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Geochemical Assessment of Groundwater Quality in Mhadei River Watershed, Goa, India

Y. Modassir, M.M. Ibrampurkar, V.D. Virginkar and R.N. Jyai Dhempe College of Arts and Science, Miramar, Panjim, Goa, INDIA

(Corresponding author: Y. Modassir) (Received 01 February, 2015, Accepted 06 March, 2015) (Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: The chemical quality of groundwater is governed by the interplay between the host litho-type, residence time of groundwater and a series of intricate adsorption-desorption and dissolution-precipitation processes. Understanding the geochemical evolution of water and its quality is important for sustainable development of groundwater resource. A detailed investigation has been carried out to understand the geochemical processes regulating the groundwater chemistry in Mhadei River watershed in Goa, India. The watershed is dominantly underlain by ferruginous laterite capping the Precambrian schistose rocks. Groundwater occurs in unconfined condition in the laterite aquifer. Twenty five groundwater samples were collected from open dug wells spread over the entire watershed during the post-monsoon and pre-monsoon periods and were chemically analysed using standard methods. The results indicate that the groundwater in the Mhadei watershed has very low dissolved constituents and is dominantly soft in nature. Calciumbicarbonate is the most common groundwater quality type in the watershed. All the major cations and anions are well within the prescribed limits of drinking water standards. However, pH of the groundwater is conspicuously low. Most of the water samples fall in the precipitation domain of the Gibb's 'Ca-Mg versus HCO₃' plot suggesting that no major constituents are added to the water during its percolation from the soil and unsaturated zones. There are no evidences of sea water intrusion or pollution through anthropogenic sources. The sodium absorption ratio and percent sodium indicates that the groundwater is suitable for irrigation purpose. However, presence of cadmium in some of the wells renders the groundwater unsuitable for drinking purpose in these areas.

Key words: Mhadei River, Goa, Groundwater quality, Laterite, Western Ghats.

I. INTRODUCTION

The chemistry of groundwater in an unconfined aquifer is a result of sum total of various geochemical processes that take place during the movement of water from the atmosphere to the aquifer through the soil zone and the unsaturated zone. The solubility of the litho-types with which the water interacts and the interaction period are the two main factors that control the chemical constituents present in the groundwater. Therefore, the suitability of groundwater for various purposes such as for drinking, domestic, agricultural or industrial use is directly governed by the litho-types in a groundwater unit and the groundwater flow dynamics. Degradation of groundwater quality occurs either by lithogenic sources or anthropogenic sources. Sea water intrusion is also a matter of serious concern in the coastal regions. The lithogenic pollutants such as arsenic and fluoride have affected groundwater in several parts of India. Anthropogenic contamination derived from industrial effluents, fertilizers, pesticides, domestic waste water and landfills has also caused groundwater quality deterioration in various parts of the country. Systematic hydrogeological studies in Goa have been carried out since last three decades by various workers [1,2,3,4,5,6,7,8,9,10]. However, most of these studies

were focused on the influence of open cast mining on the local groundwater domains and estimation of groundwater resources. The stage of groundwater development in Goa is 33% and the entire state has been categorised as safe [11]. However, there are very few studies carried out to understand the quality of groundwater. Adyalkar carried out chemical analysis of select groundwater samples from different aquifers of South Goa [12]. Central Ground Water Board reported that about 5% area along the coast of Goa and tidal river courses has been affected by sea water ingress [13]. Widespread groundwater contaminations are witnessed all along the coastal belt [14, 15, 16]. The loads of COD, BOD, NO₃, phosphate and bacterial contents have been found to be exceptionally high in coastal groundwater in Goa [17]. Gonsalves has reported high coliform content in groundwater in Calangute area [18]. Patil has reported high cadmium and nitrate in the groundwater in the Bardez taluka [19].

The aim of the present study is to understand the quality of groundwater in Mhadei River watershed which forms an important drainage system in the State of Goa. The possible relation between rock types and water quality and pollution aspects has been envisaged.

MATERIALS AND METHODS

A. The Study Area

(i) Location: The study area watershed is a sub watershed of Mandovi River in Goa, India. It lies between latitudes N 15° 22 14.85 and N 15° 42 8.3 longitudes E 74° 02 25.6 and E 74° 25 00 covering a total area of 899 km² of which 573 km² (64%) lies in Goa and 326 km² (36%) lies in Karnataka (Fig. 1). The

climate across the watershed is tropical and is characterised by high monsoon rainfall (3933mm), moderate temperature (24-34°C) and high humidity (75-90%). Over 90% rainfall occurs during the monsoon months (June to September) while the remaining 10% rainfall is received during the non-monsoon months. Rainfall is the main source of groundwater recharge in the watershed.

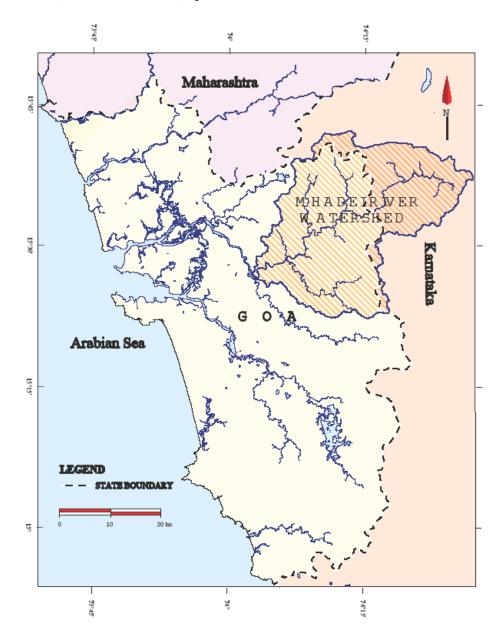


Fig. 1. Location map of Mhadei River watershed.

(ii) **Topography:** Physiographically, the Mhadei River watershed can be divided into three parts, viz., the western low lying region, the central Western Ghats escarpment and the eastern plateau region. The western region of the watershed lies in the central Midland region of Goa, this region consists of elongated hills having elevations less than 400m above mean sea level (amsl) separated by the etch plain having elevation between 30m to 100m amsl, the central part of the

watershed comprises of steep imposing hills of the Western Ghats ranging in elevation between 500m to 800m amsl while the eastern part of the watershed constitute the western fringe of the extensive Karnataka plateau (Fig. 2). The highest elevation in the watershed is 1026m amsl in the Western Ghats while the lowest elevation is near zero at the mouth of the river near Usgao. About 85% of the watershed area is covered by forest and only about 3.5% is agricultural land.

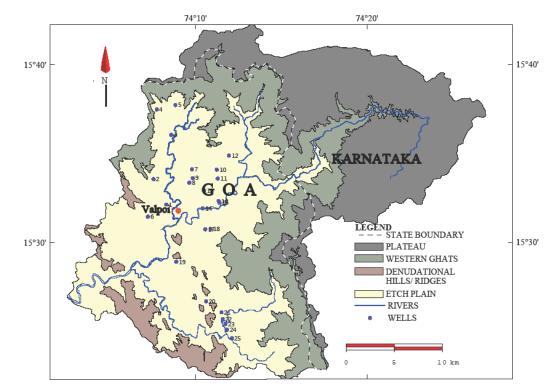


Fig. 2. Physiographic map of Mhadei River watershed.

(iii) Drainage: The Mhadei River originates at Degaon village in Khanapur taluka of Belgaum district in Karnataka. Nanode nadi, Kotrachi nadi and Ragda nadi are the major tributaries of Mhadei River. A number of smaller streams like Bail nadi, Kotni nadi, Doli nadi and Bhandura nadi also join the Mhadei River. In general, the Mhadei River watershed exhibits dendritic drainage pattern. However, most of the streams of fourth and fifth order in the western part of the watershed show a common NW-SE trend, suggesting a structural control, as the rocks in the region have a regional NW-SE trend [12]. This results in a trellis type drainage pattern in some parts of the watershed. Also, the first and second order streams flowing on the Karnataka plateau show parallel drainage pattern in the north-eastern part of the watershed as they flow on the horizontally laid Deccan Traps.

III. GEOLOGY OF THE WATERSHED

The Mhadei watershed dominantly comprises of the rocks of the Goa Group resting on the Peninsular Gneisses. Three formations of the Goa Group namely Barcem, Bicholim and Vageri Formations are exposed in the study area. They exhibit a general NW-SE trend. The rock types exposed in the study area includes gneiss, meta-basalt, quartz-sericite schist, quartzchlorite schist, pink ferruginous phyllite, BHQ with iron ore deposits, limestone and metagreywacke. The Bondla mafic-ultramafic complex represented by gabbro and pyroxenite is also exposed. The Deccan Traps (65 Ma) occur along the north-eastern margin of the study area comprising of horizontally laid basaltic flows (Fig. 3). Most of these rocks have undergone weathering to varving extent and are covered by a thick layer of laterite and/or lateritic soil.

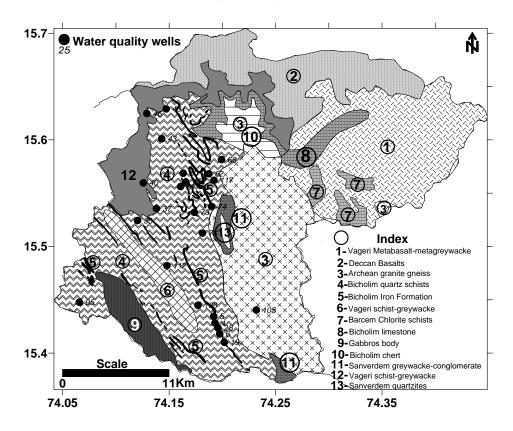


Fig. 3. Geological map of Mhadei River watershed (adopted from GSI, 1996) with observation well network.

IV. HYDROGEOLOGY OF THE WATERSHED

Laterite and valley fill deposits are the important aquifers that occur in the Mhadei watershed. Groundwater predominantly occurs in unconfined condition in these rocks. However, groundwater occurs in semi-confined condition in the fractured and weathered metamorphic rocks at depth [10]. Laterite occurs as an extensive layer capping the low lying area of the watershed that comprises of the etch-plain and the low elongated hills. However, it is often absent on the higher hills and the denudational hills of the Western Ghats.

V. HYDROCHEMISTRY

Groundwater occurs under phreatic condition over most part of the Mhadei River watershed. Open dug wells of depths ranging from 3m to 15m are used to draw water for domestic and agricultural purposes. Groundwater samples from twenty five wells were collected each during post-monsoon (November 2011) as well as during pre-monsoon (May 2012) seasons. Chemical characteristics were determined according to the analytical procedures [20]. The pH was measured in the field using pH meter. Calcium and Magnesium has been determined titrimetrically using standard EDTA. Chloride has been determined using standard AgNO₃ titration. Bicarbonate has been determined by titration with HCl. Sodium and Potassium has been determined by Flame Photometry. Sulphate has been determined by Spectrophotometric Turbidimetry. Nitrate, manganese, cadmium and chromium have been determined by Atomic Absorption Spectroscopy while iron has been determined using UV-Visible Spectrophotometry. A summary of the chemical analysis of the twenty five groundwater samples is presented in Table 1 and 2.

The pH of groundwater in the study area is acidic in nature ranging from 4.15 to 6.12 during the postmonsoon season which marginally increases to 5.12 to 7 during the pre-monsoon season. Mandrekar and Chachadi have explained following four possible geochemical reactions for low pH of groundwater in Goa [21]:

1. When ferrous iron combines with water in the presence of oxygen to precipitate iron oxide hydroxide (goethite), the reaction releases hydrogen ion resulting in lowering of pH of water.

 $4Fe^{+2} + O_2 + 6H_2O = 4FeO(OH) + 8H^+$

2. Manganese oxidation also releases hydrogen ion. $2Mn^{+2} + O_2 + 2H_2O = 2MnO_2 + 4H^+$

3. Non-availability of Ca and Mg in abundance which are buffering agents in moderating pH; thus the pH remains low.

4. Nitric acid (HNO₃) formed due to organic nitrate in soil zone releases H⁺ which reduces pH.

S.No	pН	TDS	TH	Ca	Mg	Na	Κ	HCO ₃	SO_4	Cl	NO ₃	SiO ₂	Fe	Mn	Cd	Cr
1	4.9	90	22	6.8	1.4	1.4	0.1	44	16	4.5	1.0	10.1	0.1	ND	-	-
2	6.1	30	28	6.6	2.5	4.2	0.7	18	10.2	7.5	0.3	12.1	0.1	ND	-	-
3	5.5	110	40	10.2	5.6	2.6	0.1	28	24.6	10.5	0.4	5.8	0.1	ND	-	-
4	5.1	100	24	8.6	1.0	0.8	0.9	46	8.2	7.8	1.3	8.7	0.1	ND	-	-
5	4.4	60	88	11.8	4.6	3.8	2.1	28	6.4	9.6	0.6	15.2	0.1	ND	-	-
6	4.5	50	88	10.6	4.6	4.2	0.4	24	20.1	12.6	0.9	22.5	0.1	ND	-	0.01
7	4.6	80	81	12.8	5.0	4.2	4	44	12.5	10.5	3.2	20.0	0.1	ND	-	-
8	4.6	90	53	14.2	2.8	6.1	1.8	12	17.4	12.0	1.1	18.4	0.1	ND	0.01	-
9	5.1	40	16	3.8	3.1	2.5	2.4	40	5.4	9.6	5.1	14.4	0.1	ND	0.01	-
10	4.6	60	36	6.8	3.0	5.4	0.5	36	9	7.5	0.2	12.6	0.1	ND	-	-
11	4.2	40	111	8.4	1.4	2.8	0.4	60	4.6	15.0	2.6	7.8	0.1	ND	-	-
12	5.3	30	22	5.6	2.1	4.2	1.2	60	18.4	12.0	0.6	20.0	0.1	ND	-	-
13	4.9	30	16	4.2	1.6	2.8	0.1	44	4.4	15.6	0.7	14.7	0.1	ND	0.01	-
14	4.9	10	17	5.6	0.8	3.4	1	28	10	12.6	0.6	9.5	0.1	ND	0.01	-
15	4.3	60	18	6.8	1.0	0.9	0.9	54	22.6	13.2	1.5	16.4	0.1	ND	-	-
16	4.5	10	6	3.4	0.4	4.2	1.2	30	11.7	12.0	0.1	34.5	0.1	ND	-	-
17	5.9	20	72	16.8	2.2	3.3	0.5	16	6	12.0	0.6	25.8	0.1	ND	0.01	0.01
18	5.5	10	80	12.6	3.6	4.5	0	40	26	12.6	0.7	34.7	0.1	ND	0.01	-
19	5.1	10	43	7.8	5.2	5.7	0.4	32	31.4	15.0	0.3	28.5	0.1	ND	0.01	-
20	5.2	20	17	4.8	3.1	4.2	0.7	44	14	13.8	1.1	20.4	0.1	ND	-	-
21	5.2	10	9	5.4	0.4	3.3	0.5	28	7.8	9.0	0.5	16.8	0.1	ND	-	-
22	5.7	20	12	5.8	2.3	2.4	0.5	44	14	10.8	0.7	12.5	0.1	ND	-	-
23	4.7	30	8	2.6	0.8	3.1	0.1	36	6.9	14.7	0.8	11.6	0.1	ND	-	-
24	5.2	20	40	12.6	1.1	2.1	3.1	32	12	12.0	1.5	19.0	0.1	ND	-	-
25	5.1	20	61	13.6	1.2	4.9	0.7	28	21	12.6	1.6	15.0	0.1	ND	-	0.01

 Table 1: Chemical analysis of 25 groundwater samples collected during post-monsoon season (November 2011) from Mhadei River watershed.

(Units: mg/l except pH); (ND: Not detected)

 Table 2: Chemical analysis of 25 ground water samples collected during pre-monsoon season (May 2012) from

 Mhadei River watershed.

No15.4601770.11.90.46417.07.51.16.10.1-0.01-26.2102771.05.62.03410.59.60.57.20.135.96063103.73.00.36826.213.20.52.10.10.010.010.01																	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	S.	pН	TDS	TH	Ca	Mg	Na	K	HCO ₃	SO_4	Cl	NO_3	SiO ₂	Fe	Mn	Cd	Cr
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	No																
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	5.4	60	17	7	0.1	1.9	0.4	64	17.0	7.5	1.1	6.1	0.1	-	0.01	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	6.2	10	27	7	1.0	5.6	2.0	34	10.5	9.6	0.5	7.2	0.1	-	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	5.9	60	63	10	3.7	3.0	0.3	68	26.2	13.2	0.5	2.1	0.1	0.01	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	5.6	70	23	9	0.1	1.0	1.2	108	8.4	10.5	1.6	4.0	0.1	-	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	6.0	50	63	12	3.2	5.0	2.4	32	6.7	12.6	0.9	9.2	0.1	-	-	0.01
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6	6.1	30	70	10	4.3	4.5	0.5	48	22.5	15.6	1.1	16.4	0.1	0.02	-	0.01
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	6.0	40	73	12	4.2	5.6	4.2	60	15.0	13.5	2.5	18.5	0.1	0.01	0.01	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	6.0	60	53	14	1.8	8.0	2.8	52	18.2	16.5	1.4	9.8	0.1	0.01	0.02	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9	5.5	30	16	4	0.6	3.4	2.6	100	6.8	13.2	5.5	8.6	0.1	-	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10	5.8	50	30	7	1.2	6.5	0.8	60	9.4	10.8	0.7	6.7	0.1	-	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	11	5.7	50	23	9	0.1	3.8	0.6	120	6.2	17.4	3.5	2.5	0.1	0.05	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	12	5.1	30	13	6	0.1	4.6	1.5	68	20.5	14.4	0.9	10.5	0.1	0.001	0.02	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13	5.2	20	6	3	0.1	3.2	0.3	36	7.6	16.8	1.1	5.8	0.1	0.26	0.03	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	14	5.5	20	8	5	0.5	3.4	1.2	36	12.0	15.6	0.8	4.2	0.1	-	0.01	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	15	5.4	40	17	7	0.2	1.1	1.2	100	22.8	16.2	1.8	8.1	0.1	-	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	16	5.5	10	5	4	0.5	4.8	1.4	36	14.5	15.6	0.5	21.7	0.1	-	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	17	8.6	10	68	24	0.7	4.2	0.6	16	8.5	13.8	1.0	15.6	0.1	0.02	0.02	0.01
20 5.3 30 16 4 0.7 5.4 1.0 160 16.2 15.6 1.4 13.5 0.1 - - - 21 5.5 10 8 6 0.5 3.5 0.6 28 10.7 11.4 1.0 11.4 0.1 - 0.02 - 22 5.9 10 13 5 0.1 3.8 0.7 36 16.9 13.8 0.9 9.7 0.1 0.01 - -	18	6.2	10	76	12	4.4	5.2	0.3	108	28.2	16.2	1.8	25.4	0.1	-	0.02	-
21 5.5 10 8 6 0.5 3.5 0.6 28 10.7 11.4 1.0 11.4 0.1 - 0.02 - 22 5.9 10 13 5 0.1 3.8 0.7 36 16.9 13.8 0.9 9.7 0.1 0.01 - -	19	6.1	20	78	8	5.7	6.8	0.8	136	31.8	17.4	0.6	19.8	0.1	0.01	-	-
22 5.9 10 13 5 0.1 3.8 0.7 36 16.9 13.8 0.9 9.7 0.1 0.01	20	5.3	30	16	4	0.7	5.4	1.0	160	16.2	15.6	1.4	13.5	0.1	-	-	-
	21	5.5	10	8	6	0.5	3.5	0.6	28	10.7	11.4	1.0	11.4	0.1	-	0.02	-
	22	5.9	10	13	5	0.1	3.8	0.7	36	16.9	13.8	0.9	9.7	0.1	0.01	-	-
23 5.1 20 4 3 0.3 3.2 0.4 36 7.0 16.8 1.1 8.3 0.1 - 0.02 -	23	5.1	20	4	3	0.3	3.2	0.4	36	7.0	16.8	1.1	8.3	0.1	-	0.02	-
24 5.4 20 36 13 0.4 2.4 0.4 68 13.5 13.8 1.9 10.8 0.1 0.02	24	5.4	20	36	13	0.4	2.4	0.4	68	13.5	13.8	1.9	10.8	0.1	0.02	-	-
25 6.1 30 90 14 5.5 5.3 0.9 24 23.5 15.6 2.6 9.2 0.1 0.01 0.01			30	90	14	5.5	5.3	0.9			15.6	2.6	9.2			0.01	0.01

(Units: mg/l except pH)

In the present study area, the presence of laterites rich in iron and clays rich in manganese promote for the first two reactions stated above. The carbonate rocks in Goa are almost absent thereby no contribution of Ca and Mg into the percolating water. Due to thick vegetal cover in the study area large amount of organic matrix is available in the soil zone which in turn facilitates rainwater being enriched in hydrogen ions during percolation through soil zone. The slightly more acidic water during post-monsoon is an evidence of percolating rainwater getting enriched with free hydrogen ions which are contributing in lowering the pH. During non-rainy season, as there is no percolation the availability of free hydrogen ions is less therefore the pH is slightly raised during pre-monsoon season.

The total hardness of groundwater varies from 12 to 150 mg/l in post-monsoon season and from 4 to 90 mg/l in pre-monsoon season. Though majority of the wells have soft water, some wells, viz., well no. 5, 6, 7, 11 and 18 have moderately hard water during the post-monsoon season. However, water becomes soft in most of these wells during the pre-monsoon season indicating ion exchange and adsorption of ions on clay particles in the aquifer. TDS generally varies from 10 to 110 mg/l during post monsoon suggesting low mineralisation of the groundwater in Mhadei watershed. However the TDS reduces during pre-monsoon season.

According to Douglas and Leo, three sets of major relationships exist between cations and anions in the chemistry of groundwater [22]. These are:

1. The highly competitive relationships between ions having same charge but a different valence number e.g. Ca^{+2} and Na^{+1} .

2. The affinity between ions having different charges but same valence number e g. Na^{+1} and Cl^{-1} .

3. The non-competitive relationship between ions having the same charge and the same valence number e.g. Ca^{+2} and Mg^{+2} .

The ions in Mhadei groundwater shows following relationships:

1. The highly competitive relationships: Mg^{+2} with Na^{+1} (0.40) has significant positive correlation. Ca^{+2} with Na^{+1} (0.23); Ca^{+2} with K^{+1} (0.27) and SO_4^{-2} with Cl^{-1} (0.17) have low positive correlation.

2. The affinity ions relationships: Mg^{+2} with SO_4^{-2} (0.43) has significant positive correlation. Ca^{+2} with SO_4^{-2} (0.24); Na^{+1} with CI^{-1} (0.22) and Na^{+1} with HCO_3^{-1} (0.28) have low positive correlation.

3. The non-competitive relationships: Ca^{+2} with Mg^{+2} (0.35) and HCO_3^{-1} with Cl^{-1} (0.14) have low positive correlation.

Among the cations, the order of abundance in the groundwater samples is Ca>Na>Mg>K while for the anions the order of abundance is HCO₃>SO₄>Cl. The classification of hydrochemical facies of groundwater from the Mhadei River watershed has been done using Piper's Trilinear diagram (Fig. 4) [23].

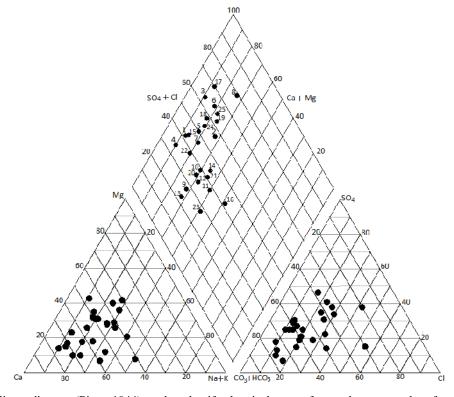


Fig. 4. Trilinear diagram (Piper, 1944) used to classify chemical types of groundwater samples of post-monsoon season from Mhadei River watershed.

All the samples lie in field 1 of the diamond shaped field of the Piper's diagram indicating predominance of alkaline earth over alkali elements both during postmonsoon as well as pre-monsoon season. Samples are distributed between fields 3 and 4 of Piper's diagram during post-monsoon season indicating equal abundance of weak and strong acids. However, most of the samples move to field 4 of the diagram during the pre-monsoon season indicating increase in strong acids over weak acids as the water flows through the aquifers.

Calcium-bicarbonate type is the most common groundwater quality type in the watershed during the post-monsoon season followed by Calcium-magnesiumchloride type. However, the groundwater becomes completely Calcium-bicarbonate type towards the onset of monsoon season suggesting precipitation of magnesium salts or adsorption of magnesium on clay particles in the aquifer by ion exchange. Alkalis (Na+K) and chloride are insignificant suggesting absence of sea water ingress in the watershed. Silica is present in significant quantities suggesting dissolution of silicate rocks in the watershed.

Gibbs (1970) suggested that plots of TDS versus the weight ratio of Na/(Na+Ca) and Cl/(Cl+HCO₃) could provide information on the relative importance of three major natural mechanisms controlling water chemistry: 1) atmospheric precipitation 2) rock weathering and 3) evaporation and fractional crystallization [24]. The composition of the groundwater in Mhadei watershed falls dominantly in the precipitation domain and partially in the rock weathering domain (Fig. 5), suggesting that the ion concentration of the water also change during its passage through the soil zone and the unsaturated zone.

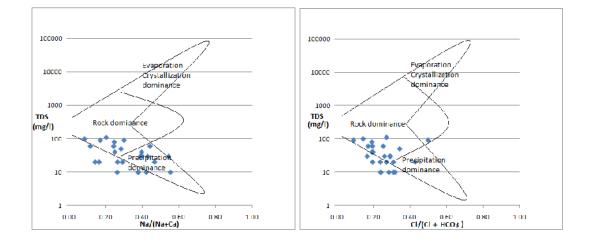


Fig. 5. Mechanism controlling chemistry of groundwater (after Gibbs, 1970).

A. Drinking water quality

All the major cations and anions are well within the prescribed drinking water quality standards by BIS and WHO [25, 26, 27]. However, the groundwater is highly acidic in nature. Low pH can facilitate dissolution of metals in water.

Nitrate is present in negligible amount in the groundwater suggesting that there are no anthropogenic and natural processes contributing nitrate in the analysed samples of the groundwater. Manganese is below detectable limit during the post-monsoon period. However, manganese is present in most of the samples during the pre-monsoon season suggesting reduction of MnO_2 formed during water percolation in the soil zone to release Mn. Water from Well no. 11 located at Nanoda village contains highest Mn content (0.05 mg/l) which is below the desirable limit of 0.1 mg/l. Manganiferous clays that occurs intercalated with phyllites and BHQ's of Bicholim Formation are likely to be the source of manganese in Mhadei watershed.

Cadmium is another heavy metal that occurs in some of the water samples. According to the WHO and BIS, the maximum contaminant level (MCL) for cadmium is 0.01 mg/l. It is observed that 11 wells of the total 25 wells in the Mhadei watershed contain cadmium at or above the desirable limit and therefore the water is toxic. These wells are located in Ambede, Carambolim, Bolcornem and Dhave villages. Cadmium can cause itai-itai disease, gastro-intestinal diseases and hypertension. It can also affect cardio-vascular system and kidneys. The source of cadmium could be both, natural (lithogenic) or anthropogenic. Cadmium occurs naturally in lead, zinc, copper and other ore minerals which can serve as sources to groundwater, especially when in contact with soft, acidic water. However, the main sources of cadmium in water are industrial activities as the metal is widely used in electroplating, pigments, plastic, stabilizers and battery industries.

In the present study area, anthropogenic sources of cadmium contamination are unlikely since there are no industries in the watershed. Therefore, the source of cadmium may be lithogenic.

B. Classification of groundwater for irrigation purpose

High salt content in irrigation water leads to formation of saline soil and affect the soil structure and permeability. This affects the water intake capacity of the plants through their roots and therefore the plant growth. According to the Salinity Laboratory of the U.S. Department of Agriculture, sodium adsorption ratio (SAR) can be considered to determine the suitability of water for irrigation purpose. Sodium adsorption ratio is a measure of relative activity of sodium ion in the exchange reaction with soil. It measures the alkali (sodium) hazard for crops and is estimated by the formula:

 $SAR = Na / ((Ca+Mg)/2)^{0.5}$

where the concentrations of all the constituents are expressed in milliequivalents per litre.

SAR of all the groundwater samples in Mhadei watershed ranges from 0.07 to 0.7 with mean values of 0.29 in post-monsoon season and 0.38 in pre-monsoon season. Thus, the groundwater in Mhadei watershed as per Richards classification [28] can be classified as low sodium water and hence is of good quality for irrigation purpose.

Wilcox [29] has classified groundwater for irrigation purposes based on percent sodium which is expressed as:

%Na = (Na + K)100 / (Ca + Mg + Na + K)

where the concentrations of all the constituents are expressed in milliequivalents per litre.

The values of percent sodium in the analysed samples range from 10 to 51 with mean values of 21 in postmonsoon season and 31 in pre-monsoon season. It is observed that during the post-monsoon season, 44% of the water samples fall in the excellent class, 48% fall in good class while 8% fall in permissible class. Whereas for the pre-monsoon season, 32% samples fall in the excellent class, 36% fall in the good class while 32% fall in the permissible class. Hence, the groundwater from the study area is suitable for irrigation purpose.

CONCLUSIONS

The quality of groundwater is governed by many factors such as physico-chemical characteristics of soil, rainfall, organic content, weathering of rocks, cation-anion exchange reactions, human and agricultural wastes and industrial effluents. The groundwater in Mhadei watershed is generally low in mineral content with all the major ions well within the permissible limits for drinking water. However, the pH of the groundwater is low. The decrease in total hardness and total dissolved solids from post-monsoon to pre-monsoon season indicate that the bases are lost by ion exchange during the flow of groundwater through the aquifer. Calciumbicarbonate type is the most common groundwater quality type in the watershed. Gibb's plot indicate that atmospheric precipitation and rock weathering are the principal mechanisms controlling the groundwater chemistry in Mhadei watershed. Small amounts of sodium and chloride indicate absence of sea water ingress in the watershed. Low nitrate content suggests that there is no anthropogenic pollution in the groundwater in Mhadei watershed. The low SAR and percent sodium indicates that the groundwater from the entire Mhadei watershed is suitable for irrigation purpose. However, the presence of cadmium in some of the wells renders the groundwater toxic for drinking purpose in these areas.

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