the area is predominantly controlled by rock dominance; i.e., an interaction exists between the litho units and the percolating water into the subsurface. Hence, it can be concluded that the overall quality of groundwater is controlled by lithology apart from other local environmental conditions. Finally, based on these studies, recommendations have been made to the local authorities to adopt conjunctive use of surface water with groundwater to stringently monitor and control low groundwater quality regions to ensure sustainable safe use of the resource.

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