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Hydrochemical analysis and assessment of groundwater quality in and around Yadadri district, Telangana, India.

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ABSTRACT

This study looks at the types of groundwater and water quality in a semi-arid watershed in southern India that includes 35 settlements. In both seasons, cation concentrations (Na+> Ca2+> Mg2+> K+) and anions (HCO3- > Cl > NO3-> SO 2-> PO43-) follow a consistent pattern across most of Peninsular India. The sodium-bicarbonate-chloride (Na+-HCO3-Cl-) classifies the groundwater. The influence of natural sources on groundwater composition across the watershed's communities is demonstrated by a Pearson correlation study of important ions. The water composition of these communities, according to Gibb's plot, is the result of rock and water interaction during infiltration and aquifer storage. Due to a severe water deficit in this region, particularly during the pre-monsoon season, deep bore wells have been drilled for both home and agricultural purposes. All of the physical dimensions and chemical contents exceed the World Health Organization (WHO) and Bureau of Indian Standards (BIS) permissible limits, rendering it unsafe for drinking, domestic, or agricultural use. Around 54 percent of groundwater samples, regardless of season, are found to be unfit for irrigation (KR 1). During the post-monsoon season, groundwater from villages near the local river (Bukleru river) is only acceptable for irrigation (KR>1).

Keywords: *Groundwater Quality, Piper, Gibb's, Drinking and Irrigation.*

1. INTRODUCTION

Despite the fact that surface water covers 71% of the Earth's surface, the availability of freshwater differs by region. As a result, in many parts of the world, particularly in developing countries, groundwater use has become unavoidable (Rodell et al. 2009; Machender et al. 2014). Because of a scarcity of surface water supplies, climate change, and developments in drilling technology, groundwater use has expanded dramatically in recent decades (Satyanarayana et al. 2017; Laxman et al. 2021; Edukondal et al. 2022). According to the World Health Organization (WHO), drinking contaminated water is responsible for around 80% of all human diseases. Geogenic contamination is the primary source of groundwater pollution (Lapworth et al. 2017; Mukherjee 2018). Human actions, on the other hand, are increasing the situation, such as deep bore well drilling, unanticipated depletion from limited potential aquifers, and shrinking of recharge zones. The exponential growth of mankind has put a pressure on current groundwater resources, as well as contributing to the deterioration of water quality that humanity is experiencing in the twenty-first century (Cooley et al. 2014). Agricultural, industrial, and home uses utilise roughly one-third of the Earth's available (renewable) freshwater (Florke et al. 2013). The water used for these activities has become contaminated with a wide range of synthetic and geogenic natural compounds, creating a significant public health concern and wreaking havoc on the planet's flora and fauna (Schwarzenbach et al. 2010). Marine salt intrusion into surface water and groundwater as a result of aquifer overexploitation and sea-level rise exacerbates the problem in many coastal areas, particularly in India and China (Rodell et al. 2009; Khan et al. 2020). The Arabian Sea and the Bay of Bengal surround India, the world's most populous tropical country (17.7% of the worldwide population). The population of India has increased from roughly 330 million at independence (1947) to over 1330 million presently. India has the world's second-largest arable land area, ranks second in farm output, and is India's greatest employer, absorbing 83 percent of the country's available water resources (Venkateswarlu and Prasad 2012).

Groundwater resources are the principal supply of drinking and irrigation water in many parts of Peniunsular India, particularly in the Telangana region (Reddy et al. 2021). Water quality assessments are based on the planned use of water, with different uses necessitating different criteria. As a result, understanding its applicability for matching purposes becomes critical (Zhang et al. 2012;

Ewaid et al. 2020). Although WHO (2011) and BIS (2012) have established permissible drinking water standards, additional water quality indices based on conventional hydro-chemical procedures provide water suited for agricultural and industrial use. To that end, Horton's (1965) water quality remains one of the most effective instruments for measuring water quality and alerting citizens and politicians. As a result, assessing the groundwater quality of undocumented semi-arid streams from crystalline areas is crucial from the standpoints of public health, socioeconomics, and ecology. As a result, the current study intends to identify the geographical and temporal variability of water quality indices in order to highlight the appropriateness of surface waters from the Bukleru watershed in the Peninsular India region for drinking, agricultural, and aquatic life.

2. STUDY AREA AND GENERAL DESCRIPTION OF GEOLOGY

Musi River is one of India's most polluted urban flowing rivers and the largest independent river in Telangana, flowing through Hyderabad, a rapidly rising metropolitan city. The Musi River has two main streams, one flowing from Hyderabad and the other from Alair, both of which merge at Janakipur before joining the Krishna River at Vadapally. The Bukleru river, a tributary of the Musi river, is part of the Alair branch of the Musi river, which flows from a semi-urban area in Telangana. This river is 42 kilometers long and 385 kilometers wide (**Fig. 1**). The Bukleru watershed is home to two mandal and 45 small to medium-sized communities. The watershed has an average height of 712 meters; the top zone is associated with undulating terrains, while the lower zone is largely related with Pediplain. Geologically, the Bukleru watershed belongs to the Peninsular Gneissic complex (PGC), with intrusion of many younger rocks such as granites, dolerites, pegmatite, and among others (Machender et al. 2014; Reddy et al. 2021). The principal lineament tendencies in the research region are NE-SW, E-W, and ENE-WSW.The location has a semi-arid tropical climate with an average annual rainfall of 840 mm, which is characteristic of the Indian peninsula's shadowed region. The Bukleru watershed has a mean annual temperature of 29 °C, with summer temperatures reaching 47 °C and winter temperatures lowering 15 °C. The region's semi-arid environment, plateau topography, and scarcity of surface water resources encourage groundwater use for household, industrial, and agricultural requirements.

3. METHODOLOGY

Sample collection

For sampling, 70 groundwater samples were chosen from the 35 representative communities in the Bukleru watershed. The sample was done on both sides of the watershed (**Fig. 1**). To better depict seasonal fluctuation, samples were obtained during the pre-monsoon (May-2018) and post-monsoon (December-2018) seasons. As a result, the current study concentrated on both the spatial and temporal fluctuations of significant ions in Bukleru's 35 settlements (**Fig. 1**). The samples were generally collected from bore wells (both agricultural and household) after a free-flowing period of 10-15 minutes before being filled into pre-cleaned high-density polyethene (HDPE) bottles.

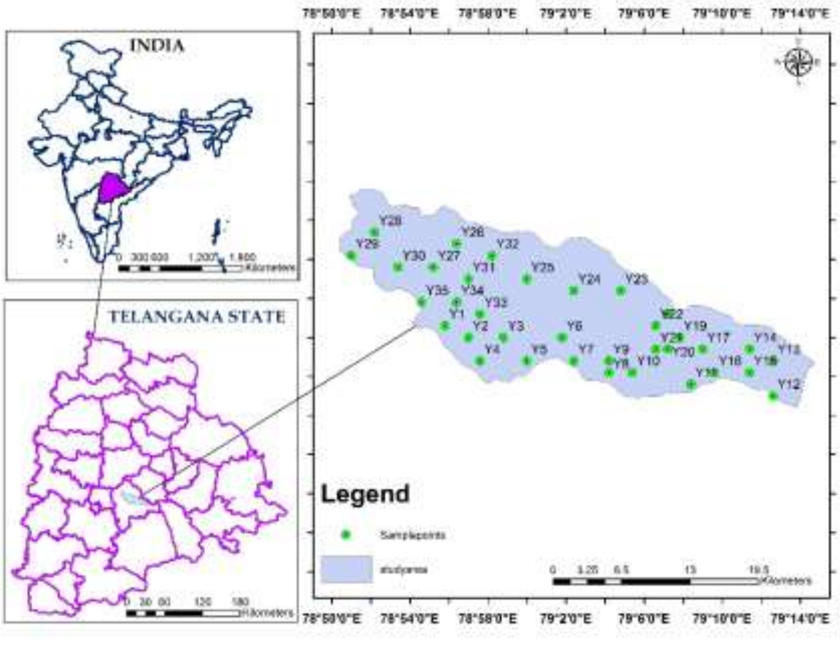

Fig. 1 Sample location map of the study area

Sample preparation

Temperature, salinity, pH, EC, and TDS were measured in situ using a portable multi probe pH meters with a precision better than 0.1. For carbonate and bicarbonate analysis, the in-situ titration method was used, as recommended by the American Public Health Association (APHA, 2005). A mild vacuum was used to filter about 100 ml of the sample using 0.45 m nylon membranes; the filtered water was stored in pre-cleaned HDPE bottles and instantly mixed with the $HgCl_2$ to stop the biological activity. After returning from the field, the samples were stored in laboratory refrigerators until they were analyzed. The principal anions and cations in the filtered water sample were evaluated in the wet chemistry lab of the Applied Geochemistry department at Osmania University.

4. RESULTS AND DISCUSSIONS

Spatial characterization of groundwater composition

Table 1 show the minimum, maximum, and mean concentrations of the commonly measured physicochemical parameters of groundwater, namely pH, EC, TDS, total hardness (TH), and main anions and cations. The pre-monsoon season's mean pH (7.8) is lower than the post-monsoon season's (7.9). (8.1). The mean EC in the pre-monsoon season (1559 S/cm) is higher than in the post-monsoon season (1282 µS/cm) (Table 1). TDS averages (905 and 821 mg l-1) from both seasons are comparable to semi-arid watersheds in peninsular India (Mondal et al. 2009; Reddy et al. 2010; Brindha et al. 2011). Regardless of the season, the concentration of cations (Na^{+}> Ca^{2+}> Mg^{2+}> K^{+}) and anions (HCO_3^{-}> Cl> NO_3^{-}> SO_4^{2}>, in all of the sampled communities, there is a consistent pattern.The somewhat greater concentrations of dissolved components in pre-monsoon seasons indicate a diluting impact after monsoon rains during the post-monsoon season (**Table 1**). The NO_3^{-} concentrations recorded are significantly higher than the WHO's allowed limit for drinking water (50 mgl-1), highlighting the involvement of sewage discharge and agricultural runoff including ammonium and N- fertilizers in the Bukleru watershed. Overall, the excess concentrations of dissolved constituents show the influence of both anthropogenic and natural sources on groundwater composition across the study region.

Table 1 Statistics of physical and chemical parameters of groundwater samples in pre and post-monsoon seasons

Parameters	Pre-monsoon season (n=35 samples)			Post-monsoon season (n=35 samples)			WHO (2011)
	Min	Max	Mean	Min	Max	Mean	
pH	7.03	8.88	8.08	7.07	8.88	8.07	6.5 - 8.5
EC	440	3600	1277	550	3160	1282	1500
TDS	282	2304	818	325	2022	821	500
Na^{+}	35	456	141	35	430	143	200
K^{+}	0	372	26	0	264	143	12
Ca^{2+}	8	232	55	8	160	53	75
Mg^{2+}	5	102	41	5	102	44	50
TH as $CaCO_3$	40	700	305	40	640	312	-
CO_3^{2-}	0	100	16	0	100	16	-
HCO_3^{-}	95	601	304	122	621	307	500
Cl^{-}	10	560	159	10	460	159	250
SO_4^{2-}	5	65	19	0	53	19	250
NO_3^{-}	1	449	85	1	518	83	45
F^{-}	0.27	4.66	1.54	0.52	4.66	1.54	1.5
Gibb's ratio I	0.05	0.87	0.43	0.05	0.87	0.43	-
Gibb's ratio II	0.28	0.96	0.64	0.35	0.96	0.64	-
SAR (meq/L)	0.76	16.12	4.26	0.76	16.12	4.21	-
%Na (mg/L)	14.13	92.78	50.69	14.13	92.78	49.41	-
RSC (meq/L)	-12.24	7.61	-0.57	-7.67	7.61	-0.68	-
KR (meq/L)	0.16	12.75	1.76	0.16	12.75	1.69	-

NOTE: Min-Minimum, Max-Maximum, Mean, CAI-Chloro Alkaline Indices, KR-Kelley's Ratio, MH- Magnesium Hazard and PI-Permeability Index

Statistical analysis

The main ions in groundwater may come from a variety of sources, including lithological, precipitation, anthropogenic, and biological inputs (Le et al. 2019). The bivariate analysis uncovers the interrelationships between the measured parameters and offers information about the key ion sources (Noori et al. 2010). In all seasons, Pearson correlation analysis of key ions shows that EC and TDS have substantial positive correlations (p 0.01) with the remainder of the variables (excluding NO^{3-}) (**Table 2a and 2b**). In both seasons, a strong relationship (p 0.01) is detected between alkaline earth elements (Ca^{2+} and Mg^{2+}) and alkalis (Na^{+} and K^{+}). Both seasons show a strong positive connection of Cl with Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} (p 0.01; **Table 2a**). Precipitation dominance is shown by a positive correlation of Cl- with the main anions and cations (Li et al. 2007). Overall, the pattern of adjustments indicates that the source of water rock interaction is the dissolved constituents in the research region's groundwaters. The presence of large amounts of HCO_3^{-} in groundwater indicates a substantial connection between infiltrating groundwater and the underlying lithology, and hence the composition of parent minerals, which supply Ca^{2+} and Mg^{2+} ions to groundwater. The predominance of silicate lithology (> 90%) and the positive connection between Ca^{2+}, Mg^{2+}, and HCO_3^{-} (**Table 2b**) support the intensive water-rock interaction and concomitant release of dissolved elements (Leaching of silicate rocks).

Table 2a Correlation matrix of the study area in pre-monsoon season

Parameters	*pH*	*Cond.*	*TDS*	*Na^+*	*K^+*	*Ca^{+2}*	*Mg^{+2}*	*CO_3^-*	*HCO_3^-*	*Cl^-*	*SO_4^{-2}*	*NO_3^-*	*F^-*	*TH*
pH	1.00													
Cond. µS/cm)	0.05	1.00												
TDS (mg/l)	0.05	1.00	1.00											
Na^+ (mg/l)	0.38	0.79	0.79	1.00										
K^+ (mg/l)	0.13	0.80	0.80	0.62	1.00									
Ca^{+2} (mg/l)	-0.54	0.32	0.32	-0.11	0.08	1.00								
Mg^{+2} (mg/l)	-0.14	0.55	0.55	0.14	0.32	0.14	1.00							
CO_3^- (mg/l)	0.77	-0.02	-0.02	0.30	0.09	-0.31	-0.38	1.00						
HCO_3^- (mg/l)	0.48	0.67	0.67	0.74	0.63	-0.22	0.34	0.20	1.00					
Cl^- (mg/l)	-0.23	0.88	0.88	0.58	0.58	0.49	0.62	-0.24	0.29	1.00				
SO_4^{-2} (mg/l)	-0.14	0.93	0.93	0.72	0.72	0.35	0.52	-0.13	0.52	0.87	1.00			
NO_3^- (mg/l)	-0.22	0.86	0.86	0.56	0.80	0.52	0.35	-0.12	0.41	0.74	0.84	1.00		
F^- (mg/l)	0.48	-0.14	-0.14	0.23	-0.21	-0.38	-0.26	0.59	0.21	-0.30	-0.19	-0.30	1.00	
TH as CaCO3	-0.45	0.58	0.58	0.02	0.27	0.75	0.76	-0.46	0.08	0.74	0.58	0.58	-0.43	1.00

Table 2b Correlation matrix of the study area in post-monsoon season

parameters	*pH*	*Cond*	*TDS*	*Na*	*K*	*Ca*	*Mg*	*CO3*	*HCO3*	*Cl*	*SO4-2*	*NO3*	*F*	*TH*
pH	1.00													
Cond	-0.04	1.00												
TDS	-0.04	1.00	1.00											
Na	0.27	0.80	0.80	1.00										
K	0.35	0.69	0.69	0.52	1.00									
Ca	-0.62	0.39	0.39	-0.05	0.06	1.00								
Mg	-0.37	0.51	0.51	0.01	0.19	0.34	1.00							
CO3	0.79	0.14	0.14	0.43	0.34	-0.34	-0.40	1.00						
HCO3	0.14	0.68	0.68	0.70	0.47	0.20	0.08	0.24	1.00					
Cl	-0.26	0.85	0.85	0.55	0.43	0.46	0.69	-0.11	0.33	1.00				
SO4-2	-0.20	0.85	0.85	0.60	0.66	0.38	0.48	0.01	0.39	0.78	1.00			
NO3	-0.06	0.69	0.69	0.47	0.66	0.24	0.38	0.03	0.17	0.49	0.71	1.00		
F	0.28	-0.03	-0.03	0.30	-0.18	-0.22	-0.33	0.48	0.27	-0.20	-0.12	-0.21	1.00	
TH	-0.59	0.55	0.55	-0.02	0.16	0.77	0.86	-0.45	0.16	0.71	0.53	0.38	-0.34	1.00

Hydrogeochemical classification of groundwater

Piper's trilinear diagram (Piper 1953) is a graphical representation of analytical data used to demonstrate the dominating hydro-chemical facies of detected main ions in groundwater. Piper diagrams for pre-monsoon and post-monsoon seasons are plotted based on essential needed constituent ionic concentrations (meql-1). The combined cation and anion composition of groundwater is shown by the diamond-shaped field between the two triangles in the piper plot. The Piper plots show that groundwater are primarily categorized into three types: In the pre-monsoon season, (I) Na^+-Cl^-, (II) mixed Ca^{2+}-Mg^{2+}-Cl^-, (III) Ca^{2+}-Na^+-HCO_3^-, and four types: During the post-monsoon season, (I) Ca2+-HCO3-, (II) mixed Ca2+-Mg2+-Cl-, (III) mixed Ca2+ Na+-HCO3-, and (IV) Na+-HCO3- were measured. According to the clustering pattern, alkaline Earth (Ca^{2+} + Mg^{2+}) outnumbers alkalis (Na^+ + K^+), while weak acids (CO_3^- + HCO_3^-) outnumber strong acids (SO_4^{2-} + Cl^-). As a result of the current investigation, it is possible to conclude that the groundwaters in the Bukleru watershed are primarily of the calcium-bicarbonate-chloride (Ca^{2+}-HCO_3^--Cl^-) type. The Piper diagrams indicate that in both seasons, a relatively small number of samples are placed in no prominent area, suggesting the dominance of Na^+ and Cl^- ions in dissolved ion concentrations (**Fig. 2**). Ca^{2+} is the most abundant cation in the pre-monsoon season, followed by Na^+ and K^+ in the non-monsoon season.

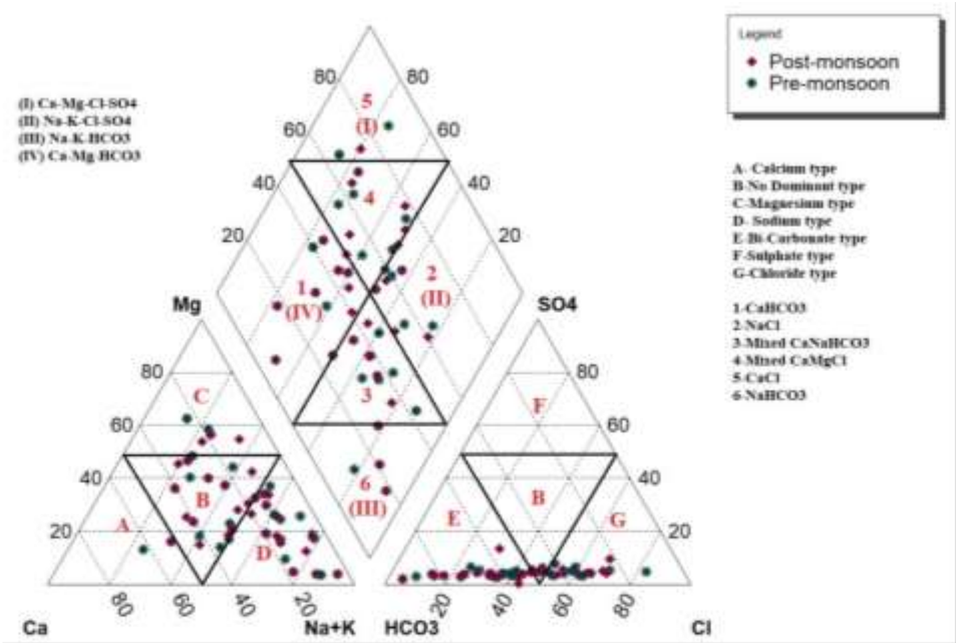

Fig. 2 Piper Trilinear diagram in pre and post-monsoon season

In terms of anions, regardless of season, Cl^- dominates the ionic concentrations in the groundwaters of the research region. Gibbs (1970) identified three key systems that regulate the chemical composition of Earth's seas. To determine the source of significant ions in groundwater, Gibbs diagrams are constructed during the pre-monsoon and post-monsoon seasons. According to Gibbs diagrams, the bulk of samples from the Bukleru watershed are in the transaction zone of rock dominance and evaporation dominance (Fig. 3).It is consistent with groundwater research in Peninsular India watersheds, where clustering is observed at the rock-dominance to evaporation-dominance transition zones (Mondal et al. 2009; Reddy et al. 2010; Brindha et al. 2015). In the case of groundwater, extended water-rock interactions during infiltration and storage in aquifers may result in high dissolved components; consequently, clustering occurs in the rock dominance zone. Overall, the Gibbs diagrams, indicate that water-rock interaction, saturated mineral dissolution, and chemical weathering of rock-forming minerals influence groundwater composition across the study region.

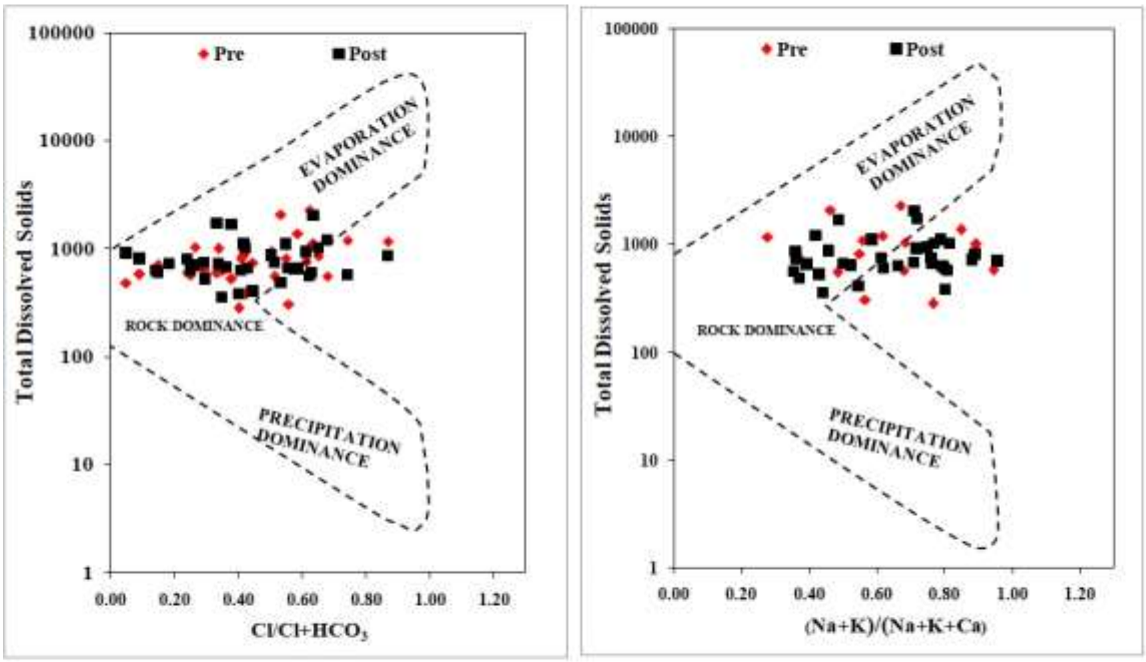

Fig. 3 Gibb's plot in the pre and post-monsoon seasons

Suitability of groundwater quality for drinking

The groundwater potability (drinking and domestic uses) of this semi-arid Peninsular India region is evaluated by comparing the measured physicochemical and hydro-chemical constituents to the desirable and maximum permissible limits recommended by the WHO and BIS for each individual quality parameter. The pH value indicates that the groundwater in this area is alkaline (Table 1). Regardless of season, the bulk (> 90%) of the samples had a pH value greater than 7.It suggests that the bulk of groundwater in the Bukleru watershed is alkaline, which is consistent with the majority of studies from the Peninsular India region (Brindha et al. 2015; Reddy et al. 2021). The elevated pH in this groundwater could be attributed to the release of significant ions during water-rock contact (**Table 1**). The majority (94 percent) of the samples have EC >500 S cm-1, indicating that the groundwater in the research location is over the allowable limits.Furthermore, all of the groundwater's TH (Ca^{2+} + Mg^{2+}) values above the allowable limit (100 mg l-1). According to the statistics in Table 1, all of the measured parameters are significantly higher above the permitted limits indicated by WHO (2011) and BIS (2012). The current study's findings indicate that the groundwater in this semi-arid watershed is unfit for drinking and domestic use.

Suitability of groundwater quality for irrigation

Around 85 percent of the study region is covered by agricultural land, with groundwater serving as the primary source of irrigation. It necessitates determining the appropriateness of groundwater for irrigation purposes. The semi-arid climate in the study region, along with good terrain, supports substantial agricultural activity, and the shortage of surface water forces the local community to rely on groundwater as a primary source of irrigation (Edukondal et al. 2022). India is one of the saltiest countries in the planet.There are numerous irrigation water quality indicators described in the literature for monitoring water quality while dealing with sodium threat (Joshi et al. 2009; Katyal 2011; Tyagi et al. 2013; Singh et al. 2015). The commonly measured irrigation water quality parameters such as sodium adsorption ratio (SAR; Richards 1954), sodium percentage (percent Na; Wilcox 1955), residual sodium carbonate (RSC; Eaton 1950), magnesium hazard ratio (MHR; Raghunath 1987), and Kelly ratio (KR; Kelley 1946) are calculated using the given Eqs. (1-5), respectively (meq-1).

Table 3 displays statistics for the indices stated previously. SAR is a metric used to compare the thickness of water for sodium ions to calcium and magnesium ions. It is critical because the use of high sodium concentration water for irrigation reduces agricultural soil permeability and structure (Richards 1954). The majority (96%) of the estimated SAR values for groundwater fall within the excellent category (10) range. According to Wilcox (1955), the appropriateness of all-natural water for irrigation purposes is determined by Na percent values.Only 1% (20), 26% (20-40), and 44% (40-60) of the surface water samples examined for Na percent levels fit into the excellent, good, and permissible categories, respectively (**Table 3**). It demonstrates that 29 percent (> 60) of groundwater samples are inappropriate for Na percent measurements (Table 3). The Na percent values in the examined villages are greater in the pre-monsoon seasons than in the post-monsoon samples. It could be due to dilution by fresh water during the post-monsoon season, especially in settlements along the Bukleru river. The RSC assesses the carbonate content of the waters (Eaton 1950).

Approximately 84 percent of the samples obtained in both monsoons followed the good category value (RSC 1.25), indicating irrigation appropriateness. Excess magnesium in water also has an impact on agricultural soils, rendering them unsuitable for irrigation (Raghunath 1987). The majority of the samples (64 percent) from the surveyed villages have MAR more than 50%, indicating that groundwater is unsuitable for irrigation (**Table 1**). Furthermore, regardless of season, the estimated KR values suggest that around 54 percent of the groundwater samples are inappropriate for irrigation (KR > 1). Reactively, half of the samples (46%) are determined to be suitable (KR 1) for irrigation, especially during the post-monsoon season. Overall, the majority of indices indicate that the groundwaters in the study region are unsuitable for irrigation. Sodium toxicity is measured in natural waters as a result of elevated sodium as Na percent and SAR ratios. For the pre-monsoon and post-monsoon seasons, SAR and Na percent values are plotted against EC (salinity hazard) (Wilcox diagrams, Wilcox 1995). The EC and Na percent values of the groundwater samples in the Wilcox Plot (**Fig. 4**) reveal that a relatively limited number of samples are excellent to good.The majority of the sample falls under the categories of good to permissible and good to dubious. Furthermore, a small number of samples from the surveyed communities fall into the questionable to inappropriate group. Overall, the Wilcox diagram supports the unsuitability of groundwater for irrigation.

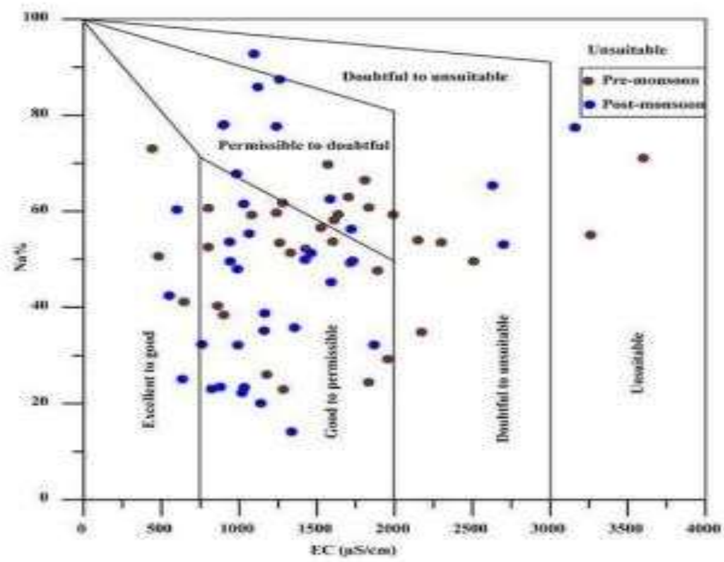

Fig. 4 Wilcox diagram of the study area

5. CONCLUSIONS

The groundwater of the Bukleru watershed in the semi-arid peninsular India region is alkaline, according to this study, especially during the pre-monsoon season. The majority of the groundwater in the research area is in the no-dominance zone, indicating that the principal ions are in balance. The major ions were distributed as follows: Na+> Ca2+> Mg2+> K+) and HCO3- > Cl > NO3-> SO2- > PO43-. The measured groundwater samples from the Bukleru watershed all exceed the WHO and BIS permissible limits, making them unsafe for drinking and domestic use. The catchment's lithological changes, together with the environment (poor rainfall and high temperatures), enable considerable chemical weathering. Dissolved constituent concentrations are regulated by the semi-arid environment, plateau topography, and rock-water interaction. The results of the factor analysis show that the region with the most geogenic and anthropogenic major inputs to groundwater contamination. Water-rock interaction during infiltration and aquifer storage, particularly during the post-monsoon season, demonstrates this. The majority (95 percent) of the groundwater in the Bukleru watershed is unsuitable for irrigation, according to generally usable irrigation water quality indexes.

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