Geochemistry of groundwater, Markandeya River Basin, Belgaum district, Karnataka State, India

Ravikumar P.* and Somashekar R.K.

Department of Environmental Science, Bangalore University, Bangalore–560 056, India * Corresponding author. E-mail: prakruthiravi@gmail.com, nisargaravi@gmail.com

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Abstract The Markandeya River Basin stretches geographically from $15^{\circ}56'$ to $16^{\circ}08'$ N latitude and $74^{\circ}37'$ to $74^{\circ}58'$ E longitude, positioned in the midst of Belgaum district, in the northern part of Karnataka. The groundwater quality of 54 pre-monsoon samples in the Markandeya River Basin was evaluated for its suitability for drinking and irrigation purposes by estimating pH, EC, TDS, hardness and alkalinity besides major cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) and anions (HCO₃⁻, Cl⁻, SO₄²⁻, PO₄³⁻, F⁻, NO₃⁻), boron, SAR, % Na, RSC, RSBC, chlorinity index, SSP, non-carbonate hardness, Potential Salinity, Permeability Index, Kelley's ratio, Magnesium hazard and Index of Base Exchange. Negative Index of Base Exchange indicates the chloro-alkaline disequilibrium in the study area and the majority of water samples fall in the rock dominance field based on Gibbs' ratio. Permeability indices of classes I and II suggest suitability of groundwater for irrigation. Based on Cl, SO₄, HCO₃ concentrations, water samples can be classified as normal chloride (96.3%) and normal sulfate (94.4%) and normal bicarbonate (44.4%) water types.

Key words Markandeya River Basin; CAI-Chloroalkaline index; PI-permeability index; KI-kelley index; PS-potential salinity

1 Introduction

Groundwater is almost globally important for human consumption as well as for the support of habitat and for maintaining the quality of base flow to rivers. Being naturally filtered in their passage through the ground, they are usually clear, colorless, and have excellent quality, being free from microbial contamination and require minimal treatment (Babiker, et al., 2007). Unfortunately, it seems that we can no longer take high quality groundwater for granted, as a threat is now posed by an ever-increasing number of soluble chemicals from urban development, industrial activities and modern agricultural practices. There has been indiscriminate exploitation of groundwater resources in the Asian countries, particularly in India, leading to a decrease in groundwater potential, lowering of water table (hence an increase in cost of groundwater withdrawal) and deterioration in groundwater quality (Prasad et al., 2008). Since, the quantity and quality of water available for irrigation in a country like India is variable from place to place, in order to meet the increasing demands for water supply due to overall development in agriculture, industry and urbanization, the dependence on groundwater has increased tremendously in recent years mainly due to the vagaries of monsoon and scarcity of surface water, contributing to the complexity of its quality assessment. And it is impossible to control the dissolution of undesirable constituents in the waters after they enter the ground (Johnson 1979; Sastri, 1994). Hence, the investigation/assessment of geochemical element distribution and the natural background of these resources are of paramount importance in reconciling the exploitation of surface and ground waters with the protection of the environment, including the well being of both mankind and local fauna and flora (Darnley et al., 1995; Edmunds et al., 2002). Because, the chemical (quality) of groundwater is not only related to the lithology of the area and the residence time the water is in contact with rock material, but also reflects inputs from the atmosphere, from soil and weathered mantle/water-rock reactions (weathering), as well as from pollutant sources such as mining, land clearance, agriculture, acid precipitation, domestic and industrial wastes (Babiker et al., 2007). 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; Majumder and Gupta, 2000; Dasgupta and Purohit 2001; Khurshid et al., 2002; Sujatha and Reddy, 2003; Sreedevi, 2004; Pulle et al., 2005; Husain et al., 2005; Sunitha et al., 2005; Subba Rao, 2006). But, so far the geochemistry of groundwater in the Markandeya River Basin has not been studied in great detail and hence, an effort has been made in the current paper to assess groundwater quality through hydrogeochemical analysis to determine suitability for domestic and irrigational purposes.

2 Study area

The River Markandeya is one of the major tributaries of River Ghataprabha in northern Karnataka that subsequently joins the River Krishna. River Markandeya originates in Bailur in western Ghats and flows for a length of 66 km towards east before joining Ghataprabha near Gokak. A dam has been constructed across the River Markandeya (16°2'0" and longitude 74°38'30") to establish reservoir at Shirur Village in the Gokak taluk. The present study area, 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 Belgaum district in the northern part of Karnataka State. The study area is covered in the survey of India (SOI) toposheets 47 L/12, 47 L/16, 48 I/9 and 48 I/I3 with a catchment area of 432 km². The command area is around 191.05 km² (19105 ha) covering part of Gokak (95.83 km²), Saundatti (80.37 km²), Hukkeri (8.90 km²) and Belgaum (5.95 km²) taluks of Belgaum District. The reservoir water has been directed by via Markandeya Left Bank Canal (MLBC, 15 km) and Markandeya Right Bank Canal (MRBC, 71 km) to irrigate an area of around 8.9 km² (890 ha) and 182.15 km² (18215 ha) respectively to provide enhanced irrigation facilities and an improved drinking water system to the villages of four taluks of Belgaum District by means of a canal system.

3 Physiography and climate

The command area comes under northern dry zone of the tenfold Agro-climatic zone of Karnataka and has a semi-arid subtropical climate. The climate condition on



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

the whole is healthy, agreeable and is characterized by general dryness excepting during monsoon season. The summer season between March and May is dry, dusty and very hot with 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 monsoon period. June to September is the period during which humidity is normally higher. Crop failures are of common occurrence mainly due to unpredictable rainfall during summer season. Heavy precipitation can be observed both from south-west (S-W) and north-east (N-E) monsoons during the months of June to 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, and it may vary between 480 m to 640 mm. On average, there are about 50 rainy days in a year. The winds are generally light with a slight increase in the force observed during the late summer and monsoon season. Two distinct cropping seasons namely, Kharif and Rabi, can be seen in the study area, grown mainly under rainfed conditions. Crops grown during 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, Safflower are grown during Rabi season.

4 Geology and hydrogeology

The Krishna River Basin covers the major portion of Belgaum district and is characterized by various geological formations belonging mainly to Upper Proteozoic followed by Archean and Lower Proteozoic periods (Fig. 1). The consolidated and unconsolidated sediments rock types cover the major portion of the district with small patches of metamorphic, plutonic, volcanic or meta-volcanic rocks. The lineaments and 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 of varying slopes such as those gentle, moderate, nearly level, very gentle, strong and very steep slope, with slope varying from 0%-35%. The topology of regions is generally flat with nearly level slope in the SSW part of the study area. The geomorphology of Belgaum district is generally marked by 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 water table are dependent on the rate of weathering and topographical factors like lithology, thickness and rock formations like weathered and fractured granites and gneisses. As the study area is dependent mainly on rainfall irrigation, chief source of groundwater is infiltration and recharge of rainwater. Considering the climatic water balance, soil characteristics account for nearly 70 percent, allowing only 20 % rainfall being added again into groundwater pool. Percolation and recharges in the ground water account for 10 percent discharge of water through wells. The depth of water table varied between 10 to 370 ft in open and bore wells from the ground level.

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

5 Methodology

5.1 Hydrochemical analysis

A total of 54 groundwater samples (Fig. 1) were collected in the command area of the Markandeya River Basin during pre-monsoon (May 2008) season. The water samples were collected after 10 minutes of pumping and transferred into pre-cleaned polyethylene bottles and stored at 10°C. Electrical conductivity, pH, temperature, redox potential (Eh) and total dissolved solids for the collected samples were measured in the field immediately after sampling. The major anionic and cationic concentrations were determined at the laboratory using the standard analytical procedures (Table 1) as recommended by APHA (2005). The accuracy of all chemical analyses was checked using the Ion Charge Balance Equation or Ion Balance Error Computation (Mathhess, 1982; Domenico and Schwartz, 1990), taking the relationship between the total cations $(Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})$ and the total anions (PO₄³⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻ and Cl⁻) for each set of complete analyses of water samples using Equation (1)

Sl. No.	Category of parameters	Characteristics	Analytical method	Unit	BIS limit (1998)
1	General	рН	Electrode	_	6.5-8.5
2		Redox potential (Eh)	Electrode	mV	NA
3		Electrical Conductivity (EC)	Conductivity-TDS meter	μS/cm	3000
4		Total Dissolved Solids (TDS)	Conductivity-TDS meter	mg/L	2000
5		Total alkalinity (as CaCO ₃)	Titrimetric	mg/L	600
6	General	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		Colour	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	1000
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		Sulphates (as SO ₄ ²⁻)	Barium chloride	mg/L	400
22	Irrigation	Boron (B)	Curcumin method	mg/L or μ g/L	_
23	water quality	Hardness (as CaCO ₃)	By Calculation	mg/L	<75
24		Salinity	using equations	‰	NA
25		Sodium Absorption Ratio (SAR)		-	<10 or 10–18
26		Residual Sodium Carbonate (RSC)		meq/L	<1.25
27		Residual Sodium Bicarbonate (RSBC)		meq/L	<5 mg/L
28		Percent sodium (Na, %)		%	<20 or 20–40
29		Permeability Index (PI)		%	Class I or II
30		Kelley Index (KI)		-	<1.0
31		Potential Salinity (PS)		meq/L	NA
32		Magnesium Hazard (MH)		%	Below 50%
33		Magnesium Ratio (MR)		-	<1.5
34		Chloro-Alkaline Indices (CAI)-1		-	+ve or -ve
35		Chloro-Alkaline Indices (CAI)-2		-	+ve or -ve
36		Soluble Sodium Percentage (SSP)		%	NA
37		Exchangeable Sodium Ratio (ESR)		_	NA

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

Note: NA. Not available.

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

where the sum of major cations and anions are expressed in meq/L and E is the error percent/reaction error/cationic and anionic balance. The reaction error of all groundwater samples was less than the accepted limit of $\pm 10\%$ (Hem, 1975) and an added proof of the precision of the data. And 'E' greater than 10% was eliminated from subsequent analyses.

Based on the physico-chemical analyses, irrigation quality parameters like SAR, Na (%), RSC, RSBC, SSP, ESR, non-carbonate hardness, Potential Salinity, Permeability Index, Kelley's ratio, Magnesium hazard/ratio, Index of Base Exchange, etc., were calculated. The correlation of analytical data has been attempted by plotting different graphical representations such as Piper (1994), Back and Hanshaw (1965), Gibbs (1970), Wilcox (1995), Richards (1954), Eaton (1950), Todd (1959) and Handa (1969) 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 groundwater sources for drinking, domestic and irrigation purposes were evaluated by comparing the values of different water quality parameters with drinking water guideline values provided by the Bureau of Indian Standards (BIS, 1998) and World Health Organization (WHO, 1984). In addition to this, visually communicating Iso-concentration/contour maps were constructed using Surfur-8.0 and ArcGIS-9.2 softwares to delineate spatial variations of physico-chemical and irrigation quality parameters in the study area.

6 Results and discussion

6.1 General parameters

The analytical results for all the physico-chemical parameters for the pre-monsoon groundwater samples from the study area are presented in Table 2. The values of pH in groundwater samples collected from the study area varied from 6.23 to 8.56 (Fig. 2), indicating slightly acidic to slightly basic in nature. Only two samples (viz., sample nos. RM7 and RM24) out of 54 samples showed pH value crossing the BIS permissible limit of 6.5–8.5. Redox potential (Eh) and temperature were measured at all water points during the monitoring survey, which varied from -103.2 to -40.9 mV and 26.1 to 28.2°C respectively. In the study area, the electrical conductivity (EC) of groundwater varies widely between 110 to 7640 µS/cm (Fig. 2) and 9.2% of the samples (i.e., sample Nos. RM9, RM12, RM32, RM47 and RM50) showed



Fig. 2. Spatial Distribution of pH, EC, TDS and salinity in the Markandeya River Basin.

	PO_4	0.35	0.07	0.52	0.38	0.69	0.07	0.76	0.59	0.38	0.06	0.31	0.48	0.55	0.03	0.59	0.31	0.01	0.11	0.07	0.31	0.28	0.59	0.45	0.42	0.13	0.14	0.00
	SO_4	47.14	77.66	29.14	42.69	116.06	0.34	7.89	118.5	349.9	9.77	234.51	314.40	45.43	40.46	156.9	22.97	1.54	103.37	91.20	36.00	20.23	50.40	59.83	1.37	110.3	12.51	13 89
or anions	NO_3	7	30	10	20	30	0.9	5	4	4	6	20	10	б	6	20	8	8	40	20	10	10	10	10	7	30	4	"
Maj	HCO ₃	427.0	366.0	366.0	340.0	549.0	90.0	366.0	485.0	549.0	345.0	650.0	595.0	330.0	396.5	675.0	427.0	328.0	488.0	615.0	610.0	549.0	376.5	366.0	170.0	545.0	350.0	366.0
	CI	110	180	190	160	320	30	80	195	670	150	525	490	85	160	280	140	95	280	260	140	100	95	145	75	245	95	150
	F	0.9	0.4	0.6	0.5	0.4	0.2	0.8	0.4	0.4	1	1	7	0.5	0.5	0.7	0.6	0.7	0.5	0.6	0.5	0.4	0.5	0.5	0.2	0.8	0.8	04
	К	40.6	60.1	3.4	3.7	67.1	1.9	14.5	17	6.8	5.1	14.4	5.8	9.5	20.6	46.2	13	11.1	42	39.8	2.5	2.4	14.7	11.6	5.1	78.9	8.8	7 8
cations	Na	54.2	68.0	59.4	54.4	73.6	4.4	37.5	121	74.3	56.1	49.7	81.1	21.8	53.9	49.7	79.3	61.7	83.9	26.4	97.9	88.4	60.2	73.3	21.5	105.6	52.6	48.4
Major	Mg	42.7	70.76	65.88	51.24	78.08	13.42	48.8	46.36	156.2	39.04	126.9	112.2	39.04	51.24	90.28	36.6	19.52	70.76	78.08	48.8	36.6	26.84	43.92	14.64	39.04	24.4	31 72
	Ca	99	112	96	52	152	18	52	72	272	56	240	236	56	68	156	64	44	132	148	88	64	60	56	36	108	56	84
Total	alkalinity	350.0	300.0	300.0	278.7	450.0	73.8	300.0	397.5	450.0	282.8	532.8	487.7	270.5	325.0	553.3	350.0	268.9	400.0	504.1	500.0	450.0	308.6	300.0	139.3	446.7	286.9	300.0
Calcium	hardness	165	280	240	130	380	45	130	180	680	140	600	590	140	170	390	160	110	330	370	220	160	150	140	90	270	140	210
	Total hardness	340	570	510	340	700	100	330	370	1320	300	1120	1050	300	380	760	310	190	620	069	420	310	260	320	150	430	240	340
	Salinity	0.44	0.57	0.45	0.46	0.82	0.05	0.2	0.66	1.82	0.68	1.38	1.6	0.4	0.4	1.04	0.35	0.28	0.81	0.7	0.4	0.32	0.32	0.38	0.15	1.18	0.26	960
	Eh	-85.6	-58.2	-61.4	-57.6	-41.8	-47.8	-68.5	-44	-42.3	-103.2	-65.7	-63.6	-78.7	-67.7	-88.6	-78.4	-75.1	-57.6	-75.1	-77.6	-77.6	-66.5	-65.1	-52.9	-90.3	-75.8	-67 5
	TDS	520	734	604	593	1030	60.6	308	717	1940	387	1560	1690	612	529	1230	488	387	1000	779	622	504	411	480	188	1340	353	308
	EC	957	1350	1110	1090	1920	110	569	1310	3590	645	2890	3110	1120	976	2280	903	713	1850	1800	1140	930	759	881	345	2500	650	735
	Ηd	7.34	6.92	6.94	7.11	7.07	6.76	8.56	7.76	7.04	7.51	7.76	7.75	7.52	7.02	7.41	7.18	7.34	6.82	7.39	7.15	6.85	6.84	7.13	6.23	7.84	6.55	689
	$T(^{\circ}C)$	27.7	26.6	27.1	27.8	27.6	26.5	28.2	27.5	26.9	27.3	27.7	27.5	26.4	26.1	26.8	27.4	27.2	26.2	27.4	27.1	26.7	26.4	27.2	26.3	27.8	26.3	26.8
Samule	D	RMI	RM2	RM3	RM4	RM5	RM6	RM7	RM8	RM9	RM10	RM11	RM12	RM13	RM14	RM15	RM16	RM17	RM18	RM19	RM20	RM21	RM22	RM23	RM24	RM25	RM26	RM27

 Table 2
 Analytical results of groundwater samples in the Markandeya command area (Pre-monsoon, 2008)

(to be continued on the next page)

											•					•		
	Ha (C	EC	TDS	Eh	Salinity	Total hardness	Calcium	Total		Majo	r cations				M	ajor anions		
))			6		hardness	alkalinity	Ca	Mg	Na	К	ц	G	HCO ₃	NO_3	SO_4	PO_4
	7.49	1050	571	-71.1	0.38	360	230	422.1	92	31.72	81.2	2.3	0.9	115	515.0	10	66.51	0.31
	7.78	747	403	-68.7	0.26	330	190	400.0	76	34.16	40.5	28.1	0.6	06	488.0	9	25.37	0.04
~	7.62	808	436	-77.7	0.32	260	130	350.0	52	31.72	91.2	14.4	1	06	427.0	10	21.43	0.42
	7.39	3520	1910) -50	1.79	1320	530	491.8	212	192.8	49.3	3.9	1	815	600.0	60	70.29	0.24
~	7.36	1530	818	-80.2	0.5	570	360	550.0	144	51.24	97.6	3	0.8	160	671.0	20	2.57	0.21
. +	7.63	1160	633	-74.4	0.44	530	380	500.0	152	36.6	84.5	1.8	7	190	610.0	30	67.37	0.31
\sim	7.18	1460	794	-72.7	0.54	650	360	470.0	144	70.76	94.3	3.2	1	190	573.4	20	96.17	0.24
4	7.16	2540	1370) -59.6	1.12	960	450	496.4	180	124.4	36.2	2.8	1	410	605.6	40	166.8	0.17
2	7.12	803	436	-71.4	0.33	290	140	270.0	56	36.6	70.8	11.3	0.6	130	329.4	2	55.37	0.14
×.	7.89	1500	815	-93.9	0.72	440	140	413.1	56	73.2	35.9	23.6	1	130	504.0	2	73.0	1.32
4	7.31	1760	958	-72.4	0.72	490	260	230.0	104	56.12	106.5	77.5	1	270	280.6	10	116.23	0.31
Ś	6.57	848	459	-65.5	0.33	320	200	320.0	80	29.28	68.6	٢	0.4	140	390.4	4	16.63	0.17
6	7.04	1290	701	-73.1	0.55	340	230	405.7	92	26.84	80.2	40.5	0.4	160	495.0	10	52.29	0.73
-	7.19	2160	1170) -40.9	0.94	1010	009	409.8	240	100	62.6	3.7	0.4	320	500.0	50	125.83	0.14
$\tilde{\mathbf{\omega}}$	7.28	1050	571	-73.1	0.35	470	250	420.0	100	53.68	58.2	0.6	0.7	95	512.4	10	33.09	0.21
9	7.53	918	496	-87	0.33	380	180	460.0	72	48.8	73.8	0.2	7	40	561.2	6	9.60	0.04
×.	6.80	1130	615	-82	0.41	400	270	433.6	108	31.72	81.7	2.3	1	115	529.0	4	104.0	0.02
4	7.42	1760	958	-67.8	0.79	740	330	380.0	132	100	26.9	14.8	1	230	463.6	50	50.91	0.03
6	7.30	7640	4150) -48.1	4.2	2050	950	460.0	380	268.4	111.2	79.8	0.9	1485	561.2	100	305.2	0.10
5	6.80	2640	1420) -49.6	1.27	870	430	260.0	172	107.4	37.3	49.6	0.6	530	317.2	40	178.11	0.03
×.	7.60	1770	962	-50.1	0.74	730	400	310.0	160	80.52	78.4	0.4	0.7	405	378.2	7	97.71	0.05
×.	7.94	3180	1720	LL- (1.62	006	450	422.7	180	109.8	65.7	0.6	7	480	515.7	7	165.0	0.21
.6	7.23	1770	959	-89.3	0.77	460	220	364.8	88	58.56	35.0	1.1	7	155	445.0	20	54.2	0.42
×.	7.81	587	319	-74.8	0.19	210	130	242.5	52	19.52	39.0	0.2	1	75	295.8	4	3.60	0.55
	8.15	193	104	-57.4	0.08	130	70	100.0	28	14.64	10.2	2.8	0.2	30	122.0	0.8	0.69	0.45
4	7.21	195	106	-59.1	0.09	150	75	102.5	30	18.3	9.6	б	0.2	30	125.0	0.8	0.69	0.45

the conductivity value crossing the permissible limit of 3000 μ S/cm (BIS, 1998). The salinity (Fig. 2) values varied from 0.05‰ to 4.2‰ for the groundwater samples. The total dissolved solid (TDS) values varied between 60.6 to 4150 mg/L (Fig. 2) and only one sample showed TDS value above the permissible limit of 2000 mg/L (i.e., sample No. RM47).

The total alkalinity (as $CaCO_3$) values were found to vary from 73.8 to 553.3 mg/L (Fig. 3) in the pre-monsoon samples, well within 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 sulphate in water. The total hardness (as CaCO₃) values range between 100 to 2050 mg/L (Fig. 3) in the pre-monsoon samples in the study area, 29.6 % of the samples had hardness values above the permissible limit of 600 mg/L (BIS, 1998). It was found that 66.67% of groundwater samples have total hardness more than total alkalinity, which indicates that the groundwater is characterized by non-carbonated hardness (Chow, 1964). The calcium hardness (as CaCO₃) values range between 75 to 950 mg/L (Fig. 3) for the groundwater samples, only 46.3% of the samples had calcium hardness values within the permissible limit of 200 mg/L (BIS, 1998).

6.2 Cation chemistry

Among the alkaline earths, the concentrations of calcium and magnesium (Fig. 4) were in the range of 18 to 380 mg/L and 13.42 to 268.4 mg/L, respectively. Of 54 samples, 11.1% and 18.5% respectively showed higher calcium and magnesium contents in comparison to their corresponding BIS permissible limits of 200 and 100 mg/L. Among the alkalies, the concentrations of sodium and potassium (Fig. 4) ranged from 4.4 to 121 mg/L and 0.2 to 79.8 mg/L, respectively. Of 54 samples, 44.5% have high potassium contents above the permissible limit of 10 mg/L (BIS, 1998), while the sodium concentration was within the permissible limit of 200 mg/L.

6.3 Anion chemistry

Bicarbonate is the predominant anion in the pre-monsoon season samples, ranging from 90 to 675 mg/L (Fig. 5) except for four samples, in which chloride concentrations were high. In the area of investigation, the chlorides value were the range of 30 to 1485 mg/L (Fig. 5), well within the permissible limit of 1000 mg/L (BIS, 1998) except for one sample (viz., sample No. RM47). The sulphate contents in pre-monsoon season in



Fig. 3. Spatial Distribution of temperature, total alkalinity, total hardness and calcium hardness in the Markandeya River Basin.



Fig. 4. Spatial Distribution of Cations (viz., Ca, Mg, Na, and K) in the Markandeya River Basin.

groundwater vary from 0.34 to 305.2 mg/L (Fig. 5), well within the permissible limit of 400 mg/L (BIS, 1998). The nitrate concentration was in the range of 0.9 to 100 mg/L (Fig. 5), with 7.40% samples (sample Nos. RM32, RM42, RM46 and RM47) having nitrate concentrations above the permissible limit of 45 mg/L (BIS, 1998). The fluoride concentrations varied from 0.2 to 2.0 mg/L (Fig. 5) in the Markandeva River Basin. The presence of low concentrations of fluoride in the majority of wells in the study area is of no minor concern as all the samples are found to have fluoride concentrations within the permissible limit of 1.5 mg/L (WHO, 1984) except 5 samples (9.26%; sample Nos. RM12, RM34, RM44, RM50 and RM51). In addition to this, phosphate concentrations were found to vary from 0.01 to 1.32 mg/L (Fig. 5), with 50% of the samples (27 samples) showing phosphate concentrations exceeding the permissible limit of 0.3 mg/L (BIS, 1998).

6.4 Hydrochemical facies

To know the hydro-geochemical regime of the study area, the analytical values obtained from the groundwater samples are plotted on Piper (1994) tri-linear diagram. These plots include two triangles, one for plotting cations and the other for plotting anions. The cation and anion fields are combined to show a single point in a diamond-shaped field, from which inference is drawn on the basis of hydro-geochemical facies concept. These tri-linear diagrams are useful for bringing out chemical relationships among groundwater samples in more definite terms rather than with 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 tri-linear diagram (Fig. 6) 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 tri-linear graphical representation of chemical data of representative samples from the study area for pre-monsoon reveal the analogies, dissimilarities and different types of waters in the study area, which are identified and listed in Table 3. This clearly explains the variations or domination of cation and anion concentrations during pre-monsoon season.



Fig. 5. Spatial distribution of anions (HCO₃, Cl, SO₄, NO₃, F and PO₄) in the Markandeya River Basin.

Hydrochemical facies of groundwater



Fig. 6. Classification diagram for anion and cation facies in the form of major-ion percentages. Water types are designed according to the domains in which they occur on the diagram segments.

The Ca-Mg type of water predominated during pre-monsoon of May 2008, accounting for 88.89% of the samples. Similarly, for anion concentrations, the HCO₃-type of water predominated in 83.33% samples. There is no significant change in the hydrochemical facies noticed during the study period (pre-monsoon), which indicates that most of the major ions are natural in origin. The reason might be that groundwater passing through igneous rocks dissolves only small quantities of mineral matter because of the relative insolubility of the

rock composition.

Further, the diamond-shaped field of Piper diagram can be further classified as (I) $Ca^{2+}-Mg^{2+}-Cl^{-}-SO_4^{2-}$; (II) Na⁺-K⁺-Cl⁻-SO₄²⁻; (III) Na⁺-K⁺-HCO₃⁻; and (IV) Ca²⁺-Mg²⁺-HCO₃⁻. Approximately, 70% of the samples belong to the Ca²⁺-Mg²⁺-HCO₃⁻ type, followed by Ca²⁺-Mg²⁺-Cl⁻-SO₄²⁻ in the study area (Fig. 7). Variations in hydrochemical facies in the samples collected from the Markandeya River basin are given in Table 4.

Based on Cl, SO₄, HCO₃ concentrations, the groundwater

Subdivision of the diamond	Characteristics of corresponding subdivisions of diamond shaned field	S	Sample
Subdivision of the diamond	Characteristics of corresponding subdivisions of diamond-snaped field	No.	Percentage
1	Alkaline earth (Ca+Mg) exceeding alkalies (Na+K)	48	88.89
2	Alkalies exceeding alkaline earths	06	11.11
3	Weak acids (CO ₃ +HCO ₃) exceeding strong acids (SO ₄ +Cl)	45	83.33
4	Strong acids exceeding weak acids	09	16.67
5	Magnesium bicarbonate type	39	72.23
6	Calcium-chloride type	09	16.66
7	Sodium-chloride type	00	-
8	Sodium-bicarbonate type	00	-
9	Mixed type (No cation-anion exceeding 50%)	06	11.11
A Calcium typ B No dominar C Magnesium D Sodium typ E Bicarbonate F Sulphate typ G Chloride typ (I)Ca ²⁺ -Mg ²⁺ -CI-S (II)Na ⁺ -K ⁺ -CI-S (II)Na ⁺ -K ⁺ -HCC (IV)Ca ²⁺ -Mg ²⁺ -H	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	CI	

Table 3 Characterization of groundwater of the Markandeya River basin based on Piper tri-linear diagram

Fig. 7. Piper-tri-linear diagram-pre-monsoon.

Hydrochemical facies	Sample No.	%
Ca-Na-Mg-HCO ₃ -Cl	20, 22, 26, 29, 33, 40, 45, 52	14.82
Mg-Ca-HCO ₃ -Cl	6, 7, 13, 38, 46, 51, 54	12.97
Mg-Ca-Na-HCO ₃ -Cl	1, 2, 3, 4, 10, 14, 28	12.97
Ca-Mg-Na-HCO ₃ -Cl	18, 24, 27, 35, 43	9.26
Ca-Mg-HCO ₃ -Cl	15, 19, 30, 53	7.40
Mg-Ca-Cl-HCO ₃	32, 36, 48, 50	7.40
Ca-Mg-Cl-HCO ₃	5, 11, 42, 49	7.40
Na-Ca-Mg-HCO ₃ -Cl	16, 17, 21	5.56
Ca-Na-HCO ₃ -Cl	25, 34, 41	5.56
Na-Mg-Ca-HCO ₃ -Cl	8, 31, 37	5.56
Ca-Mg-Cl-HCO ₃ -SO ₄	9,12	3.70
Mg-Na-Ca-HCO ₃ -Cl	23	1.85
Ca-Na-Mg-Cl-HCO ₃	39	1.85
Mg-Ca-Na-HCO ₃	44	1.85
Mg-Ca-Cl	47	1.85

sources can be 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 54 groundwater samples, about 96.3% and 94.4% samples respectively were categorized as normal chloride and normal sulfate, while only 44.4% of samples were of normal bicarbonate type.

6.5 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, both physically and chemically, thus reducing the productivity. The physical effects of these ions are 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 6) can be utilized to verify the suitability, as described as follows:

Salinity index or salinity hazard or total concentration of soluble/dissolved salt as computed in terms of measured Electrical Conductivity (EC) values;

Sodicity index or sodium hazard or relative proportion of sodium to other principal cations as expressed by Sodium Absorption Ratio (SAR);

Sodium hazard expressed as percent sodium of total cations (Na, %);

Bicarbonate hazard or bicarbonate (HCO₃) concentrations as related to the concentration of calcium plus magnesium such as Residual Sodium Carbonate (RSC) and Residual Sodium Bicarbonate (RSBC);

Boron hazard (concentrations of boron or other elements) that may be toxic;

Chlorinity index (measured chloride ion concentrations in water);

Magnesium Hazard/Ratio (MH), Kelley Index (KI), Permeability Index (PI), Potential Salinity (PS), Soluble Sodium Percentage (SSP) and index of base exchange, Exchangeable Sodium Ratio (ESR).

6.6 Salinity index

Based on the analyses, the ground water samples have been classified as various classes (Handa, 1969), as given in Table 5. It was found that all the samples collected during the pre-monsoon season (May, 2008) were categorized under low to high extensive salinity classes. The majority of samples (59.26%) belong to high salinity category. indicating that the water is of permissible quality.

EC (µS/cm)	Water salinity	Range (No. of samples)	%
0–250	Low (Excellent quality)	110-195 (3 samples)	5.55
251-750	Medium (Good quality)	345–747 (9 samples)	16.67
751–2250	High (Permissible quality)	759–2160 (32 samples)	59.26
2251-6000	Very high	2280-3590 (9 samples)	16.67
6001-10000	Extensively high	7640 (1 sample)	1.85
10001-20000	Brines weakly conc.	-	-
20001-50000	Brines moderately conc.	-	-
50001-100000	Brines highly conc.	_	-
>100000	Brines extremely highly conc.	_	_

Table 5 Classification of waters based on of EC (Handa, 1969)

Sample	$N_{c}(0/)$	CAD	DEDC	DEC	В	זת	VI	DC	MD	MIT	Inc base e	lex of exchange	CCD	ECD
ID	INA (%)	SAK	KSBC	KSC	$(\mu g/L)$	PI	KI	P5	MK	МН	CAI-1	CAI-2	_ 55P	ESK
RM1	23.11	1.28	3.71	4.85	2.49	54.60	0.35	3.59	0.647	51.61	-0.09	-0.04	33.28	0.346
RM2	18.60	1.24	0.41	-1.42	2.27	37.63	0.26	5.89	0.632	51.02	0.12	0.07	28.26	0.259
RM3	20.06	1.14	1.21	-0.22	2.94	39.34	0.25	5.66	0.686	53.08	0.50	0.40	20.73	0.253
RM4	25.52	1.28	2.98	2.47	1.82	51.51	0.35	4.96	0.985	61.90	0.46	0.30	26.54	0.347
RM5	16.91	1.21	1.41	0.98	3.14	36.03	0.23	10.24	0.514	45.85	0.46	0.35	25.98	0.229
RM6	8.54	0.19	0.58	0.46	1.35	64.09	0.10	0.85	0.746	55.14	0.72	0.41	10.70	0.096
RM7	18.94	0.90	3.40	3.38	2.35	49.52	0.25	2.34	0.938	60.74	0.11	0.04	23.25	0.247
RM8	40.16	2.74	4.36	5.83	3.56	63.79	0.71	6.74	0.644	51.49	-0.04	-0.02	43.48	0.711
RM9	10.83	0.89	-4.57	-11.44	2.21	21.01	0.12	22.54	0.574	48.63	0.82	0.95	11.42	0.122
RM10	28.45	1.41	2.86	3.41	3.32	57.04	0.41	4.33	0.697	53.47	0.39	0.28	29.97	0.406
RM11	8.67	0.65	-1.32	-4.67	2.88	22.08	0.10	17.25	0.529	46.57	0.83	0.77	10.14	0.096
RM12	14.29	1.09	-2.02	-4.77	1.60	27.11	0.17	17.10	0.475	43.94	0.73	0.62	14.89	0.168
RM13	13.17	0.55	2.61	3.00	1.93	47.08	0.16	2.87	0.697	53.47	0.50	0.19	16.55	0.158
RM14	22.37	1.20	3.11	3.21	3.04	49.17	0.31	4.94	0.754	55.40	0.36	0.22	27.40	0.308
RM15	11.65	0.78	3.28	3.21	1.63	31.59	0.14	9.53	0.579	48.82	0.58	0.31	18.02	0.142
RM16	34.54	1.96	3.80	5.45	1.48	63.13	0.56	4.19	0.572	48.53	0.04	0.02	37.87	0.556
RM17	39.65	1.95	3.18	5.15	2.69	77.14	0.71	2.70	0.444	42.24	-0.11	-0.05	43.84	0.706
RM18	21.30	1.47	1.41	0.91	3.32	40.34	0.29	8.98	0.536	46.91	0.40	0.29	27.57	0.294
RM19	7.19	0.44	2.69	2.98	2.20	28.90	0.08	8.28	0.528	46.52	0.71	0.42	13.56	0.083
RM20	33.45	2.08	5.61	8.24	1.54	58.59	0.51	4.32	0.555	47.76	-0.09	-0.03	33.96	0.507
RM21	38.03	2.18	5.80	8.78	1.63	68.11	0.62	3.03	0.572	48.53	-0.39	-0.11	38.63	0.620
RM22	31.94	1.62	3.18	5.07	1.71	65.25	0.50	3.21	0.447	42.44	-0.12	-0.04	36.53	0.503
RM23	32.23	1.78	3.20	3.58	1.23	58.75	0.50	4.71	0.784	56.39	0.15	0.08	35.23	0.498
RM24	23.00	0.76	0.99	1.64	3.02	66.17	0.31	2.13	0.407	40.13	0.50	0.37	26.20	0.312
RM25	30.19	2.22	3.54	6.27	1.45	57.46	0.53	8.06	0.361	37.34	0.04	0.03	43.46	0.534
RM26	31.28	1.48	2.94	4.75	1.81	66.05	0.48	2.81	0.436	41.80	0.06	0.03	34.35	0.476
RM27	23.12	1.14	1.81	3.19	1.59	51.14	0.31	4.38	0.378	38.37	0.46	0.30	25.31	0.310
RM28	24.75	1.22	3.80	5.25	1.74	56.18	0.34	3.15	0.610	50.14	0.23	0.10	27.10	0.339
RM29	32.73	1.86	3.85	6.86	1.76	59.98	0.49	3.94	0.345	36.24	-0.11	-0.03	33.27	0.490
RM30	19.39	0.97	4.21	6.72	1.77	54.87	0.27	2.80	0.449	42.56	0.02	0.01	27.30	0.267
RM31	41.58	2.46	4.40	6.45	1.48	72.10	0.76	2.76	0.610	50.14	-0.71	-0.24	45.44	0.762
RM32	7.48	0.59	-0.74	-10.06	3.80	18.47	0.08	23.72	0.909	59.99	0.90	1.69	7.82	0.081
RM33	27.00	1 78	3.81	6.91	1 79	48.33	0.37	4 54	0.356	36.97	0.04	0.02	27.49	0.372
RM34	27.00	1.60	2.41	6.05	1.03	17 91	0.35	6.06	0.241	28.42	0.31	0.14	25.00	0.347
DM25	23.07	1.60	2.71	2.64	2.20	41.90	0.33	6.26	0.401	14 75	0.22	0.14	23.33	0.215
DM24	23.00	0.51	2.21	2.04	2.29	41.07	0.52	12 20	0.491	44./J	0.22	0.10	24.33	0.092
KM30	1.55	1.01	0.94	-2.69	2.97	22.75	0.08	13.30	0.091	51.00	0.80	0.71	1.89	0.082
KIVI3/	22.57 14.22	1.81	2.60	5.19	0.8/	42 74	0.55	4.24	0.054	51.80	0.08	0.05	30.72	0.530
RM20	14.22 28.21	2.00	0.50	4.94	1.40	42.74	0.18	4.43 8.92	0.540	00.30 17 00	0.41	0.15	19./1	0.177
RM40	20.21	2.09 1.67	-0.39	-2.15	1.70	40.93 58 75	0.47	0.03 1 1 2	0.340	37.62	0.13	0.14	40.20 33.07	0.472
RM41	30.81	1.07	2.41	4.20	1.11	61.60	0.47	5.06	0.202	37.03	0.20	0.12	30.07	0.400
1/1/141	50.01	1.07	5.54	0.71	1.51	01.00	0.51	5.00	0.292	54.47	0.00	0.00	59.95	0.515

(to be continued on the next page)

Table	6	(Continued)
		· /

Sample	Sample Na (%)		RSBC	RSC	B	PI	KI	PS	MR	MH	Inde base ex	ex of change	SSP	ESR
ID					(µg/L)						CAI-1	CAI-2	-	
RM42	11.83	0.86	-3.78	-6.56	3.41	24.36	0.14	10.34	0.417	40.72	0.69	0.53	12.24	0.135
RM43	21.18	1.17	3.41	4.58	1.84	45.48	0.27	3.02	0.537	46.95	0.05	0.01	21.31	0.269
RM44	29.66	1.65	5.61	7.71	1.45	57.71	0.42	1.23	0.678	52.77	-1.85	-0.22	29.71	0.422
RM45	30.60	1.78	3.28	6.44	1.32	56.25	0.44	4.33	0.294	32.62	-0.11	-0.03	31.11	0.444
RM46	7.15	0.43	1.01	-2.16	3.00	24.57	0.08	7.02	0.758	55.53	0.76	0.52	9.46	0.079
RM47	10.09	1.07	-9.76	-25.72	4.92	17.15	0.12	45.07	0.706	53.80	0.84	2.04	14.35	0.118
RM48	7.99	0.55	-3.38	-8.76	3.30	20.50	0.09	16.81	0.624	50.72	0.81	1.26	14.23	0.093
RM49	18.91	1.26	-1.79	-4.28	1.88	32.74	0.23	12.44	0.503	45.34	0.70	0.96	18.97	0.233
RM50	13.68	0.95	-0.53	-3.94	2.90	27.62	0.16	15.26	0.610	50.14	0.79	0.89	13.75	0.159
RM51	14.15	0.71	2.90	2.94	1.74	39.35	0.17	4.94	0.665	52.31	0.65	0.32	14.41	0.165
RM52	28.74	1.17	2.25	3.87	1.26	66.11	0.40	2.15	0.375	38.23	0.20	0.08	28.83	0.404
RM53	14.23	0.39	0.60	0.73	0.72	61.01	0.17	0.85	0.523	46.29	0.39	0.16	16.53	0.171
RM54	12.27	0.35	0.55	0.41	0.33	54.24	0.14	0.85	0.610	50.14	0.40	0.16	14.45	0.143

Note: Na (%). Percent sodium; SAR. Sodium Absorption Ratio; RSBC. Residual Sodium Bicarbonate; RSC. Residual Sodium Carbonate; B. Boron; PI. Permeability Index; KI. Kelley Index; PS. Potential Salinity; MR. Magnesium Ratio; MH. Magnesium Hazard; CAI. Chloro Alkaline Indices; SSP. Soluble Sodium Percentage; ESR. Exchangeable Sodium Ratio.

Salinity index of the groundwater samples was computed using the measured electrical conductivity values. Water exhibiting low to moderate salinity (classes I and II) is not considered very harmful to soils or crops, whereas, that exhibiting high salinity (class III) is suitable for irrigating the medium and high salt tolerant crops. High salinity water (class IV) is suitable for irrigating high salt tolerant crops, whereas, water of salinity class V or above is generally unsuitable for irrigation. Majority of the samples (63%) in the study area were categorized as class II or III, considered as being suitable for irritation. However, about 9.26% of the water samples are found to exhibit very high to extremely high salinity (classes IV-VI), and may not be suitable for irrigation (Fig. 8).



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

6.7 Chlorinity index

Low salt tolerance crops are usually chloride sensitive. The chlorinity index of the groundwater sources was calculated using the measured chloride ion concentrations in water. Majority of the groundwater samples (~96.3%) are found to be suitable (classes I and II) for irrigation (Fig. 9).

6.8 Total hardness (TH)

In determining the suitability of groundwater for domestic and industrial purposes, hardness is an important criterion as it is involved in making the water become



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

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) (Todd, 1980; Hem, 1985; Ragunath 1987) was determined by the following equation (2)

TH=2.497 Ca^{2+} + 4.115 Mg^{2+} (2) where Ca^{2+} and Mg^{2+} concentrations are expressed in meq/L.

The classification of groundwater in the study area based on hardness (Sawyer and McCarty, 1967) is presented in Table 7. Accordingly, 42 samples (77.78%) collected during pre-monsoon season of the year 2008 fall under very hard class.

6.9 Sodium Absorption Ratio (SAR) or sodicity index

Another important factor for water quality is the sodium concentration to express reactions with the soil and known reduction in its permeability. Because high sodium depositing waters are generally not suitable for irrigating the soils as higher deposition of sodium may deteriorate the soil characteristics. Therefore, Sodium Absorption Ratio (SAR) is considered as a better measure of sodium (alkali) hazard in irrigation water as it is directly related to the adsorption of sodium on soil and is a valuable criterion for determining the suitability of the water for irrigation. Excessive sodium contents relative to the calcium and magnesium reduce the soil permeability and thus inhibit the supply of water needed for the crops. The SAR measures the relative proportion of sodium ions in a water sample to those of calcium and magnesium. 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 are evaluated by SAR (Kalra and Maynard, 1991) which is computed as

SAR =
$$\frac{\text{Na}^+}{\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}}$$
 (3)

where all cationic concentrations are expressed in epm or meq/L.

The classification of groundwater samples from the study area with respect to SAR (Todd, 1959) is presented in Table 8. During Pre-monsoon, the SAR values (Fig. 10) of all the samples are found to be less than 10, and are classified as being excellent for irrigation (i.e., S1 category).

Sodicity index was calculated using the sodium absorption ratio (SAR) and water up to class II, are generally considered suitable for irrigation. Based on the sodicity index, all the samples belongs to class-0 (Fig. 11), suitable for irrigation.

6.10 Salinity hazard

For the purpose of diagnosis and classification, the total concentrations of soluble salts (salinity hazard) in irrigation water can be expressed in terms of specific conductance. Classification of groundwater based on salinity hazard (viz., electrical conductivity) is presented in Table 9. It was found that only 1 sample during pre-monsoon, was considered unsuitable for irrigation purposes. A more detailed analysis of the suitability of water for irrigation can be made by plotting the

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

		-	
TH as CaCO ₃ (mg/L)	Water class	Range (No. of samples)	%
 <75	Soft	-	-
75–150	Moderately hard	100-130 (2 samples)	3.70
150–300	Hard	150-300 (10 samples)	18.52
 >300	Very hard	310-2050 (42 samples)	77.78

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

<10	
10–18 S2 Good –	
19–26S3Doubtful/Fairly poor-	
>26 S4 and S5 Unsuitable –	



Fig. 10. Spatial distribution of SAR, percent sodium, SSP, RSC, RSBC and boron (µg/L) in the Markandeya River Basin.



Fig. 11. Sodicity index for the groundwater samples from the study region.

	Table 9 Sa	linity hazard cl	asses
Salinity hazard class	EC in (µS/cm)	Remark on quality	Range (No. of samples)
C1	100–250	Excellent	110–195 (3 samples)
C2	250-750	Good	345–747 (9 samples)
C3	750–2250	Doubtful	759–2160 (32 samples)
C4 and C5	>2250	Unsuitable	2280–7640 (10 samples)

sodium-absorption ratio and electrical conductivity (Fig. 12) data on US Salinity Laboratory diagram (USSL, 1954). Accordingly, 32 samples fall in the category of C3S1 (59.26%), indicating high salinity/low sodium type. Of the remaining 22 samples, 10 samples belong to C4S1 and C5S1, indicating very high salinity/low sodium type, while 9 and 3 samples belong to C2S1 and C1S1, illustrating medium salinity/low sodium type and low salinity/low sodium type, respectively.

Groundwater samples that fall in the low salinity hazard class (C1) can be used for irrigation of most crops and in 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 medium salinity hazard class (C2) can be used if a moderate amount of leaching occurs. High salinity/low sodium water (C4 and C5) can be suitable for plants with good salt tolerance but can restrict 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 for irrigation of 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.



Fig. 12. US salinity hazard diagram of water samples (after Richards, 1954).

6.11 Percent sodium (Na, %)

Methods of Wilcox (1995) and Richards (1954) have been used to classify and understand the basic characteristics 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:

%Na =
$$\frac{(Na^+) \times 100}{\sqrt{(Ca^{2+} + Mg^{2+} + Na^+ + K^+)}}$$
 (4)

where the quantities of Ca^{2+} , $Mg^{2+}Na^{+}$ and K^{+} are expressed in milliequivalents per litre (epm or meq/L).

When the concentrations of sodium are 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 Ca²⁺ and Mg^{2+} in soil would reduce the permeability and eventually give rise to soil with poor internal drainage. Hence, air and water circulation is restricted under wet conditions and such soils will become usually hard when dry (Saleh et al., 1999).

The classification of groundwater samples with respect to percent sodium (Fig. 10) is given in Table 10 and it was found that 52 samples (96.3%) 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 of 54 samples, 39 (72.23%) belong to good to permissible, 4 samples (7.40%) to excellent to good, 6 samples (11.11%) to doubtful to unsuitable and 5 samples (9.26%) to unsuitable category.

Table 10 Sodium	percent water	class (Wilco	ox, 1955)
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Sodium (%)	Water class	Range (No. of samples)
<20	Excellent	7.15-19.39 (23 samples)
20-40	Good	20.06-39.65 (29 samples)
40-60	Permissible	40.16-41.58 (2 samples)
60-80	Doubtful	-
>80	Unsuitable	-
Table 11 Sadium navaant watau alaga (Fatan 1050)		

Table 11	Sourdin percent water class (Eaton, 1950)		
Sodium (%)	Water class	Range (No. of Samples)	
>60	Unsafe	_	
<60	Safe	7.15-41.58 (54 samples)	



Fig. 13. Percent sodium vs. EC plot (after Wilcox, 1995).

6.12 Soluble sodium percentage (SSP)

Water quality for agricultural purposes in the Markandeya River Basin shows variation between excellent to good categories based on Todd's classification of soluble sodium percentage (SSP) values, which is defined as:

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

where all concentrations are expressed in meq/L. SSP values range from 7.82 to 45.44 for pre-monsoon season of year 2005 (Fig. 32).

6.13 Residual sodium carbonate (RSC)

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 concentrations of bicarbonate, there is a tendency for calcium and magnesium to precipitate as the water in the soil becomes more concentrated. An excess quantity 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 is denoted by Residual Sodium Carbonate (RSC) is calculated as follows (Eaton, 1950; Ragunath, 1987):

$$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+})$$
(6)

where all ionic concentrations are expressed in epm.

According to the US Department of Agriculture, water with more than 2.50 epm of RSC is not suitable for irrigation purposes. Groundwater samples for the pre-monsoon season were classified on the basis of RSC (Fig. 10) and it was foud that 33 samples (61.11%) showed RSC values more than 2.50 epm and all positive RSC values indicate that dissolved Ca^{2+} and Mg^{2+} ions were less than CO_3^{2-} and HCO_3^{-} contents, while 19 samples (35.19%) have RSC values below 1.25 epm and only two samples (3.70%) belong to the doubtful category (Table 12).

6.14 Residual sodium bicarbonate (RSBC)

Gupta and Gupta (1987) defined RSBC (Residual Sodium Bicarbonate) as given in equation (4)

$$RSBC = (HCO_3^- - Ca^{2+})$$
(7)

The RSBC values varied from (-9.76) to 5.8 meq/L during Pre-monsoon (Fig. 10) and all the 54 samples collected during pre-monsoon were found to be satisfactory (<5 mg/L) according to the criteria set by Gupta and Gupta (1987).

6.15 Boron (B)

Boron concentrations (Fig. 10) in the groundwater of the study area during May 2008 range between 0.327 μ g/L and 4.918 μ g/L (i.e., 0.0003–0.0049 mg/L) with an average value of 2.12 μ g/L (i.e., 0.00212 mg/L). Iron is also toxic to crops at high concentrations. The proposed limits of boron concentrations in irrigation water and the number of groundwater samples from the study area representing the boron classes (McCarthy and Ellery, 1994) are presented in Table 13. All values are within the excellent category for both tolerant and semi-tolerant crops.

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

RSC (epm)	Remark on quality	Range (No. of samples)
<1.25	Good	(-25.72)-0.98 (19 samples)
1.25-2.50	Doubtful	1.64-2.47 (2 samples)
>2.50	Unsuitable	2.64-8.78 (33 samples)

Poron alass	Semi-sensitive crop		Sei	Semi-tolerant & tolerance crop	
Boron class	Range (mg/L)	Total No. of wells (May-08)	Range	Total No. of wells (May-08)	
Excellent	<0.33	0.0003-0.0049 (54 samples)	<0.67	0.0003-0.0049 (54 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	

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

6.16 Permeability index (PI)

The Permeability Index (PI) values also indicate the suitability of groundwater for irrigation, as the soil permeability is affected by long-term use of irrigation water, as influenced by Na⁺, Ca²⁺, Mg²⁺ and HCO₃⁻ contents of the soil. Doneen (1964) and Ragunath (1987) evolved a criterion for assessing the suitability of water for irrigation based on a Permeability Index (PI) and waters can be classified as Class I, Class II, and Class III. Permeability Index (PI) can be written as follows:

$$PI = \frac{(Na^{+} + \sqrt{HCO_{3}} \times 100)}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})}$$
(8)

where the concentrations are reported in meq/L.

The permeability index (Fig. 15) of the Markandeya River Basin ranged from 17.15% to 77.14% during premonsoon season of May 2008. It was found that all the samples categorized under classes I and II of Doneen's chart (Domenico and Schwartz, 1990; WHO, 1989) (Fig. 14).

6.17 Potential salinity (PS)

Doneen (1954, 1962) pointed out that the suitability of water for irrigation is not dependent on the concentrations of soluble salts. Doneen (1962) is of the opinion that the low soluble salts gets precipitated in the soil and accumulated with each successive irrigation, whereas the concentrations of highly soluble salts enhance the salinity of the soil. "Potential salinity is defined as the chloride concentration plus half of the sulfate concentration".

Potential Salinity =
$$Cl^- + \frac{1}{2}SO_4^{2-}(meq/L)$$
 (9)

The PS values are more pronounced in samples from the estuarine region than those from the fresh region. The high 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



Fig. 14. Donean chart of permeability index for the Markandeya command area.

varied from 0.85 to 77.14 during pre-monsoon season of May 2008 (Fig. 15).

6.18 Ion-exchange processes

Control on the dissolution of undesirable constituents in water is impossible during the subsurface runoff, but it is essential to know various changes in chemical composition undergone by groundwater during their trend/travel in the sub-surface (Johnson 1979; Sastri, 1994). The chloro-alkaline indices CAI-1 and CAI-2 are suggested by Schoeller (1965, 1967, 1977), which indicates ion exchange between the groundwater and its host environment during residence or travel. If there are Na⁺ and K⁺ ions in water which are exchanged with Mg²⁺ and Ca²⁺ ions, the indices are positive, indicating direct



Fig. 15. Spatial distribution of Permeability Index (PI), Potential Salinity (PS), Chloro Alkaline Indices-1 and Chloro Alkaline Indices-2 in the Markandeya River Basin.

base Exchange reaction or chloro-alkaline equilibrium. 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 reactions viz., ion exchange between the groundwater and its host environment during residence or travel in the sub-surface. The chloro-alkaline indices used in the evaluation of Base Exchange are calculated using the following formulae

Chloro alkaline index 1=[Cl-(Na+K)]/Cl Chloro alkaline index 2=

$$[Cl-(Na+K)]/(SO_4+HCO_3+CO_3+NO_3)$$
(10)

It was found from the chloro-alkaline indices (Fig. 15) calculated for pre-monsoon samples that 20.37% of the samples from the Markandeya River Basin showed negative ratios indicating an indirect base exchange reaction. In contrast, 79.63% of the samples showed positive chloro-alkaline indices, illustrating that they had direct base exchange reaction. During this process, the host rocks are considered to be the primary sources of dissolved solids in the water. Schoeller indices of the groundwater samples revealed that cation–anion exchange (chloro-alkaline equilibrium) to exist all over the area (Table 6), except at 11 sites where the values

were negative. Groundwater with a base-exchange reaction in which the alkaline earths have been exchanged for Na⁺ ions (HCO₃⁻>Ca²⁺+Mg²⁺) may be referred to as base-exchange-softened water, and that in which the Na⁺ ions have been exchanged for the alkaline earths (Ca²⁺+ Mg²⁺ > HCO₃⁻) may be referred to as base-exchangehardened water (Handa, 1979). In the study area, 98.15% of the samples had higher HCO₃⁻ concentrations over alkaline earths, indicating the base exchange-softened water nature.

6.19 Kelley's index (KI)

Sodium measured against Ca^{2+} and Mg^{2+} is used to calculate Kelley's ratio (Kelley, 1940, 1951; Paliwal, 1967). However, now-a-day SAR is a better measure for sodium and this particular ratio 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 Kelley's index of more than one indicates an excess level of sodium in waters. Hence, waters with a Kelley's index less than one are suitable for irrigation, while those with a ratio more than one are unsuitable. Kelley's index (Fig. 16) in the present study varied from 0.079 to 0.762 and all the water samples are considered suitable for irrigation.



Fig. 16. Spatial distribution of Kelley Index (KI), Magnesium Hazard (MH), Magnesium Ratio (MR) and Exchangeable Sodium Ratio (ESR) in the Markandeya River Basin.

6.20 Magnesium hazard (MH)

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. High level of Mg²⁺ is usually due to the presence of exchangeable Na⁺ in irrigated soils. In equilibrium, more Mg²⁺ 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 index of more than 50% would adversely affect the crop yield as the soils become more alkaline.

Magnesiumratio =
$$\frac{(Mg^{2+}) \times 100}{(Ca^{2+} + Mg^{2+})}$$
 (11)

In the Markandeya River Basin, the magnesium hazard (MH) values were reported to be in the range of 28.42% to 68.3% (Fig. 16). Of the 54 samples, 55.55% of the samples showed magnesium index value below 50%, suggesting their suitability, while only 44.45% fall in the unsuitable category with MH more than 50%, indicating their adverse effect on crop yield.

6.21 Magnesium ratio (MR)

Based on the Mg/Ca ratio (Fig. 16), waters can be classified as suitable or unsuitable for irrigation. Accordingly all the samples belong to the safe category (Table 14).

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

Class	Remark	Range (No. of samples)
<1.5	Safe	0.241-1.307 (all samples)
1.5-3.0	Moderate	-
>3.0	Unsafe	-

6.22 Exchangeable sodium ratio (ESR)

Exchangeable sodium ratio (ESR) can be defined as:

ESR =
$$\frac{Na^{+}}{Ca^{2+} + Mg^{2+}}$$
 (12)

Water quality for agricultural purposes in the Markandeya River Basin based on ESR values varied from 0.079 to 0.762 (Fig. 16).

6.23 Mechanisms controlling groundwater chemistry

Lastly, to know the groundwater chemistry and relationship of the chemical components of water from their respective aguifers such as chemistry of the rock types, chemistry of precipitated water and rate of evaporation, Gibbs (1970) has suggested a diagram in which ratios of dominant anions and cations are plotted against the values of total dissolved solids (TDS). Gibbs diagrams, representing the ratio-I for cations [(Na+K)/(Na+K+Ca)] and ratio-II for anions [Cl/ (Cl+HCO₃)] as a function of TDS are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance and evaporation dominance. The chemical data of groundwater samples are plotted in Gibbs diagram (Figs. 17 and 18) and it was found that majority of the samples suggested the chemical weathering of rock-forming minerals influencing the groundwater quality by means of dissolution of rocks through which water is circulating. Only few samples represent evaporation dominance and most of the samples falling in the evaporation dominance were collected from dug wells. Evaporation makes salinity increase bv increasing Na⁺ and Cl⁻ with relation to the increase of TDS and anthropogenic activities (agricultural fertilizers and irrigation-return flows) also influence the evaporation by increasing Na⁺ and Cl⁻, and thus TDS.



Fig. 17. Gibbs variation diagram {TDS vs. [(Na+K)/(Na+K+Ca)]}.



Fig. 18. Gibbs variation diagram {TDS vs. [Cl/(Cl + HCO₃)]}.

7 Conclusions

The groundwater sources in the Markandeya River Basin were evaluated for their chemical composition and suitability for drinking, irrigation and industrial uses. It is evident from the higher values of physico-chemical parameters like hardness, alkalinity, bicarbonates, potassium that most of the groundwater samples analyzed in the present investigation might had natural and anthropogenic influences, through infiltration and percolation during monsoon. The groundwater in the region is classified as moderately to very hard category based on hardness, while RSC values specify that water samples belong to good to unsuitable classes. Permeability index recommends that the water samples from the Markandeya River Basin are suitable for irrigation. Majority of the samples had positive chloro-alkaline indices, illustrating that they had direct Base Exchange reaction and only few samples with negative Index of Base Exchange indicated chloro-alkaline disequilibrium. The suitability of groundwater for irrigation was evaluated based on the irrigation quality parameters, revealing that the majrority of the samples fall in excellent to suitable categories for irrigation. The samples which are not suitable based on the irrigation quality parameters may be suitable in well-drained soils.

Based on the attempt made to study the hydrochemis-

try of groundwater, it was found that HCO₃ type predominated the anions and Ca-Mg type dominated the cations during the pre-monsoon period of May 2008. The water type that predominates in the study area is of Ca²⁺-Mg²⁺-HCO₃⁻ type, followed by Ca²⁺-Mg²⁺-Cl⁻- SO_4^{2-} . It was also noticed that alkaline earth elements exceeded alkalies concentrations and weak acids exceeded the strong acid elements. Based on Cl, SO₄, HCO₃ concentrations, the groundwater sources were categorized as normal chloride (96.3%) and normal sulfate (94.4%) and normal bicarbonate (44.4%) types. From U.S. Salinity hazard diagram, it is evident that about 59.26% of the samples are grouped within C3S1 classes, indicating high salinity and low sodium type and need better drainage to overcome salinity problem. From Wilcox plot, it is observed that most of the samples from the study area fall in the good to permissible classes for irrigation purpose. Further, Gibbs plot indicated that the chemistry of 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. Finally, it can be concluded that the overall quality of groundwater controlled by lithology apart from other local environmental conditions. 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 groundwater resource.

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