

Groundwater depletion and quality deterioration due to environmental impacts in Maheshwaram watershed of R.R. district, AP (India)

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Received: 20 November 2009 / Accepted: 4 July 2010 / Published online: 28 July 2010
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Abstract Maheshwaram watershed is situated in Ranga Reddy district of Andhra Pradesh at a distance of about 30 km south of Hyderabad, capital of Andhra Pradesh. The watershed has an area of 60 km² and has hard rock aquifers with semi-arid climate. The study area has been expanding at a fast pace and now has the distinction of being one of the fastest growing urban centers facing the problem of groundwater depletion and quality deterioration due to the absence of perennial source of surface water and also due to over exploitation. Human activities involving industrial and agricultural development and the inadequate management of land and water resources have, directly or indirectly resulted in the degradation of environment viz. water and soil. In the present study chemical analysis of groundwater samples of the study area, collected during pre- and post-monsoon seasons of 2007–2008 has been carried out. The analyzed data are utilized to characterize the hydro chemical process dominant in the area. Various classification methods such as Piper, Back and Hanshaw, Wilcox, USA. Salinity Laboratory are employed to critically study the geochemical characteristics of groundwater of the study area. Finally, principal component analysis (PCA) is also employed to the chemical variables of groundwater to characterize the hydro chemical process that is dominant in the area. In the analysis four principal components emerged as significant contributors to the groundwater quality. The total contribution of these four

components is about 85–87%. The contribution of the first component is about 49–50% and has significant positive loadings of Ca²⁺, Mg²⁺, Na⁺, and Cl⁻ ions. The second, third, and fourth principal components have significant positive loadings of F⁻, NO₃⁻, SO₄²⁺, and HCO₃⁻ ions.

Keywords Principal component analysis · Piper trilinear diagram · Residual sodium carbonate

Introduction

A small watershed at the Maheshwaram village, located 30 kms south of Hyderabad city agglomeration, is about 60 km² in area. There are no prominent rivers in the area. The watershed is facing the problem of groundwater depletion and quality deterioration, due to the absence of perennial source of surface water, inadequate rainfall, and over exploitation. Water quality in the area has deteriorated due to increased human population, rapid urbanization, un-scientific disposal of wastes, and improper water management. Anthropogenic activities like poultry farms, various industries including chemical and pharmaceuticals, and sewage release of reactive pollutants by chemical industries are the main cause for the degradation of water and soil quality in the watershed. It is with this background that the present investigations are carried out: to know the impact of urbanization and industrialization and to suggest adequate strategies and mitigative measures to be implemented to avoid further deterioration of the environment for sustainable development.

In order to assess the groundwater quality and its suitability for drinking and irrigation purposes, chemical analysis of groundwater samples of the area, collected during the pre- and post-monsoon seasons of 2007–2008 has been carried out (Tables 1 and 2). Principal component

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Table 1 Analytical results of major ions (units in mg/l) in groundwater samples collected during pre-monsoon season

Sample location	X	Y	Pre-monsoon													
			pH	Ec	TDS	TH	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃	NO ₃	Fluoride	
SMP 1 MRO OFF	225,008	1,897,404	6.8	1260	670	356.55	53.6	53.8	85.3	22	143.5	54	219.6	245	0.85	
SMP 2 QTZ PUL UNT	224,764	1,897,684	6.75	797	424	397.1	89.3	42	35.9	1.6	48.9	12.1	292.8	39.2	1	
SMP 3 TMLR COMM	229,679	1,895,423	6.8	1870	1,000	768.71	217.8	54.2	128.1	3.8	243.8	120.4	298.9	383.2	0.84	
SMP 4 AWARE	223,875	1,897,603	7.43	1,100	590	284.66	42.5	43	91.9	1.8	58.4	80.5	320.3	89.1	1.8	
SMP 5 RNHG CO	225,067	1,896,034	6.2	6,450	3,500	3,134.63	705	223.1	598.9	5.7	2,646	2,214	256.2	–	0.8	
SMP 6 IR SUGR	226,856	1,896,038	6.3	2040	1090	908.63	213.1	90.7	119.1	10	446.8	184.9	277.6	–	1	
SMP 7 BLND COL	226,876	1,896,416	6.65	1,390	740	511.26	97.7	64.5	59.7	1.9	288.7	115.4	336.2	338.5	0.85	
SMP 8 PRNK OIL	225,879	1,894,611	6.81	862	459	417.21	1011	39.8	45	1.8	98.8	127.8	262.3	36.8	0.85	
SMP 9 DATR ASHRM	226,034	1,894,455	6.12	2810	1500	1566.86	427.8	120.5	170.3	4.9	326.4	1514.9	280.6	–	1.2	
SMP 10 SANTHORM	229,089	1,895,310	7.05	790	420	279.96	67.6	26.7	84.4	1.9	23	10	503.3	15.5	1.5	
SMP 11 JJ PHRM COMM	229,679	1,895,423	6.71	744	396	319.81	91.3	22.1	50.9	2.1	68.9	18	289.8	14.9	1.4	
SMP 12 RECH SITE	229,690	1,896,256	6.91	704	375	259.93	69.8	20.4	70.4	0.6	63.8	26.9	509.4	17.7	1.4	
SMP 13 MSHRM COMI	230,272	1,896,248	6.54	1,920	1,030	881.73	213.1	83.6	99.1	3.4	271	47.6	241	86.2	0.9	
SMP 14 UPGD THND	230,895	1,698,384	6.75	1,230	660	314.5	67.8	31.4	141.9	2.7	50	22.8	302	64.5	1.8	
SMP 15 KBTHND	231,228	1,899,693	7	891	475	368.13	88.3	35.3	96.2	1.5	71.9	52.2	308.1	86.5	1.6	
SMP 16 GANGARAM	231,019	1,899,779	6.84	704	375	183.96	38.8	20.9	98.4	2	29.7	60.6	396.4	96.7	1.5	
SMP 17 SIRGPR	231,065	1,899,880	6.53	1,150	610	457.71	134.6	29.1	76	3.1	165.7	70.8	170.8	129.1	1.72	
SMP 18 KC THND	230,983	1,899,921	6.75	1,230	660	458.92	106.3	46.3	96.2	2	126.5	55.3	353.8	91.2	1	
SMP 19 MOHBT NGR	230,922	1,899,790	6.59	2,060	1,110	940.4	203.6	104.4	73.1	4.4	305.2	166.4	295.3	238.5	1.2	
SMP 20 IFFI-9 SITE	231,416	1,900,023	6.75	1,420	760	370.57	55.7	55.4	176.1	1.6	154.1	112.2	390.4	6.9	1.6	

Table 2 Analytical results of major ions (units in mg/l) in groundwater samples collected during post-monsoon season

Sample location	X		Y		Postmonsoon													
	Latitude	Longitude	pH	Be	TDS	TH	Ca	Mg	Na	K	Cl	SO	HCO	NO	Fluoride			
SMP 1 MRO OFF	225,008	1,897,404	7.08	1,978	1,265	671.6	101.2	101.5	161	4.1	274.7	65.8	9094	194.8	0.49			
SMP 2 Qiz PUL UNT	224,764	1,897,684	6.99	832	532	378.98	64.7	52.6	44.6	2	61.3	15	581.6	43.6	0.44			
SMP 3 TMLR COMM	229,679	1,895,423	6.77	255MS	1,504	1155.1	327.6	81.5	192.6	5.7	366.6	132.8	733	415.1	0.59			
SMP 4 AWARE	223,875	1,897,603	7.19	997	638	306.77	45.9	46.4	93.3	1.9	63.1	78.8	534.2	107.5	1.74			
SMP 5 RNGH CO	225,067	1,896,034	7.15	6,250	4,000	3146.9	805.7	254.9	684.4	6.5	3024	215	711	-	1.15			
SMP 6 IR SUGR	226,856	1,896,038	7.04	2,180	1,395	1,160.1	272.7	116	152.4	12.7	571.5	218.8	473	-	1.19			
SMP 7 BIND COL	226,876	1,896,416	6.91	1,300	832	573.56	109.8	72.5	67.1	2.1	324.5	80.6	500.6	229.4	0.88			
SMP 8 PRNK OIL	225,879	1,894,611	7.5	970'	620.8	563.43	136.7	53.8	60.8	2.4	133.6	40.8	536.2	33.2	0.92			
SMP 9 DATR ASHRM	226,034	1,894,455	6.36	3.66	2342	2445.9	667.9	188.1	265.8	7.6	509.6	1796	604.7	33.8	1.6			
SMP 10 SANTHORM	229,089	1,895,310	7.14	834	534	355.2	85.9	33.9	107.3	2.4	29.2	12.7	663	38.1	1.67			
SMP 11 JJ PHRM COMM	229,679	1,895,423	6.96	786	503	406.59	116.3	28	64.6	2.6	87.5	26.5	464	43	0.53			
SMP 12 RECH SITE	229,690	1,896,256	7.2	845	541	372.09	100.6	29.4	101.5	0.86	92	26.8	536.8	8	0.64			
SMP 13 MSHRM COMI	230,272	1,896,248	7.04	1322	846	720.07	175	68.6	81.3	2.8	222.5	68.3	383.2	259.7	0.54			
SMP 14 UPGD THND	230,895	1,898,384	7.01	1390	890	404.12	91.4	42.3	191.3	3.6	67.4	38.8	699.1	107.4	1.27			
SMP 15 KBTHND	231,228	1,899,693	7.1	812	491	378.28	91.2	36.4	99.4	1.5	74.3	41.4	441.3	64.6	0.82			
SMP 16 GANGARAM	231,019	1,899,779	7.12	1201	768	375.51	79.4	42.8	201.5	4	60.8	33.9	456.8	161.1	1.57			
SMP 17 SIRGPR	231,065	1,899,880	7.14	1124	719	538.54	158.6	34.2	69.5	3.6	195.3	55.9	438.5	76.9	1.88			
SMP 18 KC THND	230,983	1,899,921	7.15	813	520	359.73	83.7	36.4	75.7	1.5	99.6	41.9	379.6	81.7	0.6			
SMP 19 MOHBT NCR	230,922	1,899,790	7.1	896	573	484.72	105.1	53.8	37.7	2.2	157.5	54.5	223.5	190.2	1.16			
SMP 20 IFP1-9 SITE	231,416	1,900,023	6.87	1490	953	460.94	69.8	69.4	222.2	2	193.2	87.4	829.8	12.6	1.41			

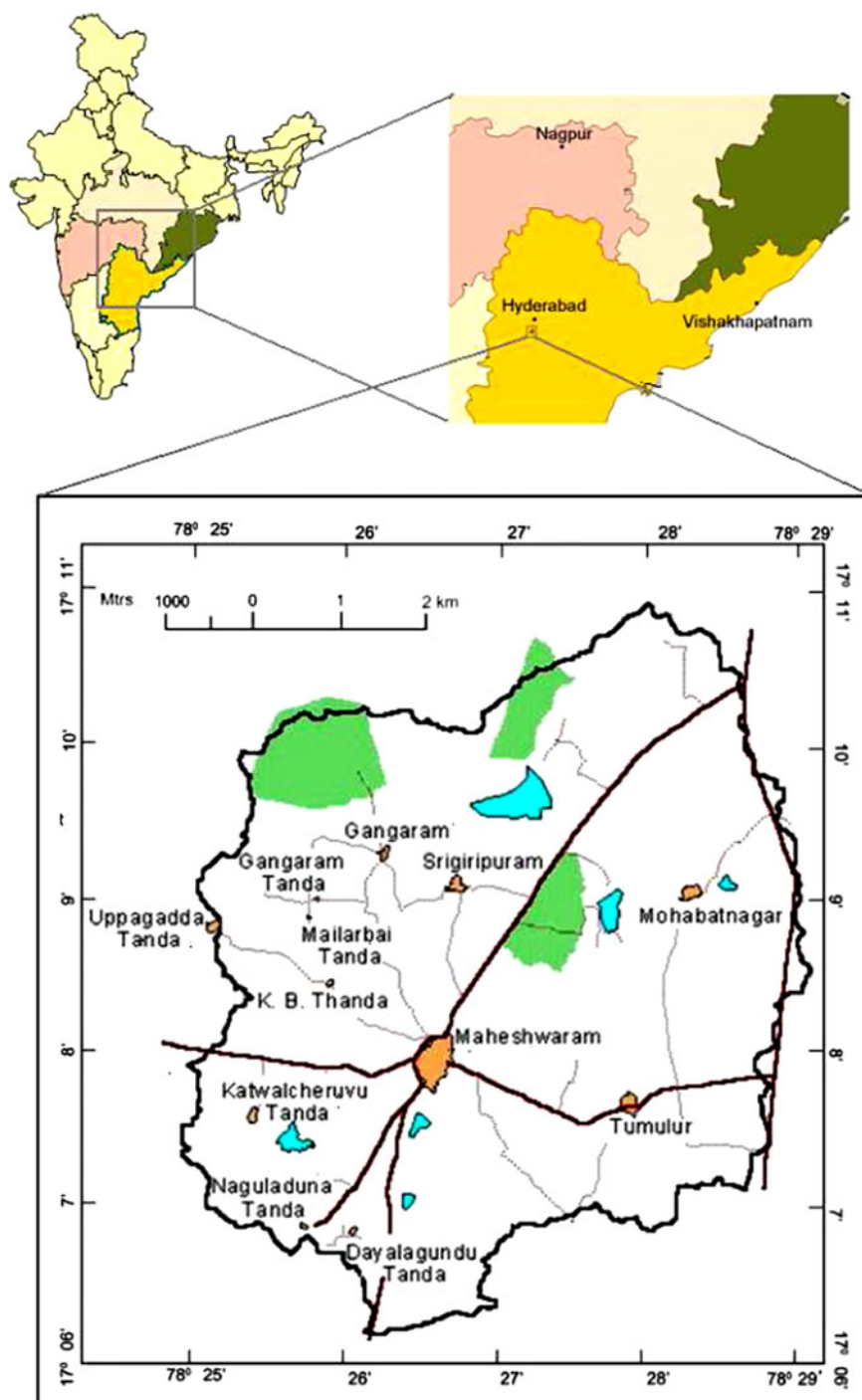
analysis (PCA) is also employed to the chemical variables of groundwater to characterize the hydro chemical process that is dominant in the area.

Study area

The present study is carried out at the Maheshwaram watershed which is situated in the Ranga Reddy district of

Andhra Pradesh at a distance of about 30 km from Hyderabad, capital of the state of Andhra Pradesh (Fig. 1). The watershed has an area of 60 km². The study area is situated between longitude 78°24'30"E–78°29'00"E and latitude 17°06'20"N–17°11'00"N. The region receives an average annual rainfall of 573 mm from the south west monsoon. The area can be classified as semi-arid. In general, the topography is undulating. A network of 1st and 2nd order streams shows dendritic to sub-dendritic type of

Fig. 1 Location map of Maheshwaram watershed



drainage pattern with no major streams. All streams drain into Mankal Tank which ultimately drains into Musi river.

Geology of Maheshwaram

Geology of the area is relatively homogenous, comprising of Precambrian granite mostly pink and gray (Figs. 2, 3) Dewandel et al. (2006). Basic enclaves, aplite, pegmatite, epidote and quartz veins, and dolerite dykes frequently traverse the area. Biotite granite covers a major part of Maheshwaram with porphyritic feldspars. Granites are intruded by quartz and dolerite dykes of several generations and are well exposed in northern and western parts of watershed. These dykes form important structural feature controlling the movement of groundwater in the region. Joints are the most commonly observed structural feature in the study area. Vertical joints act as conduits for transfer of water whereas horizontal joints help in maintaining the lateral continuity of the aquifer.

Sampling and chemical analysis

A random sampling is used to select sampling sites (Fig. 3). The pH of water is very important indication of its quality

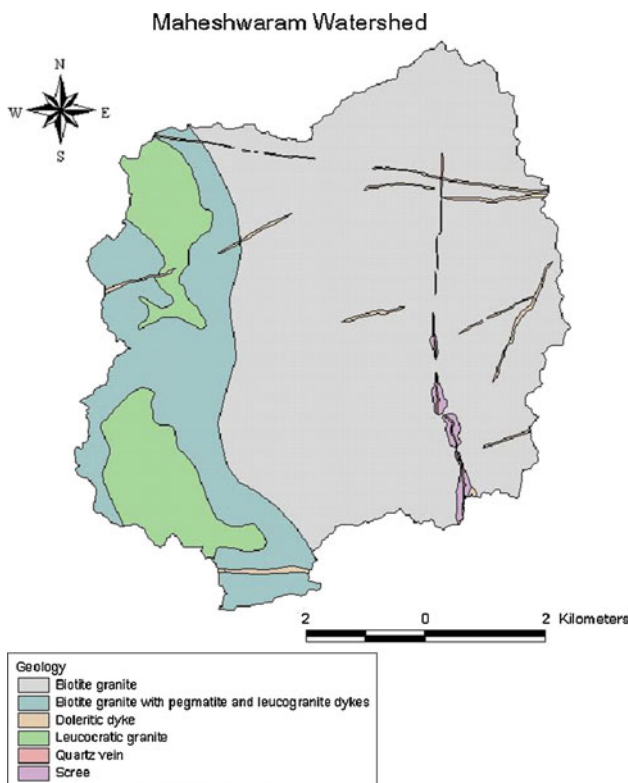


Fig. 2 Geological map of Maheshwaram watershed (Adapted and modified from Dewandel et al. 2006)

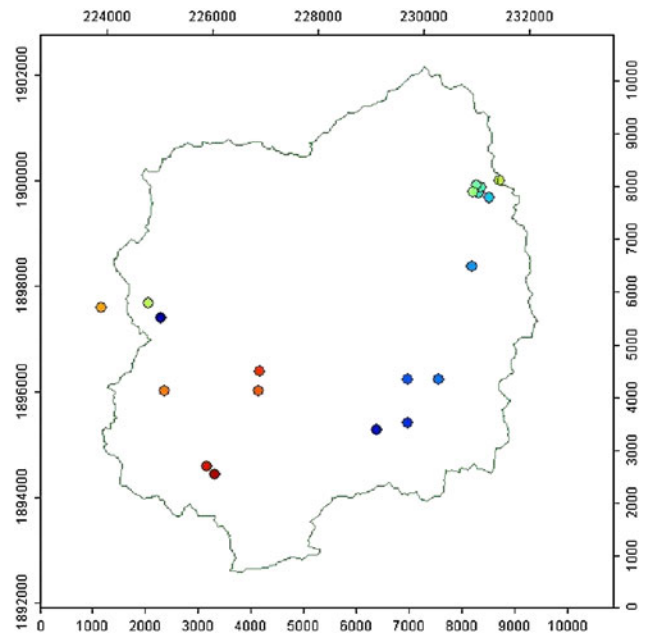


Fig. 3 Water sample locations of Maheshwaram watershed

and provides important piece of information regarding types of geochemical equilibrium (Hem 1985). Hydrogen ion concentration pH indicates the strength of the water to react with the acidic or alkaline material present in the water. The pH value is reciprocal of log of hydrogen ion concentration. The pH of groundwater in the study area is varying in the range (6.12–7.5). The pH values of all samples are within the desirable limits (6.5–9.5, World Health Organization 2006). Though pH has no direct effect on human health, all biochemical reactions are sensitive to variation of pH (Subba Rao and Krishna Rao 1991).

The salt concentration of water is generally measured with the help of electrical conductivity (Ec). The Ec of water is directly proportional to the salt concentration and vice versa. Hence, the conductivity measurement provides an indication of ionic concentrations. It depends upon temperature, concentration and types of ions present (Hem 1985). The electrical conductivity of groundwater of the study area varies between 704 and 6,450 $\mu\text{S}/\text{cm}$ at 25°C. The acceptable limit of Ec in drinking water is <1,500 $\mu\text{S}/\text{cm}$ at 25°C World Health Organization (2006). High conductance (>1,500 $\mu\text{S}/\text{cm}$) was observed in 15–30% of the groundwater samples, and this may be attributed to high chloride concentrations in groundwater (Davis and Dewist 1966).

According to Fetter classification (1990) of waters based on the total dissolved solids, 70–75% of the samples come under fresh water (TDS < 1,000 mg/l) and 25–30% under brackish water (TDS > 1,000 mg/l). Total hardness of groundwater of the study area is varying from 156.7 to 7,199.28 mg/l. TH was calculated (Sawyer et al. 2003) as

$$\text{TH(as CaCO}_3\text{) mg/l} = (([\text{Ca}^{2+}] + [\text{Mg}^{2+}]) \times 50) \text{ mEq/l} \quad (1)$$

The limit of total hardness for drinking water is specified as 500 mg/l World Health Organization (2006). Nearly 30–45% of the groundwater of the area exceeded the desirable limits. Water hardness is primarily due to the result of interaction between water and the geological formations (Angino 1983). The hardness of water is due to the presence of alkaline earths such as calcium and magnesium. However, iron, strontium, barium, manganese, and aluminum also contribute to hardness (Brown et al. 1974). High concentrations are observed in the Raghunath Steel & Co. industrial area, where calcium and magnesium are also high.

Among the cationic (Ca^{2+} , Mg^{2+} , Na^+ , K^+) concentrations, Ca (38.8–805.7 mg/l) is dominant followed by Na (35.9–684.4 mg/l), Mg (20.4–264.9 mg/l), and K (0.6–12.7 mg/l). Among the anionic (HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , and F^-) concentrations, bicarbonate is the dominant ion (170.7–909.8 mg/l), followed by chloride (23–3,024 mg/l), sulfate (10–1,796 mg/l), nitrate (8–415.1 mg/l), and fluoride (0.44–1.88 mg/l). Maximum concentrations of Ca (805.7 mg/l), Mg (254.9 mg/l), Na (684.4 mg/l), and Cl (3,024 mg/l) are observed at Raghunath Steel & Co. industrial area.

Geo-chemical characterization of groundwater

Classification schemes developed are mainly based on the concentrations of various predominant cations and anions or on the interrelationship of ions. In the present study, the methods such as Piper (1994), Back and Hanshaw (1965), Wilcox (1955), and US Salinity Laboratory method Richards (1954) are used to study the geochemical characteristics of the groundwater of the study area.

Hydro-chemical facies

To identify the water composition in different zones, Back and Hanshaw (1965), Morgan and Winner (1962), and Seaber (1962) developed the concept of hydro-chemical facies. Hydro-chemical facies are different zones in an aquifer that differ in their chemical composition. Groundwater of the study area for pre- and post-monsoon seasons is classified (Figs. 4, 5) using Back and Hanshaw diagram (1965). The percentage of groundwater of the area falling in different groups (Table 3) clearly explains the variation of cation and anion concentrations during pre- and post-monsoon seasons.

Piper trilinear method

The Piper trilinear diagram (Piper 1994) is one of the most useful graphical representations in groundwater quality

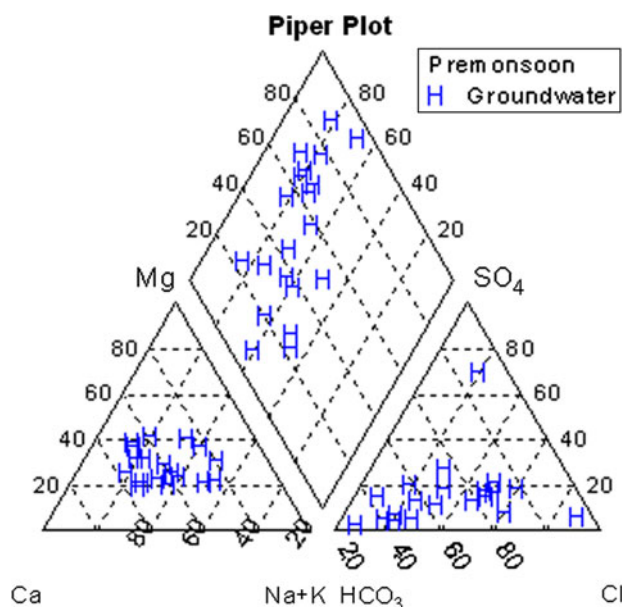


Fig. 4 Piper tri-linear diagram representing the chemical analysis of pre-monsoon

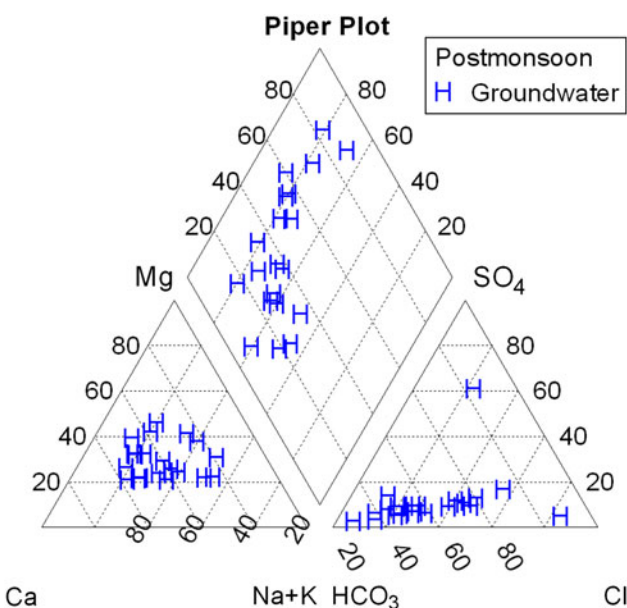


Fig. 5 Piper tri-linear diagram representing the chemical analysis of post monsoon

studies and helps in understanding the geochemistry of shallow groundwater. These tri-linear diagrams are very useful in bringing out chemical relationships among groundwater in more definite terms than with the other possible plotting methods (Walton 1970). Chemical composition of analyzed groundwater of the study area is represented in the Piper diagrams (Figs. 4, 5) for pre- and post-monsoon seasons. Distribution of the groundwater samples in different subdivisions of the diamond-shaped field of the piper diagram reveals the analogies and

Table 3 Classification of water on the basis of hydro-chemical facies

Type	Pre-monsoon percent of GW	Post-monsoon percent of GW	Ratio for pre to post monsoon
Cations			
Ca type (A)	40	35	1:0.90
Mg type (B)	NIL	NIL	NIL
Na/K type (C)	15	20	1:1.33
No dominant type (D)	45	45	1:1
Anions			
HCO ₃ type (E)	60	15	1:0.25
SO ₄ type (F)	5	5	1:1
Cl type (G)	15	5	1:0.33
No dominant type (H)	20	15	1:0.75

dissimilarities. Different types of waters are identified and are given in Table 4. The plot of chemical data on the diamond-shaped tri-linear diagram reveals that majority of the groundwater samples fall in the fields of 1, 3, and 5, suggesting that alkaline earths exceeds alkalis. Weak acids exceed strong acids and the ions representing carbonate hardness (secondary alkalinity) exceed 50%, respectively (Table 4). From the diagram (Figs. 4, 5) it is clear that the hydrochemistry of groundwater is dominated by alkaline earths and weak acids.

Classification of groundwater for irrigation purpose

The suitability of groundwater for irrigation purposes depends upon its mineral constituents. The salts present in

the water affect the soil structure, permeability, and aeration, which indirectly affect the plant growth. The sodium concentration in irrigation water is very useful for understanding the quality of irrigation water as sodium by the process of Base Exchange replaces calcium in the soil, thereby reducing the permeability of soil.

Wilcox (1955) has classified groundwater for irrigation purposes based on percent sodium and electrical conductivity. Eaton (1950) has recommended the concentration of residual sodium carbonate for determining the suitability of water for irrigation purposes. According to the US Salinity Laboratory method Richards (1954), electrical conductivity and sodium adsorption ratios are considered in determining the suitability of water quality for irrigation.

Classification by percent sodium (Wilcox method)

The sodium in irrigation waters is usually denoted as percent sodium and can be determined by the following formula (Wilcox 1955), Zhu et al. (2010):

$$\%Na = ([Na^+] \times 100) / ([Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+]) \tag{2}$$

where the quantities of Na, Ca, Mg, and K are taken in mEq/l. The classification of groundwater samples from the study area with respect to percent sodium and electrical conductivity is shown in Figs. 6 and 7.

It is observed that during pre-monsoon season, 75% of the groundwater is confined to the good to permissible class, while 10% of the groundwater fall in the excellent to good class, and another 15% in the doubtful to unsuitable class (Fig. 6). Hence, 85% of the groundwater fall between

Table 4 Characterization of groundwater of the study area on the basis of Piper tri-linear diagram

Sub division number of the diamond-shaped fields	Characteristics of corresponding sub division of diamond-shaped fields	Pre-monsoon % of sample	Post-monsoon % of sample
1	Alkaline Earths (Ca + Mg) exceeds alkalis (Na K)	85	85
2	Alkalis exceeds alkaline earths	15	15
3	Weak acids (CO ₃ + HCO ₃) exceeds strong acids (SO ₂ + Cl + F)	50	80
4	Strong acids exceed weak acids	50	20
5	Carbonated hardness (secondary alkalinity) exceeds 50%; i.e., chemical properties of the groundwater are dominated by alkaline earths and weak acids	35	65
6	Non-carbonate hardness (secondary alkalinity) exceeds 50%, i.e., chemical properties of the groundwater are dominated by alkalis and strong acids	15	NIL
7	Non-carbonate alkali (primary salinity) exceeds 50%, i.e., chemical properties of the groundwater are dominated by alkalis and weak acids	NIL	NIL
8	Non carbonate alkali (primary salinity) exceeds 50%, i.e. chemical properties are dominated by alkalis and weak acids	NIL	NIL
9	No one cation–anion exceeds 50%	45	15

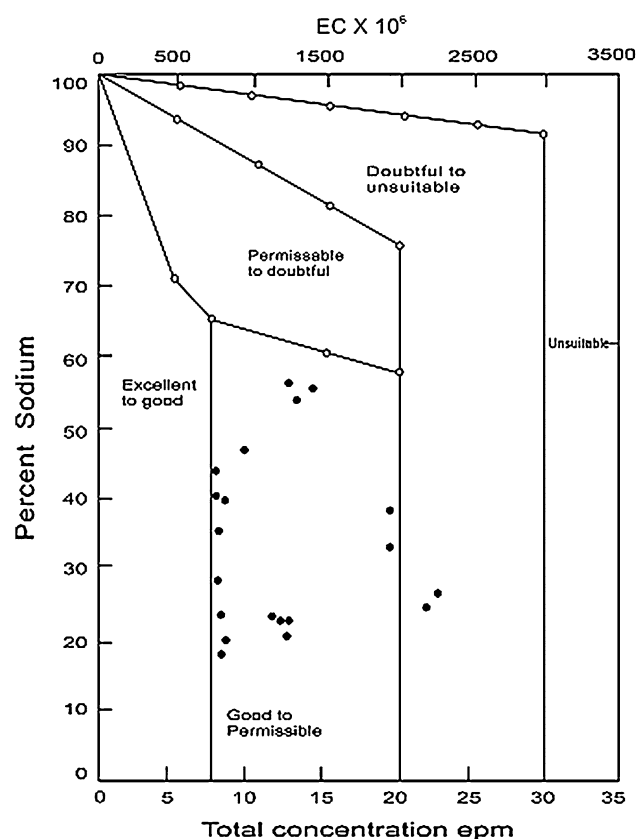


Fig. 6 Classification of groundwater based on Ec and Na% (Wilcox) of pre-monsoon

permissible to excellent class and is suitable for irrigation purposes, whereas for the post-monsoon period, 90% of the groundwater is confined to the good to permissible class, and 10% in the doubtful to unsuitable class (Fig. 7).

Classification by residual sodium carbonate (RSC)

The sodium hazard to the crops can also increase significantly with rise in bicarbonate concentration. Water containing high concentrations of carbonate and bicarbonate ions tends to precipitate Ca and Mg as their carbonates. As a consequence, the relative proportion of sodium increases and gets fixed in the soil there by decreasing the soil permeability. Residual sodium carbonate is calculated by the following equation (Eaton 1950):

$$\text{RSC} = ([\text{CO}_3^{2-}] + [\text{HCO}_3^-]) - ([\text{Ca}^{2+}] + \text{Mg}^{2+}) \quad (3)$$

where all the concentrations are expressed in mEq/l. On the basis of RSC (Tables 5 and 6), it is observed that 65% of groundwater of the area is safe for irrigation and 35% of groundwater of the area is unsuitable for irrigation purposes during pre-monsoon season, whereas for the post-monsoon, it is observed that 45% of groundwater of the

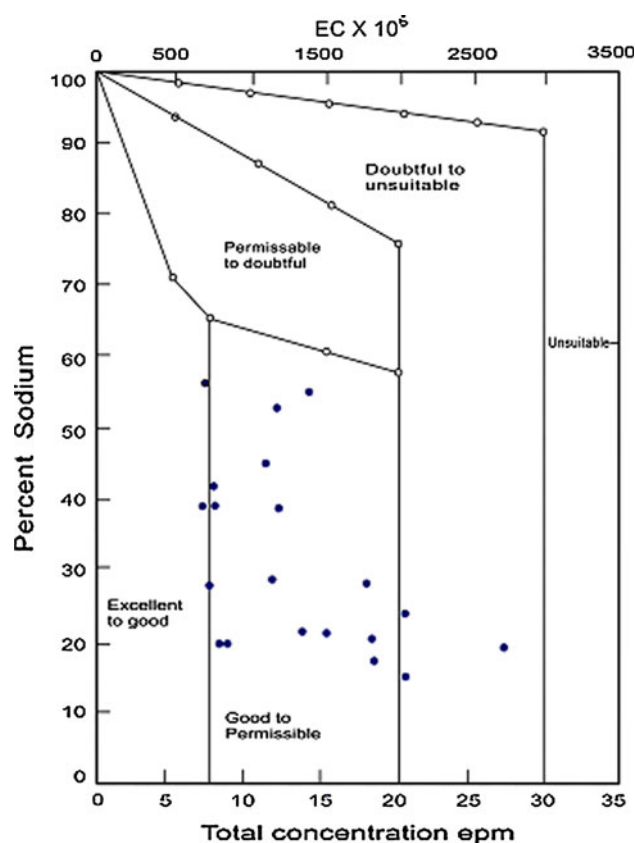


Fig. 7 Classification of groundwater based on Ec and Na% (Wilcox) of post-monsoon

Table 5 Classification of groundwater of the study area during pre-monsoon season on the basis of RSC

RSC (mEq/l)	Suitability for irrigation	No. of samples
<1.25	Safe for irrigation	13
1.25–2.5	Moderately safe for irrigation	Nil
>2.5	Unsuitable for irrigation	7

Table 6 Classification of groundwater of the study area during post-monsoon season on the basis of RSC

RSC (mEq/l)	Suitability for irrigation	No. of samples
<1.25	Safe for irrigation	9
1.25–2.5	Moderately safe for irrigation	1
>2.5	Unsuitable for irrigation	10

area is safe for irrigation, 5% is moderate, and 50% is unsuitable for irrigation purposes.

Classification of groundwater by U.S. Salinity Laboratory method

The U.S. Salinity Laboratory Richards (1954) proposed a diagram for studying the suitability of groundwater for

irrigation purposes based on sodium adsorption ratio (SAR) and (Ec). SAR is an important parameter for determining the suitability of irrigation water, as it measures the alkali/sodium hazard for crops. SAR can be estimated by taking individual values of Na⁺, Ca²⁺, and Mg²⁺ in mEq/l and substituting in the following expression (Wilcox 1955), Zhu et al. (2010):

$$SAR = [Na^+] / \left(\sqrt{([Ca^{2+}] + [Mg^{2+}]) / 2} \right) \quad (4)$$

The chemical parameters of the groundwater of the area are represented in the U.S.S.L. diagram (Figs. 8, 9) and the results are shown in Tables 7 and 8. During pre-monsoon season it is observed that 15% of the groundwater falls under C2S1 class indicating medium salinity, low-sodium waters; 80% of the groundwater falls under C3S1 class, indicating high salinity and low sodium waters; and 5% of the groundwater falls under C4S1 class, indicating very

Table 7 U.S.S.L. classification of irrigation waters (after Richards 1954) during pre-monsoon season

Class	Number of samples	Percentage of samples
C2S1	3	15
C3S1	16	80
C4S1	1	5

Table 8 U.S.S.L. classification of irrigation waters (after Richards 1954) during post monsoon season

Class	Number of samples	Percentage of samples
C2S1	20	100

high salinity, low sodium waters. During post monsoon season it is observed that 100% of the groundwater falls under C3S1 class, indicating high salinity and low sodium waters. It is observed that 95% of the groundwater samples, for both pre- and post-monsoon fall in the fields of C2S1 and C3S1 waters, indicating high salinity and low sodium water type. This type of water can be used for irrigation with little danger of exchangeable sodium.

Principal component analysis

Principal component analysis is a variable reduction procedure. It is useful when one has obtained data on a large number of variables, and believes that there is some redundancy in those variables. In this case, redundancy means that some of the variables are correlated with one another, possibly because they are measuring the same construct. When this happens, one can take advantage of this redundancy of information and simplify the problem by replacing observed variables into a smaller number of principal components that will account for most of the variance in the observed variables. All the principal components are orthogonal to each other so there is no redundant information, Davis (1986).

The chemical analysis data of ground water sampled during pre- and post-monsoon seasons of 2007–2008 were subjected to principal component analysis (PCA) to understand the controlling covariance structure between the variables. Each variable was standardized to the mean 0.0, and variance 1.0, to avoid the problem of having one variable with large variance unduly influencing the determination of component loadings. PCA code from Matlab 6.5 (2002) is used for the purpose.

The correlation matrices between 13 variables for pre- and post-monsoon data are shown in Tables 9 and 10. Principal component analysis is carried out only on nine independent (Ca, Mg, Na, K, HCO₃, Cl, SO₄, NO₃, F) variables. The result of principal component analysis based

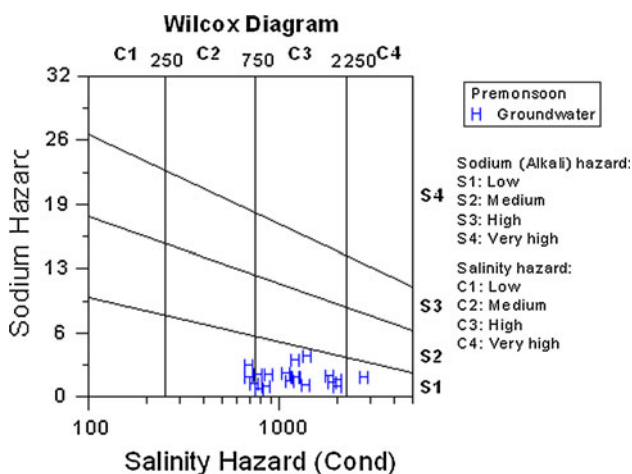


Fig. 8 Classification of groundwater based on USSL of pre-monsoon season

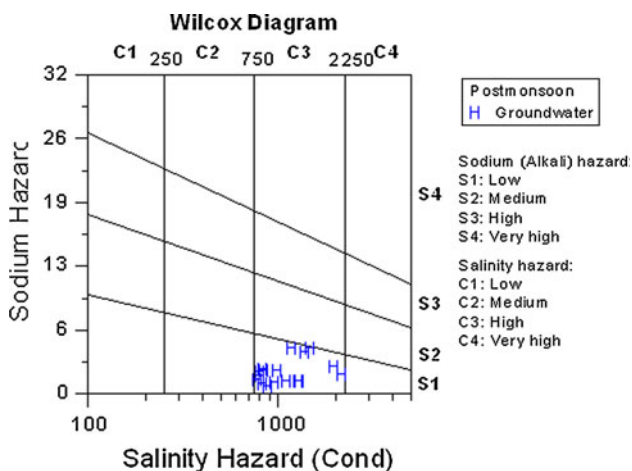


Fig. 9 Classification of groundwater based on USSL of post-monsoon season

Table 9 Correlation matrix of 13 variables (pre-monsoon)

	pH	Ec	TDS	TH	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃	NO ₃	Fl
pH	1.00	-0.65	-0.64	-0.70	-0.73	0.69	-0.47	-0.70	-0.54	-0.55	0.44	0.13	0.46
Each	-0.65	1.00	1.00	0.99	0.96	0.97	0.93	0.57	0.96	0.35	-0.31	-0.10	0.40
TDS	-0.64	1.00	1.00	0.98	0.96	0.97	0.93	0.57	0.96	0.35	-0.31	0.10	-0.40
TH	-0.70	0.99	0.98	1.00	0.99	0.97	0.89	0.58	0.93	0.44	-0.31	-0.14	-0.44
Ca	-0.73	0.96	0.96	0.99	1.00	0.94	0.85	0.60	0.89	0.51	-0.33	-0.15	-0.43
Mg	-0.69	0.97	0.97	0.97	0.94	1.00	0.84	0.62	0.89	0.43	-0.33	-0.08	-0.48
Na	-0.47	0.93	0.93	0.89	0.85	0.84	1.00	0.39	0.95	0.20	-0.14	-0.23	-0.20
K	-0.70	0.57	0.57	0.58	0.60	0.62	0.39	1.00	0.46	0.38	-0.39	-0.09	-0.32
Cl	-0.54	0.96	0.96	0.93	0.89	0.89	0.95	0.46	1.00	0.14	-0.24	-0.14	-0.39
SO ₄	-0.55	0.35	0.37	0.46	0.51	0.48	0.20	0.38	0.14	1.00	-0.15	-0.17	-0.10
HCO ₃	0.44	-0.31	-0.31	-0.32	-0.33	-0.33	-0.14	-0.39	-0.24	-0.15	1.00	-0.21	0.29
NO ₃	0.13	-0.10	-0.10	-0.14	-0.15	-0.08	-0.23	-0.09	-0.14	-0.17	-0.21	1.00	-0.33
Fl	0.46	-0.40	-0.40	-0.44	-0.43	-0.48	-0.20	-0.32	-0.39	-0.10	0.29	-0.33	1.00

Table 10 Correlation matrix of 13 variables (post monsoon)

	pH	EACH	TDS	TH	Ca	Mg	Na	K	Cl	So ₄	HCO ₃	NO ₃	F
pH	1.00	0.26	-0.32	-0.41	-0.42	-0.38	-0.18	-0.36	-0.02	0.74	-0.23	-0.20	-0.06
EACH	0.26	1.00	0.73	0.60	0.54	0.67	0.80	0.31	0.90	-0.14	0.25	-0.28	0.05
TDS	-0.32	0.73	1.00	0.97	0.94	0.97	0.93	0.59	0.92	0.47	0.39	-0.09	0.13
TH	-0.41	0.60	0.97	1.00	0.99	0.97	0.84	0.62	0.86	0.63	0.26	-0.13	0.13
Ca	-0.42	0.54	0.94	0.99	1.00	0.93	0.81	0.61	0.83	0.65	0.21	-0.12	0.14
Mg	-0.38	0.67	0.97	0.97	0.93	1.00	0.85	0.63	0.86	0.58	0.35	-0.13	0.10
Na	-0.18	0.80	0.93	0.84	0.81	0.85	1.00	0.44	0.91	0.29	0.46	-0.18	0.19
K	-0.36	0.31	0.59	0.62	0.61	0.63	0.44	1.00	0.43	0.45	0.15	-0.07	0.20
Cl	-0.02	0.90	0.92	0.86	0.83	0.86	0.91	0.43	1.00	0.17	0.26	-0.18	0.05
SO ₄	0.74	-0.14	0.47	0.63	0.65	0.58	0.29	0.45	0.17	1.00	0.10	-0.15	0.28
HCO ₃	-0.23	0.25	0.39	0.26	0.21	0.35	0.46	0.15	0.26	0.10	1.00	-0.01	0.00
NO ₃	-0.20	-0.28	-0.09	-0.13	-0.12	-0.13	-0.18	-0.07	-0.18	-0.15	-0.01	1.00	-0.29
F	-0.06	0.05	0.13	0.13	0.14	0.10	0.19	0.20	0.05	0.28	0.00	-0.29	1.00

on the most significant first four components shows that these components explain about 85 and 87% of the total variance of observed variable, for pre- and post-monsoon periods, respectively. Hence, the first four components can be used to explain the background hydro chemical processes, without losing any significant characteristics. The principal components, the corresponding Eigen values and the percent of variance contribution by each component is given in Tables 11, 12, 13, and 14.

Principal component-I (PC-I)

The contribution of the principal component PC-I is about 49 and 50% of the total variance and has the largest Eigen value in the range 4.46–4.54, for pre- and post-monsoon periods, respectively (Tables 12, 14). PC-I has moderate positive loadings (0.40–0.46) of (Ca²⁺, Mg²⁺, Na⁺, Cl⁻)

ions (Tables 11, 13). The correlation between (Ca²⁺, Mg²⁺, Na⁺, Cl⁻) ions is more than 0.84, and that between TDS (salinity) and Ca²⁺, Mg²⁺, Na⁺, Cl⁻ ions is more than 0.90, which is significant at 1% level. Salinity of the soil is directly controlled by the concentrations of Na⁺ and Cl⁻ ions, which is derived from interactions of water and rock, and gets enriched in the ground waters due to their higher solubility Zhu et al. (2010). Alkaline earths such as calcium and magnesium contribute to the hardness of water. Hence, PC-I can be a salinity and hardness component.

Principal component-II (PC-II)

The contribution of the principal component PC-II is about 17 and 15% of the total variance and has the second largest Eigen value in the range 1.34–1.51, for pre- and post-

Table 11 Principal components (pre-monsoon)

	I	II	III	IV
Ca	0.46	−0.06	0.02	−0.10
Mg	0.45	0.00	−0.05	−0.08
Na	0.40	−0.24	−0.32	0.06
K	0.32	0.10	0.33	0.26
Cl	0.43	−0.10	−0.36	0.07
SO ₄	0.21	−0.11	0.72	−0.47
HCO ₃	−0.19	−0.44	−0.29	−0.67
NO ₃	−0.06	0.69	−0.19	−0.23
Fl	−0.23	−0.50	0.14	0.42

Table 12 Percent contribution of each component (pre-monsoon)

Principal components	Eigen values	Percent contribution	Elements with high loadings
I	4.54	50	Ca, Mg, Na, Cl
II	1.51	17	NO ₃
III	1.07	12	SO ₄
IV	0.74	8	Fl

Table 13 Principal components (post-monsoon)

	I	II	III	IV
Ca	0.45	0.00	0.18	−0.13
Mg	0.46	−0.09	0.09	−0.05
Na	0.43	−0.18	−0.26	−0.03
K	0.32	0.14	0.34	0.07
Cl	0.41	−0.23	−0.20	−0.36
SO ₄	0.28	0.39	0.43	0.25
HCO ₃	0.18	−0.32	−0.36	0.80
NO ₃	−0.10	−0.47	0.61	0.26
Fl	0.11	0.64	−0.21	0.27

Table 14 Percent contribution of each component (post-monsoon)

Principal component	Eigen value	Percent contribution	Elements with high loadings
I	4.46	49	Ca, Mg, Na, Cl
II	1.34	15	Fl
III	1.05	12	NO ₃
IV	0.85	9	HCO ₃
V	0.66	7	SO ₄

monsoon periods, respectively. For the pre-monsoon period NO₃ dominates and has a high positive loading of 0.69 on the component, whereas for the post monsoon period F dominates and has a high positive loading of 0.64 on PC-II.

Principal component-III (PC-III)

The contribution of the principal component PC-III is about 12% of the total variance and has the Eigen value varying from 1.05 to 1.07, for pre- and post-monsoon periods, respectively. For the pre-monsoon period SO₄ dominates and has a high positive loading of 0.72 on the component, whereas for the post-monsoon period NO₃ dominates and has a high positive loading of 0.61 on PC-III.

Principal component-IV (PC-IV)

The contribution of the principal component PC-IV is about 8 and 9% of the total variance and has the Eigen value varying from 0.74 to 0.85, for pre- and post-monsoon periods, respectively. For the pre-monsoon period F dominates and has a moderate positive loading of 0.42 on the component, whereas for the post-monsoon period HCO₃ dominates and has a high positive loading of 0.80 on PC-IV.

Although all anions (NO₃[−], F[−], SO₄[−], HCO₃[−]) are present in the PC-II, PC-III, and PC-IV, the common anions that appear both in pre- and post-monsoon are NO₃[−] and F[−]. Hence, these can be named as anthropogenic and litho logical components, respectively.

Results and discussions

Groundwater samples collected from the study area during pre-and post-monsoon seasons have been analyzed for various ionic and non-ionic parameters to assess their worth for drinking and irrigational purposes. Parameters to assess groundwater potability were compared with specifications of World Health Organization (2006) and Bureau of Indian Standards (BIS, 1983) in Table 15 and are discussed in the following:

It is observed that 25–30% of the samples come under brackish water (TDS > 1,000 mg/l, World Health Organization 2006). The pH of groundwater is varying between 6.12 and 7.5 and is within the desirable limits (6.5–9.5; World Health Organization 2006). The electrical conductivity of groundwater of the study area varies between 704 and 6,450 μS/cm at 25°C (acceptable limit is <1,500 μS/cm at 25°C; World Health Organization 2006). High conductance (>1,500 μS/cm) was observed between 15 and 30% of the groundwater samples, and this may be attributed to high salinity in groundwater. Total hardness of groundwater of the study area is varying from 156.7 to 7,199.28 mg/l and nearly 30–45% of the groundwater of the area exceeded the desirable limits (<500 mg/l; World Health Organization 2006). The hardness of water is due to

Table 15 Drinking water quality standards

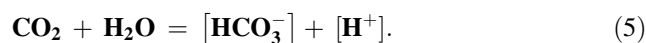
Parameter	BSI (1983)	WHO (2006)	Analysed samples range	% of samples exceeding desirable limits
pH	6.5–8.5	6.5–9.5	6.12–7.5	–
Ec ($\mu\text{s}/\text{cm}$)	–	(<1,500 $\mu\text{s}/\text{cm}$)	704–6,450	15–30
TDS (ppm)	500	(<1,000)	274–4,000	25–30
TH (ppm)	500	500	156.7–7,199.28	30–45
Ca (ppm)	500	500	38.8–805.7	0–10
Mg (ppm)	30	–	19.5–264.9	75–90
Na (ppm)	100	100	35.9–684.4	30–50
K (ppm)	10	10	0.6–12.7	5
HCO ₃ (ppm)	300	–	170.7–909.8	45–95
Cl (ppm)	250	250	23–3,024	30
SO ₄ (ppm)	200	200	10–1,796	10
NO ₃	45	45	5.6–4,151	55
F (ppm)	0.6–1.0	1.5	0.44–1.95	20–35

the presence of alkaline earths such as calcium and magnesium.

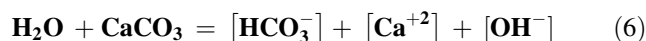
Among the cationic (Ca, Mg, Na, K) concentrations, the order of abundance is $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$. The concentration of Ca, Mg, and Na in the groundwater is due to the weathering of pyroxenes, plagioclase feldspars, apatite and sphene present in the granites, and alaskites of the study area. The Ca of groundwater of the study area varies from 30.1 to 805.7 mg/l. Around 0–10% samples exceed the desirable limit (<500 mg/l; World Health Organization 2006). The sources of Ca^{2+} consists mainly of carbonate rocks containing calcite CaCO_3 and dolomite $\text{CaMg}(\text{CO}_3)_2$. The Mg of groundwater of the study area varies from 19.5 to 264.9 mg/l and nearly 75–90% exceed the desirable limit (<30 mg/l; BSI 1983). Mg–silicate minerals, chiefly amphiboles, pyroxene, olivine, biotite, and dolomite constitute the main source of Mg (Berner and Berner 1987). Excess of magnesium affects the quality of soil, which results in poor crop yield. The high concentration of magnesium and calcium impairs the potability of water and may cause encrustation in the water supply structure. Apart from natural sources, human activities have significant influence on the concentration of sodium in groundwater. Sewage, industrial effluents, the use of sodium compounds for corrosion control, and water softening processes have all contributed to Na concentrations in groundwater of the study area. Sodium concentrations in the groundwater is varying from 35.9 to 684.4 mg/l of the area and around 30–50% of the samples exceed the desirable limit (100 mg/l; World Health Organization 2006). The K of groundwater of the study area varies between 0.6 and 12.7 mg/l. Nearly 5% of the samples exceed the desirable limit (10 mg/l; World Health Organization 2006).

Among the anionic (HCO₃, SO₄, Cl, NO₃, and F) concentrations, the order is $\text{HCO}_3 > \text{Cl} > \text{SO}_4 > \text{NO}_3 > \text{F}$.

Bicarbonate concentrations are varying from 170.8 to 909.8 mg/l in the groundwater of study area. Around 45–95% of samples exceed the desirable limit (300 mg/l; BSI 1983). The maximum concentration of bicarbonate 909.8 mg/l is observed at the Mandal Revenue Office, near Maheshwaram. Bicarbonate, usually the primary anion in groundwater, is derived from the carbon dioxide released by the organic decomposition in the soil (Todd 1980)



According to Subba Rao et al. (2002), ground waters saturated with CaCO_3 lead to precipitation of CaCO_3 . This indicates the occurrence of kankar in the soil zone. The precipitation of CaCO_3 could decrease the Ca^{2+} and carbonates (HCO₃ and CO₃) in the ground waters, but leaching of CaCO_3 from the kankar can increase them and consequently increase the level of pH, Hem (1985) as

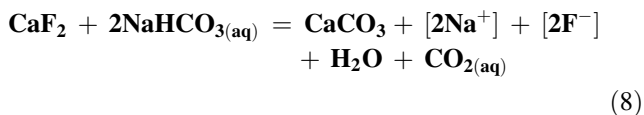
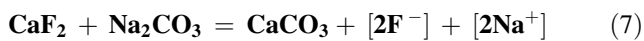


In the present analysis HCO₃ has increased during post monsoon period; hence leaching of CaCO_3 from the kankar has taken place.

Sulfate concentrations vary from 10 to 1,796 mg/l and around 10% of the samples exceed the desirable limit of (200 mg/l; World Health Organization 2006). It is observed that high concentrations of sulfate in groundwater are distributed at Dattatreya Ashram, near Maheshwaram. The distribution of sulfate is due to sulfur minerals, sulfides of heavy metals, which are common occurrence in igneous rocks and metamorphic rocks. Apart from these natural sources, sulfates can be introduced through the application of sulfuric soil conditioners (Karanth 1987). Sulfates are also discharged into the groundwater from different industrial effluents. Excessive sulfate concentration has laxative effect World Health Organization (2006).

The source of chloride in groundwater is due to the domestic sewage and industrial effluents (Karanth 1987; Craig and Anderson 1979). Chloride concentrations are varying from 23 to 3,024 mg/l. It is observed that nearly 30% of groundwater from the area exceeds the desirable limit (250 mg/l; World Health Organization 2006). Excessive chloride concentration leads to salinity, which deteriorates the soil, Saadatmand et al. (2007). Nitrate concentrations vary from 5.6 to 415.1 mg/l and nearly 55% of water sample exceeds the permissible limit of 45 mg/l World Health Organization (2006). Numerous sources in the environment contribute to the total nitrate content of natural waters (Handa et al. 1982) viz., atmosphere, atmospheric nitrogen fixation, and anthropogenic sources which include (a) industrial wastes containing N-compounds (b) human and animal wastes and agricultural activities. Urea (NH₂)₂CO and ammonium nitrate NH₄NO₃ are the most commonly used fertilizers contributing nitrates to the ground water. Although commercial fertilizers are suspected as major source of nitrate in groundwater, researchers have also identified natural organic nitrogen, livestock, septic tank, and atmospheric inputs as contributories in the absence of fertilizer application; high nitrate concentrations observed may be attributed to the anthropogenic sources like leakage of septic tanks, sewer pipes, and improper disposal of domestic and industrial wastes (Sudarshan and Sravanthi 1996; Sravanthi et al. 1997).

Fluoride concentration varies from 0.44 to 1.88 mg/l. Around 20–35% of samples exceed the limit of 0.8–1.5 mg/l World Health Organization (2006). High fluoride content in groundwater leads to dental and skeletal fluorosis such as mottling of teeth, deformation of ligaments, and bending of spinal cord. Maximum concentration of F 1.88 mg/l is observed in the groundwater collected from a bore well located in smp-17 SIRGPR area. Fluorite (CaF₂) is the main solid-phase fluoride in rocks. F⁻ ions are released when CaF₂ reacts with carbonate waters, (Saxena and Ahmed 2001)



The NaHCO₃-rich water accelerates the dissolution of CaF₂ and thereby releases fluoride into groundwater. High fluoride concentration in the groundwater may be attributed to the presence of fluorine-bearing minerals like biotite, apatite, and sphene from the granites of the study area and due to use of the phosphoric fertilizers (Fluoroapatite Ca₅[PO₄]₃[F,Cl]), (Handa 1975) at these areas, for agricultural activities before settlements. Most of the industries

in the study area are steel, chemical industries (Uma Organic Ltd., Sai Teja Electroplating, etc. at SMP-5), brick tiles, oil refineries, and other anthropogenic activities which contribute to the fluoride concentrations. The fluoride concentrations increased at some places (SMPS 5–10, 16 and 17 = 40%) and decreased in the rest (60%) during post-monsoon season. The presence of fluoride is due to lithology as well as due to pollution by chemical industries.

The tri-linear plot in the piper diagram suggests that alkaline earths exceed alkalis, weak acids exceed strong acids, and the secondary alkalinity exceeds 50%. The Wilcox diagrams reveals that 85% of the groundwater samples fall between permissible to excellent class and another 15% in the doubtful to unsuitable class for irrigation purposes. Results of residual sodium carbonate analysis indicate that 35% of groundwater in that area is unsuitable for irrigation purposes during pre-monsoon season, whereas during the post-monsoon season this reaches to 50%. From the U.S. Salinity Laboratory diagrams, it is observed that 95% of the groundwater samples, for both pre- and post-monsoon fall in the fields of C2S1 and C3S1 waters, indicating high salinity and low sodium water type. This type of water can be used for irrigation with little danger of exchangeable sodium.

The result of principal component analysis based on the most significant first four components shows that these components explain about 85–87% of the total variance of observed variables, for pre- and post-monsoon periods, respectively. These four components cover eight out of total nine elements considered for PCA. The contribution of the PC-I is about 49–50% of the total variance and has moderate positive loadings (0.40–0.46) of (Ca²⁺, Mg²⁺, Na⁺, Cl⁻) ions. The correlation between TDS and Ca²⁺, Mg²⁺, Na⁺, Cl⁻ ions is more than 0.90. Hence, PC-I can be a salinity and hardness component. Nearly 30% of groundwater from the area exceeds the desirable limit of Cl (250 mg/l; World Health Organization 2006) and around 30–50% of the samples exceed the desirable limit of Na (100 mg/l; World Health Organization 2006). These two factors make groundwater saline Zhu et al. (2010). High salinity reduces the osmotic activity of plants and thus interferes with the absorption of water and nutrients from the soil, (Saleh et al. 1999). Presence of alkaline earths Ca and Mg make groundwater hard.

The contribution of the PC-II is between 15 and 17%; the PC-III accounts 12% and the PC-IV between 8 and 9% for pre- and post monsoon seasons. For the pre-monsoon period, NO₃, SO₄, and F have high loading on PC-II, PC-III, and PC-IV, whereas for the post-monsoon period F, NO₃, and HCO₃ have high loadings on PC-II, PC-III, and PC-IV. The anions that appear both in pre- and post-monsoon seasons are NO₃⁻ and F⁻. Hence, these can be named as anthropogenic and litho logical components,

respectively. Contamination of groundwater due to septic tanks and nitrogen fertilizers increases the level of NO_3^- .

Conclusion

Maheshwaram watershed is facing the problem of groundwater depletion and quality deterioration due to the absence of perennial source of surface water, inadequate rainfall, and overexploitation. Water quality has deteriorated due to increased human population, rapid urbanization, unscientific disposal of wastes, and improper water management. Change in land use pattern directly resulted in the degradation of hydro-geological environment. Weathered zone has become dry and the existing wells tap the fractured and fissured aquifers (Hashimi and Engerrand 1999). Unscientific agricultural practices are the prime cause for deterioration of groundwater quality. The anthropogenic activities like poultry farms, various industries including chemical and pharmaceuticals, indiscriminate use of fertilizers/pesticides, and sewage release of reactive pollutants into the atmosphere by chemical industries are the main causes for deterioration of air, water, and soil quality in the watershed.

The groundwater in the study area is slightly alkaline in nature. Based on the TDS, about 25–30% of groundwater samples exceed the desirable limits of the drinking water ($\text{TDS} < 1,000 \text{ mg/l}$; World Health Organization 2006). The Wilcox diagram reveals that 15% of the groundwater samples are in doubtful to unsuitable class for irrigation purposes. From the RSC analysis it is observed that 35–50% of samples are unsuitable for irrigation purposes. More than 30% of samples exceed the desirable limits for $\text{Na} < 100 \text{ mg/l}$, $\text{Mg} < 30 \text{ mg/l}$, $\text{Cl} < 250 \text{ mg/l}$, and $\text{HCO}_3 < 300 \text{ mg/l}$ (BSI 1983) concentrations. Excess of Na, Mg, Cl, and HCO_3 concentrations deteriorates the soil quality and damage sensitive crops. Hence, these soils require gypsum treatment to improve permeability of soils and crop yield. It is observed that more than 55% of samples exceed the desirable limits for NO_3 concentrations. Salinity and pollution problems of the study area should be solved by installing distillation plant, adopting rain harvesting method, and by providing proper drainage facilities. To avoid further deterioration of the environment and to ensure sustainable development, the following measures need to be adopted: (a) Practice of drip irrigation should be encouraged as it helps in preventing leaching and weathering of rocks. (b) The zones of high fluoride are to be avoided for exploiting water for drinking purposes. (c) Periodical monitoring of the environment-related parameters is recommended.

Acknowledgments We are thankful to Dr. V. P. Dimri, Director, NGRI for his encouragement and permission to publish this paper.

Purushotham thanks Dr. Shakeel, Scientist, for extending all logistic support during the field work. Thanks are also due to Dr. V. Balram and Dr. D. Venkat Reddy for helping in analysis of water samples.

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