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ORIGINAL ARTICLE

Hydrogeochemistry of the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

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Abstract Systematic hydrogeochemical survey has been carried out for understanding the sources of dissolved ions in the groundwaters of the area occupied by Sarada river basin, Visakhapatnam district, Andhra Pradesh, India. Khondalites, charnockites and granite gneisses and calc-granulites of Precambrians and alluvial deposits of Quaternaries underlie the study area. Groundwaters are both fresh and brackish; the latter waters being a dominant. Most groundwaters are characterized by Na^+:HCO_3^- facies due to chemical weathering of the rocks. Enrichment of Na^+, K^+, Cl^-, SO_4^{2-}, NO_3^- and F^- in some groundwater samples is caused by seawater intrusion, locally accompanied by ion-exchange, and anthropogenic activities, resulting in an increase of brackish in the groundwaters. Based on the results of this hydrogeochemical study, suitable management measures are recommended to solve the water quality problems.

Keywords Hydrogeochemistry · Water quality management · Sarada river basin · Visakhapatnam district · Andhra Pradesh · India

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Introduction

The Sarada river basin is one of the groundwater potential areas in Visakhapatnam district, Andhra Pradesh, India (Fig. 1). The area has been known as a centre for agriculture. Demand for groundwater use for drinking and irrigation has increased from year to year due to shortage of the surface water supply. Excessive irrigation has detrimentally affected the groundwater quality.

The study of geochemistry of groundwaters is an important aspect for drinking, irrigation and industrial purposes. Each groundwater system in any area has a unique chemistry due to chemical alteration of meteoric water, recharging the aquifer system (Back 1966; Drever 1988; Hem 1991). The changes in the chemical quality of meteoric water depend on many factors, such as soil–water interaction, duration of solid-water interaction, dissolution of mineral species, and seawater and anthropogenic impacts (Stallard and Edmond 1983; Faure 1988; Karanth 1991; Subba Rao 2001, 2002, 2006; Subba Rao et al. 2002, 2005, 2006).

Earlier studies in the present study area were focused on geomorphological evaluation (Prudhviraj and Vaidyanadhan 1981), hydrogeological conditions for the development of groundwater resources (CGWB 2001), drainage characteristics for the watershed management (John Devadas et al. 2006a), the role of rain gauge network in assessment of water resources (Ammineedu et al. 2002) and hydrogeomorphological conditions for the location of groundwater potential zones (John Devadas et al. 2006b), whereas no study has so far been carried out on hydrogeochemistry. The aim of the present paper is, therefore, to understand the sources of dissolved ions

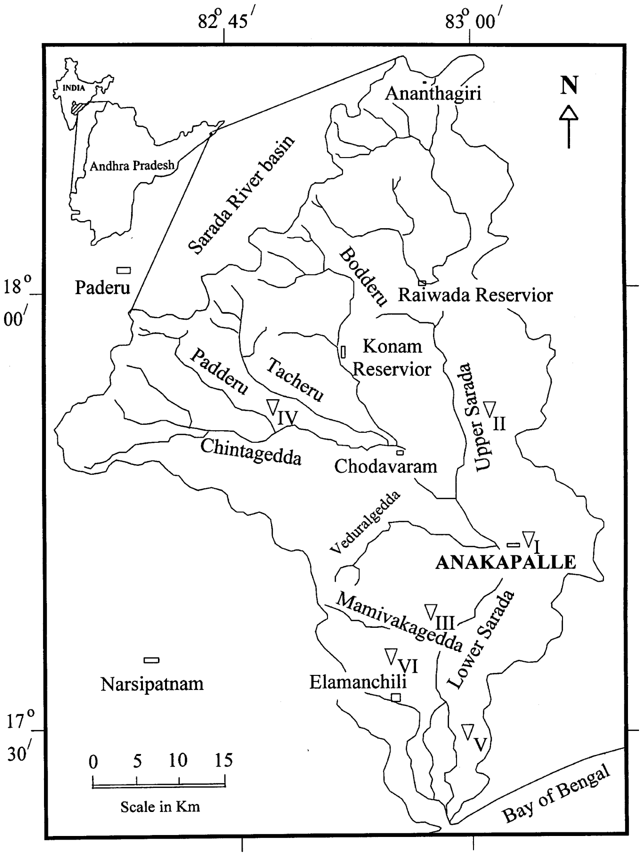

Fig. 1 Location of the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India. Symbol ∇_{III} denotes the location of the lithologs

in the groundwaters of the area occupied by Sarada river basin.

Study area

The Sarada river basin lies between latitude 17°25′N–18°17′N and longitude 82°13′E–83°5′E (Fig. 1), covering an areal extent of about 2,590 km^2 . The area enjoys a semi-arid to dry sub-humid climate. The lowest temperature recorded is 18°C in January, while the maximum temperature recorded is 37°C in May. The average annual rainfall is 1,068 mm. Most rainfall (75%) receives from southwest monsoon.

The area is characterized by undulating topography. The river Sarada originates from the Ananthagiri hill ranges at a height of 1,500 m, flows towards south and finally joins the Bay of Bengal (Fig. 1). The maximum length of the river basin is 55 km from east to west and is 90 km from north to south. The drainage is mainly sub-dendritic to dendritic and is ephemeral nature.

The soil cover includes sandy soils, loamy soils, clayey loamy soils and clayey soils. The area is underlain by khondalites, charnockites, granite gneisses and calc-granulites of Precambrians, and alluvial deposits of Quaternaries (Fig. 2). Dykes and veins (quartzite and pegmatite) occur in the rocks. The rocks exhibit NE-SW strike with deviations of SSE-NNW, N–S and NNE–SSW, and show SE dip. The alluvial deposits are confined to the river course. Younger alluvium is, generally, inundated by flood during monsoon. The alluvium consists of alternate beds of clay and sand with intercalated $CaCO_3$ concretion, locally known as kankar.

Lithologs collected from the well owners of the study area (Fig. 1) show that the depth of the zone of topsoil varies from 1.5 to 6 m from the ground surface (Fig. 3). The topsoil zone is followed by the clay zone (2–7 and 12–15 m), sand zone (8–11 and 16–25 m), weathered zone (2–43 m) and fractured zone (5–41 m). Hard rock is observed at different depth levels of 23–41 m, after encountering the weathered zone/fractured zone.

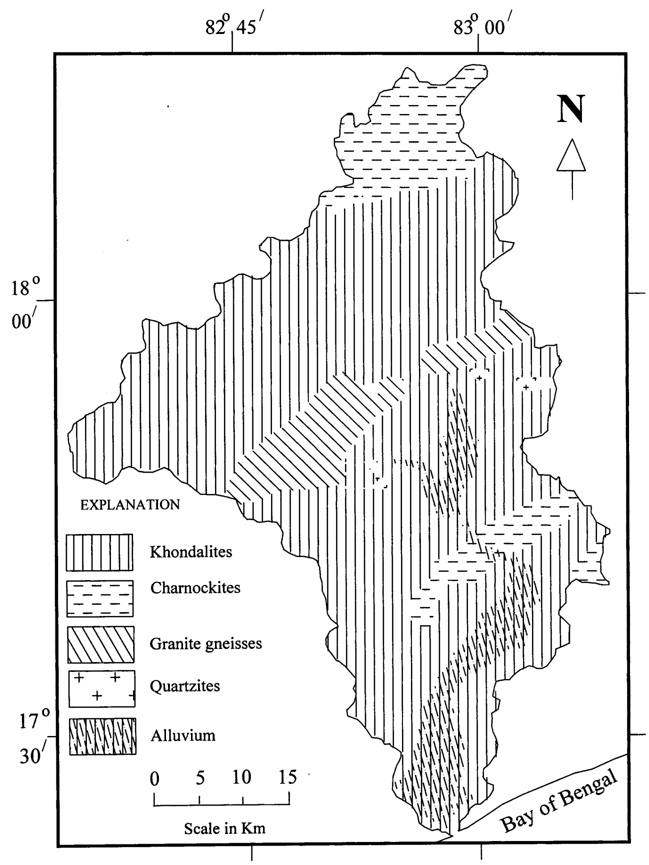

Fig. 2 Geology of the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

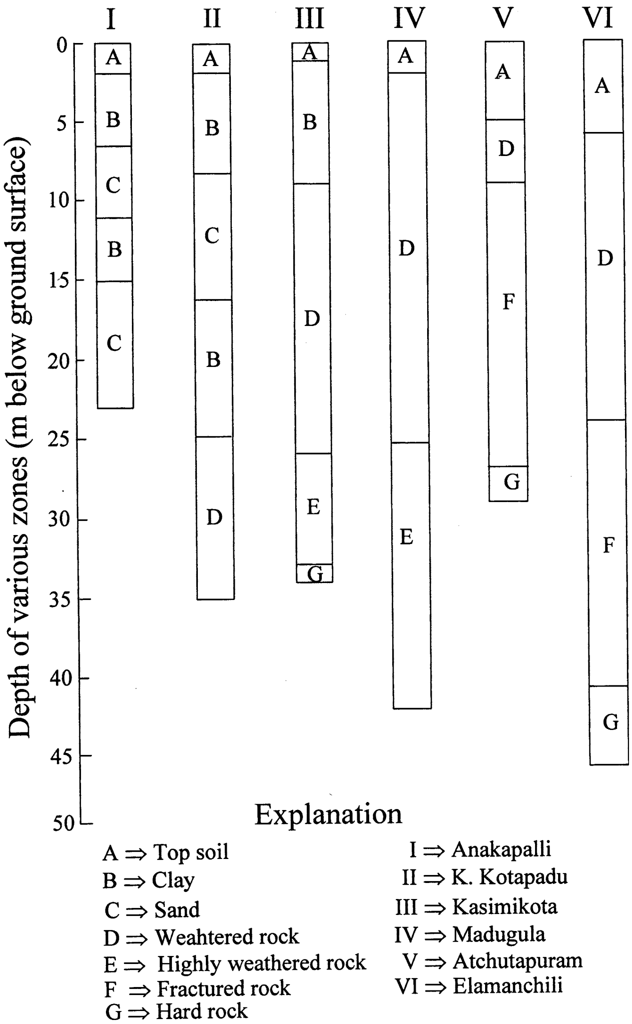

Fig. 3 Lithologs of the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Groundwater exists under water table conditions in the shallow weathered zone and under semi-confined to confined conditions in the fractured zone at depth. Whereas, the water occurs under a multi-aquifer system due to occurrence of alternating layers of clay and sand in the alluvial sediments (Fig. 3). The depth to water table level is in the range of 3.9 below ground level (bgl) at site 36 to 18.3 m bgl at site 11 during pre-monsoon and is between 2.1 m bgl at site 36 and 9.8 m bgl at site 11 during post-monsoon (Table 1 and Fig. 4). Annual water level fluctuation is 1.8–8.5 m. The water table map of the study area prepared on the basis of pre-monsoon and post-monsoon data of 2004 (Fig. 5) shows that the direction of groundwater flow is from northeast and northwest to southeast, following the topography and drainage.

The important crops grown in the study area are paddy, jowar, bajra, maize, sugarcane, blackgram, horsegram and groundnut.

Methodology

Thirty-six water samples from the shallow aquifer zone were collected during pre-monsoon and post-monsoon of 2004 from the study area (Fig. 4). The water levels in the wells were recorded, using a water level recorder. The water samples were collected in a clean half litre polyethylene bottles. The sampling bottles were soaked in 1:1 HCl for 24 h were rinsed, with deionized waters, and were washed again prior to each sampling with the filtrates.

The groundwater samples were analysed for various chemical parameters, following the standard water quality methods (Table 2) of APHS (1992). The parameters include pH, total dissolved solids (TDS), total hardness (TH) as $CaCO_3$, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-) and fluoride (F^-).

The pH and electrical conductivity (EC) of the groundwater samples were measured in the field, using pH and EC digital instruments. The value of EC was used to compute the value of TDS, as suggested by Hem (1991). The rest of the chemical parameters were determined in the laboratory immediately, after sampling. For each groundwater sample, the concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and anions (CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- and F^-) were used to compute the ionic-balance-error, which resulted to be within the standard limit of ±5%.

Results and discussion

Groundwater quality

Groundwaters are slightly alkaline with a pH interval of 7–8.7 in pre- and post-monsoon periods (Table 3).

Table 1 Summary of the seasonal depth to water table levels (m bgl) in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Season	Depth to water table level (m bgl)				
	Minimum	Maximum	Mean	Standard deviation	Coefficient of variation
Pre-monsoon	3.9	18.3	12.32	5.53	44.89
Post-monsoon	2.1	9.8	6.74	5.22	77.45

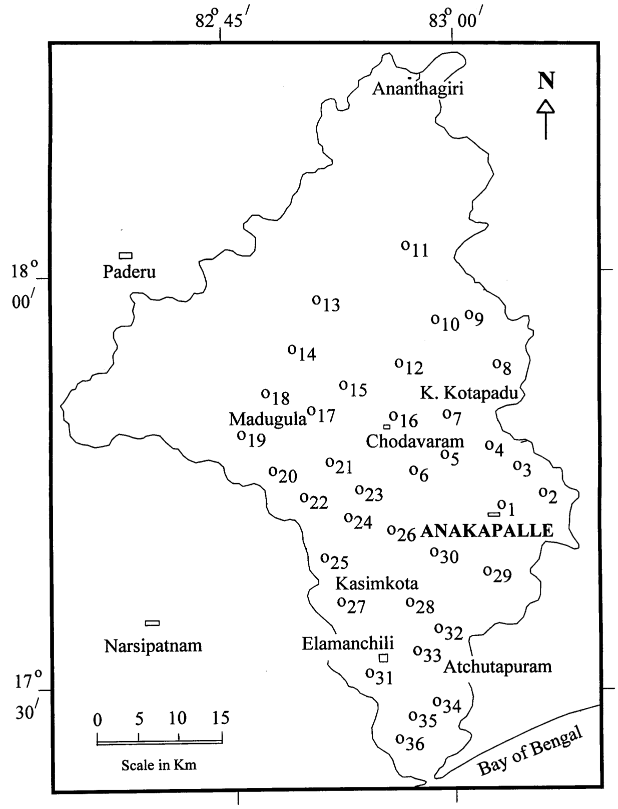

Fig. 4 Location of the groundwater samples in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

TDS ranges from 350 to 2,600 mg/l in both the seasons. As per the TDS classification (Fetter 1990), about 36% of the total pre-monsoon groundwater samples and 28% of the total post-monsoon groundwater samples come under a fresh water category (TDS < 1,000 mg/l; Table 4), while 64% of the total pre-monsoon groundwater samples and 72% of the total post-monsoon groundwater samples are brackish (TDS > 1,000 mg/l). This suggests that the pre-monsoon fresh groundwater samples become brackish during post-monsoon. Iso-TDS lines of pre-monsoon and post-monsoon groundwater samples (Fig. 6) show that higher TDS values are observed at topographic-lows and lower TDS values at topographic-highs.

Total hardness ranges from 40 to 920 mg/l (Table 3). Groundwaters, therefore, are soft (TH < 75 mg/l) to very hard (TH > 300 mg/l; Sawyer and McCarty 1967). Calcium and Mg^{2+} have concentrations ranging from 6 to 163 and 10 to 131 mg/l, respectively. Na^{+} is the most abundant ion among the cations, with concentration varying from 37 to 943 mg/l. High K^{+} values up to 124 mg/l are observed. Among the anions, $HCO_3^{-} + CO_3^{2-}$ is the dominant ion, followed by Cl^{-}, SO_4^{2-}, NO_3^{-} and F^{-}, and their concentrations (mg/l) vary from 60 to 1,012, 54 to 1,383, 8 to 270, 1 to 180 and 0.1 to 2.8, respectively. All the dissolved ions, except Ca^{2+}, show higher concentrations in monsoon than in pre-monsoon. Referring to the concentrations in milliequivalents per litre (meq/l), the order of abundance of ions is $Na^{+} > Mg^{2+} > Ca^{2+} > K^{+}$: $HCO_3^{-} + CO_3^{2-} > Cl^{-} > SO_4^{2-} > NO_3^{-} > F^{-}$.

Drinking purpose

Total dissolved solids, TH, pH and the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-} and F^{-} in most

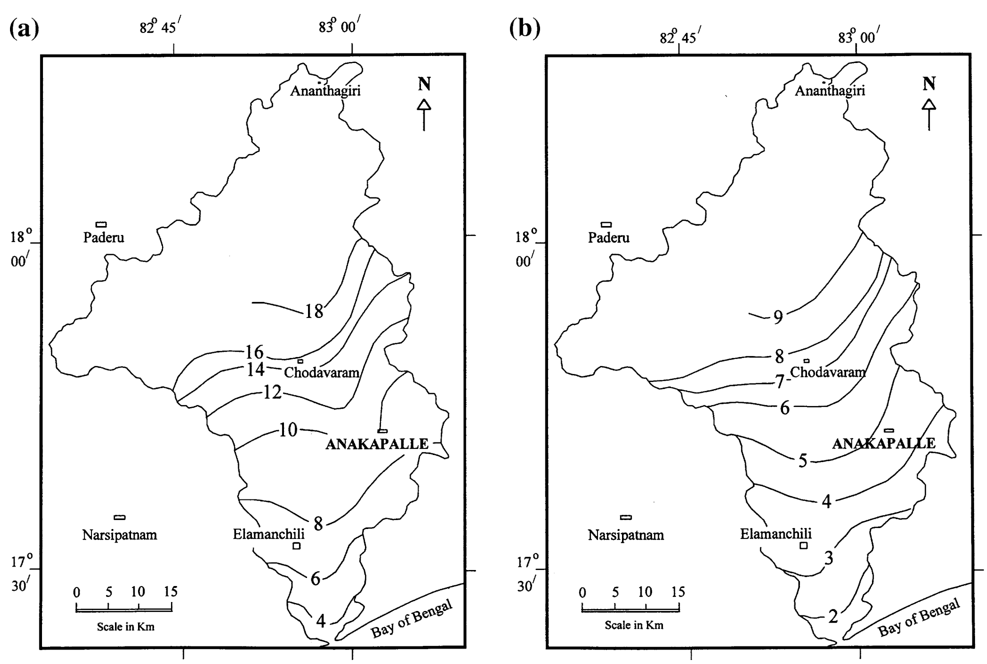

Fig. 5 Depth to groundwater levels (m bgl) of **a** pre-monsoon and **b** post-monsoon in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Table 2 Analytical methodology adopted for analysis of groundwater samples collected from the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Analysis	Method/instrument	Standard solution
pH	pH instrument	Buffer solutions 4, 7 and 9
EC	Electrical conductivity instrument	KCl
TDS	EC × 0.55 to 0.65	–
TH	Titrimetric	EDTA solution, and ammonium hydroxide and erichrome black-T indicators
Ca^{2+}	Titrimetric	EDTA solution and ammonium purporate indicator
Mg^{2+}	Calculation (TH-Ca^{2+})	–
Na^{+}	Flame photometer	–
K^{+}	Flame photometer	–
CO_3^{2-}	Titrimetric	H_2SO_4 solution and phenolphthalein indicator
HCO_3^{-}	Titrimetric	H_2SO_4 solution and methyl orange indicator
Cl^{-}	Titrimetric	$AgNO_3$ solution and potassium chromate indicator
SO_4^{2-}	Spectrophotometer	–
NO_3^{-}	Spectrophotometer	–
F^{-}	Spectrophotometer	–

groundwater samples are higher than the highest desirable limits of 500, 300, 8.5, 75, 30, 200, 250, 150, 45 and 1.2 mg/l, respectively, prescribed for drinking purpose by WHO (1984) and BIS (1991; Table 5). The number of unsuitable groundwater samples increases in post-monsoon. Values of the chemical parameters higher than the specified thresholds cause a development of mucous membrane, gastrointestinal irritation, encrustation effects on water supply structures, hypertension effects, laxative effects and respiratory problems, Methemoglobinemia and Fluorosis (BIS 1991). In about 33% of the total pre-monsoon groundwater samples (8–19) and in about 17% of the total post-monsoon groundwater samples (8–11, 16 and 19; Table 3), the concentration of F^{-} is less than the minimum safe limit of 0.6 mg/l for drinking. This causes a dental caries (BIS 1991).

Irrigation purpose

To assess the degree of water quality for irrigation purpose, the sodium or alkali-hazard expressed in terms of sodium adsorption ratio (SAR) is widely used. If waters used for irrigation are high in Na^{+} and low in Ca^{2+}, the ion-exchange complex may become saturated with Na^{+}, which destroys the soil structure, because of dispersion of the clay particles (Todd 1980). Such soils reduce the plant growth.

The SAR is computed, using the formula (Hem 1991):

$$\mathrm{SAR} = \mathrm{Na}^{+}/\{[\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}]/2\}^{0.5}, \tag{1}$$

where the ion concentrations are expressed in meq/l. The computed SAR values range from 1.33 to 31.63 and the TDS values vary from 350 (EC: 540 µmho/cm) to 2,600 (EC: 4,000 µmho/cm) mg/l for pre- and post-monsoon groundwater samples of the study area (Tables 3, 6). The SAR versus EC plot (Fig. 7) shows that most groundwater samples come under the moderate water quality (72%) to bad water quality (17%) types with increasing percent of the water samples (44–56%) towards post-monsoon (Table 7). Very few groundwater samples (6%) fall in a good water quality category in pre-monsoon. The moderate to bad quality waters have Na^{+} concentrations higher than the good quality waters. Therefore, inferior (moderate to bad) quality waters are not suitable for irrigation as good quality waters.

Hydrogeochemical relations

In $HCO_3^{-} + CO_3^{2-}$ versus $Cl^{-} + SO_4^{2-}$ diagram (Fig. 8a), most groundwater samples fall below the equiline (1:1). This suggests that most waters are characterized by $Cl^{-} + SO_4^{2-} > HCO_3^{-} + CO_3^{2-}$. To assess the relation between Na^{+}+K^{+} and Cl^{-}, they are plotted, as illustrated in Fig. 8b. Most water samples fall above the theoretical line (1:1), suggesting that the waters are dominated by alkalis (Na^{+} and K^{+}). This excess alkalis, with respect to those associated with Cl^{-}, is ascribable to silicate weathering (Stallard and Edmond 1983). Significantly, the excess alkalis are accompanied by an excess of HCO_3^{-} over Cl^{-} in the groundwaters (Fig. 8c), indicating that most groundwaters are characterized by Na^{+}:HCO_3^{-} facies.

Graphical presentation of groundwater quality

In the Langelier–Ludwig plot of Fig. 9, the groundwater samples situated in the $Ca^{2+} + Mg^{2+} + HCO_3^{-}$

Table 3 Chemical composition (concentration in mg/l) of pre-monsoon (**a**) and post-monsoon (**b**) groundwaters of the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Site number, as shown in Fig. 4	pH	TDS	TH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}	F^{-}
1a	7.7	1,800	320	64	39	449	48	–	585	458	100	76	1.7
1b	7.9	1,900	480	64	78	515	22	–	793	456	224	88	1.9
2a	8.4	1,800	80	8	15	590	12	60	524	480	135	1	1.6
2b	8.3	2,000	100	8	19	713	15	38	539	683	200	13	1.8
3a	8.3	1,850	440	88	53	438	28	40	561	506	606	111	0.7
3b	7.6	1,880	940	160	131	528	5	–	195	711	160	120	1.2
4a	7.6	1,620	740	104	117	209	8	–	573	330	117	62	0.7
4b	8.4	1,520	80	16	10	548	10	76	556	345	212	95	2.5
5a	8.2	1,430	460	32	92	308	14	–	597	274	102	12	1.0
5b	8.4	1,200	540	8	127	242	23	57	705	205	206	20	1.2
6a	7.9	1,210	520	96	68	190	2	–	561	271	40	100	0.8
6b	7.1	1,200	620	136	68	207	50	–	500	203	80	180	1.5
7a	8.8	1,050	80	8	15	341	2	93	453	209	26	14	1.5
7b	8.3	1,100	300	24	58	358	2	57	486	213	127	19	1.8
8a	8.4	1,150	320	24	63	259	1	40	390	306	57	15	0.3
8b	7.4	1,150	560	120	63	130	51	–	378	247	90	26	0.5
9a	8.3	790	420	16	31	112	3	40	366	130	74	35	0.3
9b	7.7	900	260	48	34	161	84	–	390	182	81	33	0.5
10a	8.2	590	300	16	63	75	6	–	371	87	34	33	0.5
10b	7.7	800	400	96	39	110	30	–	414	80	28	25	0.1
11a	7.8	350	180	32	24	41	3	–	170	54	21	2	0.5
11b	8.4	600	60	8	10	243	1	57	545	40	30	22	2.0
12a	8.4	600	220	16	44	92	7	40	230	70	38	90	0.8
12b	7.7	750	260	48	34	161	84	–	314	167	81	103	0.5
13a	8.3	400	240	24	44	37	6	20	180	40	27	28	0.5
13b	8.3	650	240	32	39	132	2	–	456	20	8	33	0.9
14a	7.6	500	280	24	53	39	3	–	200	80	26	17	0.5
14b	7.7	720	400	96	39	110	30	20	390	90	28	22	1.1
15a	8.2	600	220	64	15	103	10	–	250	38	35	57	0.3
15b	7.7	900	500	88	68	142	6	–	397	74	106	69	1.5
16a	8.7	520	180	6	39	197	2	40	561	145	10	86	2.1
16b	7.9	1,000	300	56	39	237	2	–	428	149	86	90	0.5
17a	8.2	700	220	64	15	125	10	–	250	123	35	57	0.3
17b	7.7	980	500	88	68	142	6	–	397	74	106	99	0.8
18a	8.1	610	300	56	39	59	4	–	220	80	33	53	0.5
18b	7.7	850	260	48	34	161	84	–	314	167	81	103	0.7
19a	8.2	630	220	64	15	103	10	–	250	38	35	57	0.3
19b	7.8	850	160	16	29	150	19	–	505	88	80	66	0.3
20a	8.3	790	420	16	31	112	3	40	366	120	74	35	1.3
20b	7.9	1,000	540	48	102	218	3	–	350	216	95	56	1.6
21a	8.0	950	280	40	34	197	22	–	414	163	62	113	1.2
21b	8.3	1,050	300	24	58	268	2	57	399	195	127	99	1.5
22a	8.3	1,030	200	24	34	260	11	–	471	226	70	48	1.4
22b	7.1	1,100	620	136	68	107	50	–	360	209	80	180	1.6
23a	7.4	1,130	510	64	58	213	2	–	353	181	56	24	1.4
23b	8.2	1,200	400	24	83	378	52	–	650	307	214	75	1.8
24a	8.3	1,180	240	16	49	317	2	–	570	195	80	53	1.5
24b	7.5	1,250	760	144	97	172	1	–	720	237	140	95	1.9
25a	7.9	1,210	370	76	55	213	2	–	622	278	40	90	1.3
25b	8.2	1,450	400	24	83	378	52	40	250	465	14	110	2.4
26a	8.4	1,300	320	24	63	305	1	–	451	119	57	50	1.3
26b	8.0	1,300	300	40	49	380	124	–	460	345	192	62	1.5
27a	8.2	1,420	410	32	79	307	14	–	597	236	156	22	1.4
27b	7.6	1,650	940	160	131	228	5	–	60	651	202	32	1.6
28a	8.3	1,530	520	128	49	257	58	40	390	153	101	21	1.4
28b	8.3	1,800	100	8	19	666	15	38	342	698	135	33	0.8
29a	8.3	1,600	280	16	58	430	1	100	610	361	130	5	1.8
29b	8.3	1,700	280	8	63	550	3	84	380	595	157	19	2.1
30a	8.0	1,480	420	48	97	131	57	–	230	280	86	61	1.4
30b	7.6	1,500	740	120	106	374	5	–	510	651	60	120	1.8

Table 3 continued

Site number, as shown in Fig. 4	pH	TDS	TH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}	F^{-}
31a	8.5	1,620	460	24	97	329	6	60	427	410	144	74	2.0
31b	8.4	2,100	800	136	112	421	6	84	928	707	212	95	2.4
32a	8.6	1,570	300	16	63	412	8	100	300	503	116	14	1.4
32b	8.3	1,950	100	8	19	713	15	38	342	698	135	33	2.8
33a	8.5	1,590	460	24	97	352	6	60	488	410	144	14	2.2
33b	6.9	2,050	920	163	112	329	87	–	330	818	206	22	1.8
34a	8.3	1,710	440	88	53	461	28	40	110	707	118	33	2.7
34b	7.2	2,300	800	136	112	421	6	–	428	816	212	75	2.8
35a	8.3	1,780	540	108	65	369	28	40	110	661	118	11	1.7
35b	8.3	2,350	760	136	102	477	61	–	219	835	276	26	2.1
36a	8.3	2,000	640	64	56	395	1	40	260	817	110	66	1.4
36b	7.7	2,600	340	40	58	943	5	–	219	1,383	196	89	1.8

quadrant can be interpreted as slightly evolved meteoric-derived groundwaters. This Ca^{2+} + HCO_3^- to Ca^{2+} + Mg^{2+} + HCO_3^- compositions is typically originated through dissolution of calcite and dolomite, respectively. Indeed, White et al. (2005) have recently demonstrated the ubiquitous nature of accessory calcite in crystalline rocks. Although the surface areas of calcite and dolomite are comparatively low, their dissolution rates are so high, with respect to those of silicate minerals, to control the composition of poorly evolved groundwaters of meteoric origin.

In addition to these waters, three limiting processes are also recognizable in Fig. 9, corresponding to the evolution towards Na^+ + HCO_3^-, Na^+ + Cl^- and Ca^{2+} + SO_4^{2-} compositions. The first evolutionary trend reflects dissolution of Na–Al–silicates governed by conversion of carbonic acid (H_2CO_3) to HCO_3^- ion. Owing to the low dissolution rates of these minerals, this evolution is a relatively slow process. The second trend may be related to addition of seawater in the coastal area. The third trend is ascribable to either dissolution of Ca-sulphates (e.g. gypsum and/or anhydrite) or oxidative dissolution of sulphide (mainly pyrite) accompanied by neutralization through interaction with carbonates and silicates. Because of the high concentrations of Na^+, K^+, SO_4^{2-}, Cl^-, NO_3^- and F^- in some groundwaters (Table 3), which cannot be explained through the water-rock interaction alone, other processes are to be invoked. For example, potash feldspar is not easily weathered and K^+ experiences sorption on clay minerals or other ion exchangers (Hem 1991). Besides, oxidative dissolution of sulphides (Davis and Dewiest 1966) is not expected to play a significant role in the study area.

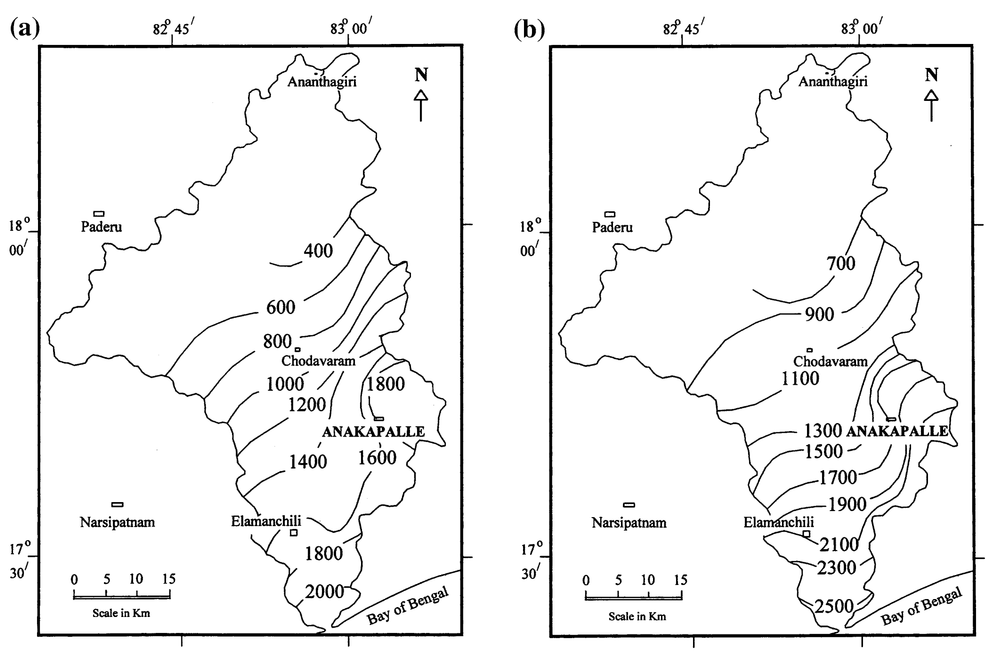

Fig. 6 Iso-TDS lines (mg/l) of **a** pre-monsoon and **b** post-monsoon in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Table 4 Classification of groundwaters in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

TDS (mg/l)	Classification of water type	Distribution of groundwater samples			
		Pre-monsoon	%	Post-monsoon	%
<1,000	Fresh water	9–21	36.11	9–18	27.77
>1,000	Brackish water	1–8 and 22–36	63.89	1–8 and 19–36	72.23

Percent is computed for each water type on the basis of the total groundwater samples

Agricultural practice is intensive and long-term without any control of using chemical fertilizers for higher crop yields in the study area. Fertilizers used contain potash, sulphate, nitrate and phosphate. Besides, gypsum is widely used to reduce the concentration of Na^+ in the soils, as higher concentration of Na^+ in the soils tends to become impermeable layers, which retard the crop growth. These explain higher values of K^+, SO_4^{2-}, NO_3^- and F^- ions in the groundwaters (Table 3), as is also observed in the other regions (Pawar and Shaikh 1995; Zhang et al. 1995; Singh et al. 2000; Subba Rao 2006).

Some groundwaters samples (34–36; Table 3) close to the sea (Fig. 4) show high concentrations of Cl^- and Na^+, suggesting that they may be polluted by seawater intrusion into the inland aquifers. Cl^-/Na^+ ratios higher than the seawater value suggest that seawater intrusion is accompanied by Na^+–Ca^{2+} exchange, which is a common phenomenon in coastal areas (Appelo and Willemsen 1987; Appelo et al. 1990, 1993; Appelo 1994). These waters show higher TDS values compared to other waters (Fig. 6). Indeed, Cl^-/Na^+ ratios lower than the seawater value suggest the presence of a Na^+–HCO_3^- component ascribable to dissolution of Na^+–Al–silicates governed by conversion of H_2CO_3 to HCO_3^-, as discussed already. A general reaction for the weathering of silicate rocks with H_2CO_3 is show below:

$$\text{(cations) silicates} + H_2CO_3 \rightarrow H_4SiO_4 + HCO_3^- + \text{cations} + \text{clay products} \quad (2)$$

Fluoride concentration in natural waters is usually limited by saturation (equilibrium) with respect to fluorite (CaF_2). Owing to this constraint, the waters, containing high concentrations of dissolved Ca^{2+}, are characterized by low F^- contents. In contrast, Na^+–HCO_3^- waters have low Ca^{2+} concentrations (owing to high HCO_3^- contents and saturation with respect to $CaCO_3$) and can acquire high F^- concentrations. This is a typical characteristic of Na^+–HCO_3^- waters, which should not be used for drinking purpose. In the present study, high concentration of F^- (>1.20 mg/l) in the groundwaters (Table 5) is caused by leaching of fluoride-bearing minerals of the soils and country rocks, apart from the influences of chemical fertilizers. Similar observations are reported in the other regions (Hem 1991; Wodeyar and Srinivasan 1996; Subba Rao et al. 1998; Subba Rao 2003; Subba Rao and John Devadas 2003). However, very low concentration of F^- (<0.6 mg/l) in some groundwater samples, as stated above, is caused by soil erosion due to shifting cultivation, which is common and severe in the region (Subba Rao et al. 1999). Thus, the highly erodable region has greater loss of topsoil, which contains

Table 5 Distribution of groundwater samples exceeding the drinking water standards in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Chemical parameter	WHO (1984)	BIS (1991)	Distribution of groundwater samples			
			Pre-monsoon	%	Post-monsoon	%
pH	7–8.5	7–8.5	7, 16 and 32	8.33	No samples	–
TDS	500	500	1–10, 12 and 15–36	91.66	1–36	100
TH	100	300	1, 4–6, 8–11, 18, 23, 25–28 and 30–36	55.55	1, 3, 5, 6, 8, 10, 14, 15, 17, 20, 22-25, 27 and 30–36	58.33
Ca^{2+}	75	75	3, 4, 6, 25, 28, 34 and 35	19.44	3, 6, 8, 10, 14, 15, 17, 22, 24, 27, 30, 31 and 33–35	41.66
Mg^{2+}	30	30	1, 3–6, 8–10, 12–14, 16, 18 and 20–36	83.33	1, 3, 5–10, 12–18, 20–27, 29–31 and 33–36	83.33
Na^+	200	200	1–5, 7, 8 and 22–36	61.11	1–8, 11, 16, 20, 21, 23, 25, 27–29 and 31–36	66.67
Cl^-	200	250	1–6, 8, 23-26 and 29–36	52.77	1–6, 8, 14, 16, 22, 25 and 27–36	58.33
SO_4^{2-}	200	150	1–3, 5, 27 and 36	16.66	1, 4, 5, 23, 26, 27, 29, 31 and 33–35	30.55
NO_3^-	45	45	1, 3, 4, 6, 15, 17-19, 21, 23–26, 28, 31 and 33–35	50.00	1, 3, 6, 8–10, 12, 14–18, 22–27, 30, 31, 34 and 35	61.11
F^-	1.5	1.2	1, 2 and 20–36	52.77	1, 2, 4, 6, 7, 15 and 20–36	63.88

Percent is computed for each chemical parameter on the basis of the total groundwater samples

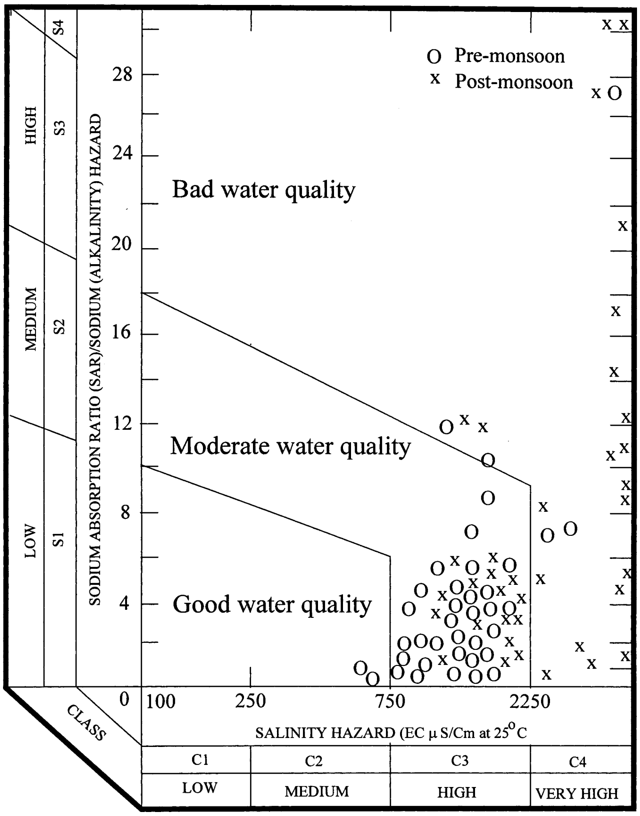

Fig. 7 Groundwater quality for irrigation purpose (after Richard 1954) in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

valuable salts. As a result, the chemical constituents, including F^- from the soils, are not leached properly into the groundwaters.

Tipper et al. (2006) suggest that the chemical changes, in small rivers sampling uniform lithologies, result from a different response of carbonate and silicate mineral dissolution to climatic forcing. Carbonate weathering is more sensitive to monsoonal run-off, because of its faster dissolution kinetics. Silicate weathering increases relative to carbonate weathering during dry season, and may be more predominant in groundwater with longer water-rock interaction times. Despite this kinetic effect, silicate weathering fluxes are dominated by monsoon flux. Hence, the groundwaters observed after monsoon show the higher concentrations of various ions in the present study area (Table 3).

The groundwaters of the study area are not suitable for drinking and irrigation (Tables 5, 6, 7), owing to their chemical characteristics, which are governed by chemical weathering of the rocks, seawater intrusion, locally accompanied by ion-exchange, and anthropogenic activities. Therefore, the study emphasizes the need for groundwater quality management measures, before using the waters for a particular purpose.

Groundwater quality management

While suggesting the water quality management techniques to prevent, control and overcome the environmental constraints, it is essential to adopt appropriate groundwater quality management measures that should not be a burden. On the other hand, the selection of the measures should be on the basis of the characteristic features of an area for effective management practice.

The simplest and the most efficient method is recharging through rainwater harvesting, because of undulating topography of the study area, apart from the other techniques like water softening, ion exchange, defluoridation, etc. If run-off waters are stored, it would help not only in improving the groundwater conditions, but also in reducing the concentrations of various ions, including Na^+, K^+, Cl^-, SO_4^{2-}, NO_3^- and F^-, and thus TDS (Table 3), well below the safe limits, and could be used for drinking and irrigation. Fluoridation of water is also essential to control the effects of dental caries on human health, where the concentration of F^- is below the recommended limit of 0.6 mg/l.

However, people's participation is a key factor for the success of rainwater harvesting and fluoridation of water techniques. In this context, environmental awareness and education are necessary to the people for proper understanding about the water availability, and its use and quality at different levels of management. This method could also help reduce the health risks, increase the crop growth and thereby improve the agriculture income of the people.

Conclusions

Groundwater samples studied from the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Table 6 Summary of the computed seasonal SAR values for the groundwaters of the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Season	SAR values				
	Minimum	Maximum	Mean	Standard deviation	Coefficient of variation
Pre-monsoon	1.33	28.55	6.51	5.02	71.11
Post-monsoon	1.82	31.63	8.07	8.38	103.84

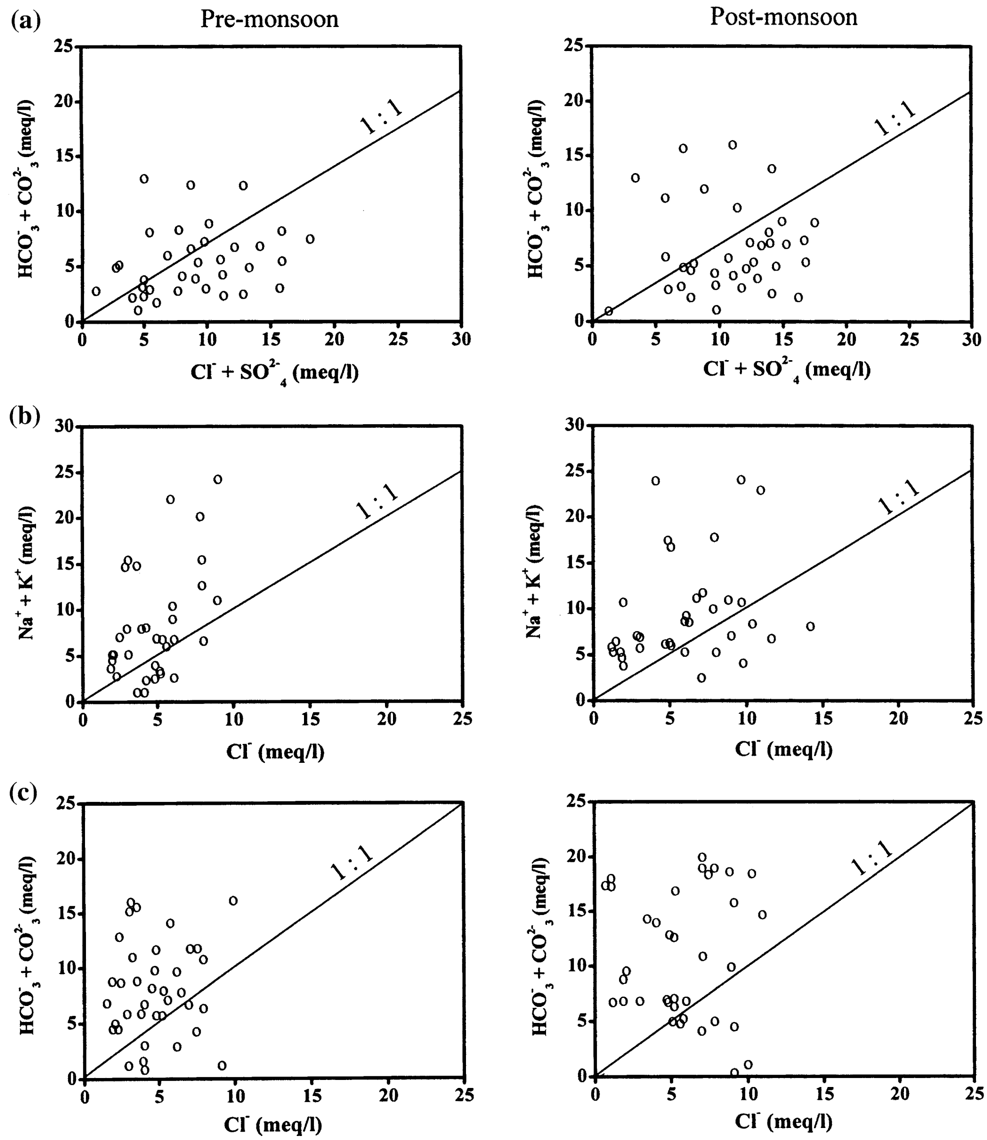

Fig. 8 Relation of **a** $HCO_3^- + CO_3^{2-}$ with $Cl^- + SO_4^{2-}$, **b** $Na^+ + K^+$ with Cl^- and (**c**) $HCO_3^- + CO_3^{2-}$ with Cl^- in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

have both fresh and brackish nature; the latter waters being a dominant. Most waters belong to $Na^+ + HCO_3^-$ facies due to chemical weathering of the country rocks. The occurrence of higher concentrations of K^+, SO_4^{2-}, NO_3^- and F^- in the groundwaters is attributable due to extensive use of fertilizers. High concentrations of Cl^- and Na^+ suggest a seawater intrusion, whereas Cl^-/Na^+ ratios higher than the seawater value indicate that this process is accompanied by Na^+-Ca^{2+} exchange. These waters cause high TDS. A graphical presentation of the quality of groundwaters identifies the various types of chemical composition of groundwaters from meteoric origin to other ones, resulting from a mixing of chemically distinct waters in the different mixing

Table 7 Classification of groundwater quality for irrigation purpose in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

Degree of water quality	Distribution of groundwater samples			
	Pre-monsoon	%	Post-monsoon	%
Good	11 and 12	5.56	No samples	–
Moderate	2, 4–6, 8–10, 12–20 and 33	77.78	5, 6, 8, 10, 12–22 and 24	44.44
Bad	1, 3, 7 and 34–36	16.66	1–4, 7, 9, 11, 23 and 25–36	55.56

Percent is computed for each water type on the basis of the total groundwater samples

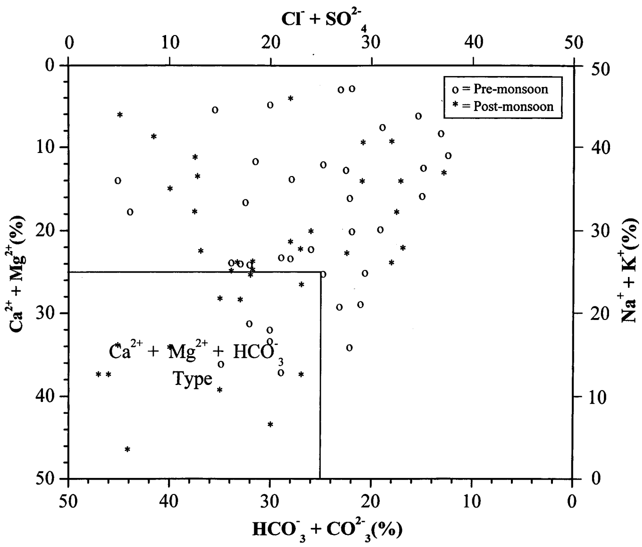

Fig. 9 Graphical diagram showing the classification of groundwater chemistry (after Langelier and Ludwig 1942) in the Sarada river basin, Visakhapatnam district, Andhra Pradesh, India

ratios, supporting the above views. Owing to the occurrence of chemical weathering of rocks and soils, seawater intrusion, locally accompanied by ion exchange, and anthropogenic activities, most groundwaters of the Sarada river basin are unsuitable for drinking and irrigation. Based on the results of this hydrogeochemical study, appropriate management measures to improve the groundwater quality and people's participation are mandatory.

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