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Suchismita Senapati

PhD Scholar, Department of
Earth Sciences, Jyoti Vihar,
Sambalpur University,
Sambalpur, Odisha, India

Dr. Nandita Mohanta

Professor, Department of
Geology, Utkal University,
Vanivihar, Bhubaneswar,
Odisha, Odisha, India

Dr. Babita Bakhara

Guest faculty, Department of
Earth Sciences, Jyoti Vihar,
Sambalpur University,
Sambalpur, Odisha, Odisha,
India

Dr. Subhasmita Parida

Lecturer, Department of
Geography, Udaynath
Autonomous College of Science
and Technology, Adaspur,
Cuttack, Odisha, Odisha, India

Corresponding Author:

Suchismita Senapati

PhD Scholar, Department of
Earth Sciences, Jyoti Vihar,
Sambalpur University,
Sambalpur, Odisha, India

Hydrochemical analysis and evaluation of the suitability of groundwater for irrigation purposes in khariar blocks of Nuapada district, Odisha, India

Suchismita Senapati, Nandita Mohanta, Babita Bakhara and Subhasmita Parida

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Abstract

Groundwater serves as a key source of drinking water in Nuapada District, Odisha, and supports the region's agricultural practices, particularly under irregular rainfall conditions. It acts as a critical resource for irrigation, sustaining both livelihoods and crop productivity. Therefore, the sustainable management of groundwater is vital to maintain its long-term availability, especially in light of the rising population and increasing water demand. The present study was conducted in the Khariar Block of Nuapada District, Odisha (India), with the primary objective of assessing groundwater quality and determining its suitability for irrigation. A comprehensive hydrochemical investigation was undertaken to gain insights into the physicochemical characteristics of groundwater in the region. During the pre-monsoon season of 2019, water samples were collected from various locations within the study area for detailed analysis. The samples were analyzed for physical parameters such as pH, electrical conductivity (EC), and total dissolved solids (TDS), along with chemical constituents including calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), and fluoride (F^-). The irrigation suitability of groundwater was evaluated using multiple standard indices, namely the Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), Percent Sodium ($\text{Na}\%$), Permeability Index (PI), Potential Soil Salinity (PSS), Magnesium Ratio (MR), and Kelly's Ratio (KR). To interpret the hydrochemical facies and geochemical processes influencing water quality, Piper's trilinear diagram and Gibbs diagram were employed. The Gibbs diagram revealed that most of the groundwater samples fall within the rock dominance zone, indicating that rock-water interactions play a significant role in controlling the groundwater chemistry. The analysis of irrigation indices, particularly SAR and $\text{Na}\%$, suggested that the groundwater in the area is generally suitable for irrigation purposes. However, elevated concentrations of nitrate and fluoride were detected in several samples, posing potential health and agricultural concerns. The primary sources of these contaminants are likely soluble chemical fertilizers and livestock waste infiltration into the subsurface aquifer system.

Keywords: Groundwater quality, Statistical and GIS method, SAR, Khariar block

Introduction

Groundwater and surface water are essential for agricultural irrigation (Worqlul *et al.*, 2017) [25]. Groundwater is an essential source of water for many countries, serving both rural and urban areas (Mansour *et al.*, 2020) [19]. The steady increase in the global population has led to a growing demand for water across agricultural, domestic, industrial, environmental, and recreational sectors. With finite freshwater resources, this escalating need underscores the importance of efficient management and regulation of water supplies, especially when the water is meant for human consumption. (Kumar *et al.*, 2017; Bhardwaj and Sam, 2022) [13, 6]. Polluted water can cause numerous serious and long-term health problems, such as gastrointestinal disorders, cholera, and various waterborne infections. (Ali *et al.*, 2021) [1]. In many regions, particularly in developing countries, access to clean water is limited, contributing to high mortality rates, especially among vulnerable populations like children and the elderly.

The impacts of inadequate water quality extend beyond immediate health issues; they also affect education, economic stability, and overall community well-being. Efforts to improve water quality such as infrastructure development, water purification technologies, and public

health initiatives are crucial for preventing illness and promoting healthier communities (US Environmental Protection Agency (USEPA, 2007, Li & Wu, 2019 and Aly *et al.*, 2015) [24, 14, 3]. The chemical characteristics of groundwater are shaped by a range of hydrogeochemical interactions and processes occurring within the subsurface environment. (Davis *et al.*, 1966) [8]. Comprehending these processes is crucial for evaluating groundwater quality and its interaction with the surrounding geological formations. Additionally, such geochemical mechanisms play a significant role in causing the spatial and temporal variations observed in groundwater composition. (Ali *et al.*, 2016) [2].

Regular spatiotemporal monitoring and evaluation of groundwater are vital to ensure its safe and sustainable utilization, especially for drinking and irrigation. The hard rock landscape of the Khariar Block, located within the Eastern Ghats and the Chhattisgarh Plateau, depends predominantly on groundwater resources to meet these essential needs. The marginal contributions of fluoride in groundwater primarily arise from the natural dissolution of fluoride- and nitrate-due to excesses use of fertilizer in agricultural land. (Dhakate *et al.*, 2021) [10]. In granitic aquifers, rock-water interactions are the primary source of fluoride contamination (Nakayama *et al.*, 2022) [20]. Moreover, human activities, including the discharge of fly ash from fossil fuel burning, also lead to increased fluoride levels in groundwater (Aslam *et al.*, 2024) [5].

Geographic Information Systems (GIS) are increasingly recognized as a valuable tool for addressing diverse problems and managing geographical data holistically. They effectively capture the spatiotemporal variability that is

crucial for assessment and decision-making (Pandey *et al.*, 2020) [21]. The main aim of this research is to evaluate the quality of groundwater for drinking purposes, with a special focus on the use of GIS-based techniques. For this assessment, 15 key water quality parameters were analyzed, including pH, electrical conductivity (EC), total hardness (TH), total dissolved solids (TDS), total alkalinity (TA), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), nitrate (NO_3^-), bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}), fluoride (F^-), and iron (Fe). These parameters were selected to comprehensively assess groundwater quality. Consequently, this study seeks to evaluate the marginal dynamic behaviour of fluoride and nitrate in groundwater using a qualitative approach, alongside statistical analysis and vulnerability assessments related to irrigation.

2. Materials and Methods

2.1 Study area

Khariar Block is situated in the southeastern part of Nuapada District, Odisha, along the southeastern edge of the Chhattisgarh Plateau. The region experiences a tropical monsoon climate with hot and humid summers, where daytime temperatures range from 35 to 40°C, while winter temperatures vary between 12 and 25°C. The average annual rainfall is approximately 1247 mm. Geographically, Khariar Block is bounded by Komna Block to the north, Boden Block to the west, and Sinapali Block to the south, covering a total area of about 412 sq. km (Fig. 1). The average elevation of the study area is around 560 meters above mean sea level (MSL).

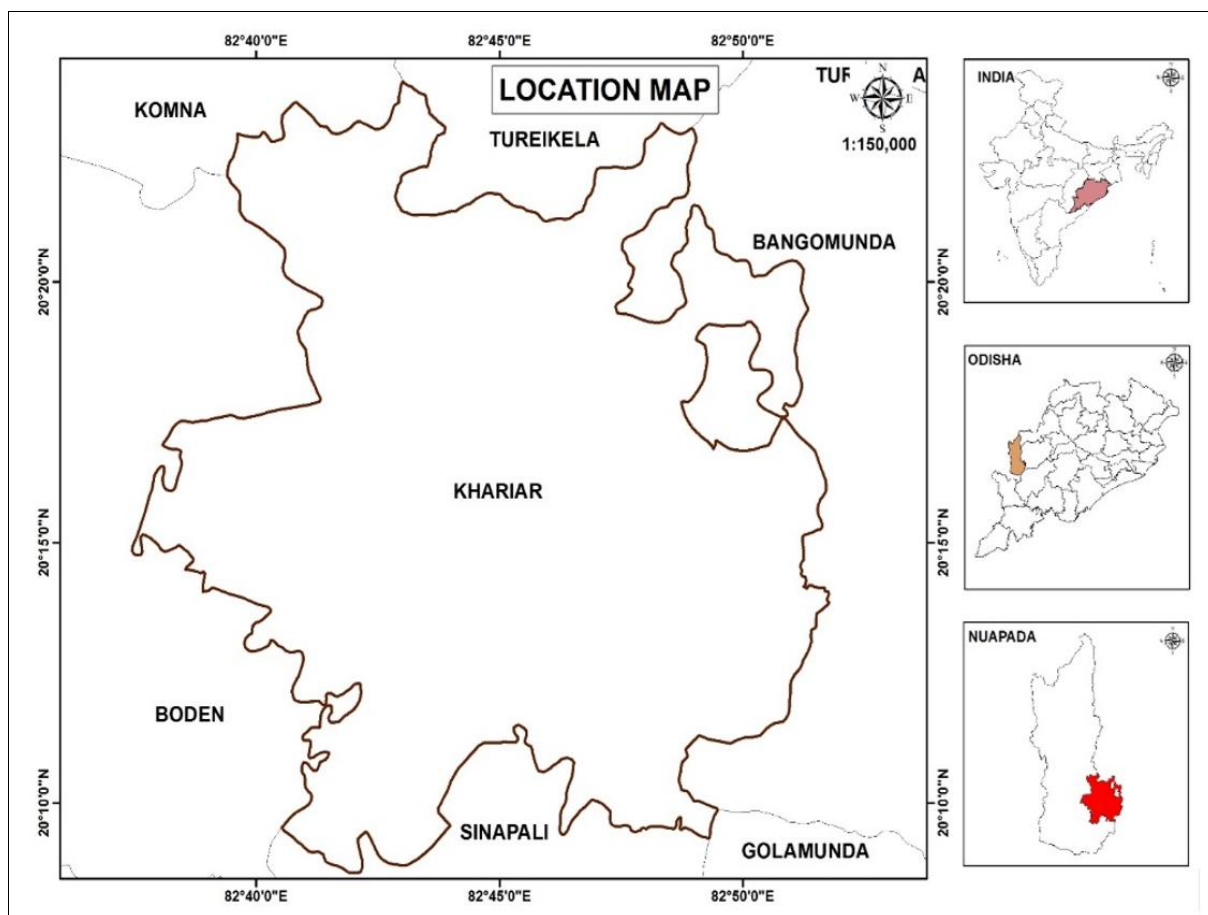


Fig 1: Location map of the study area.

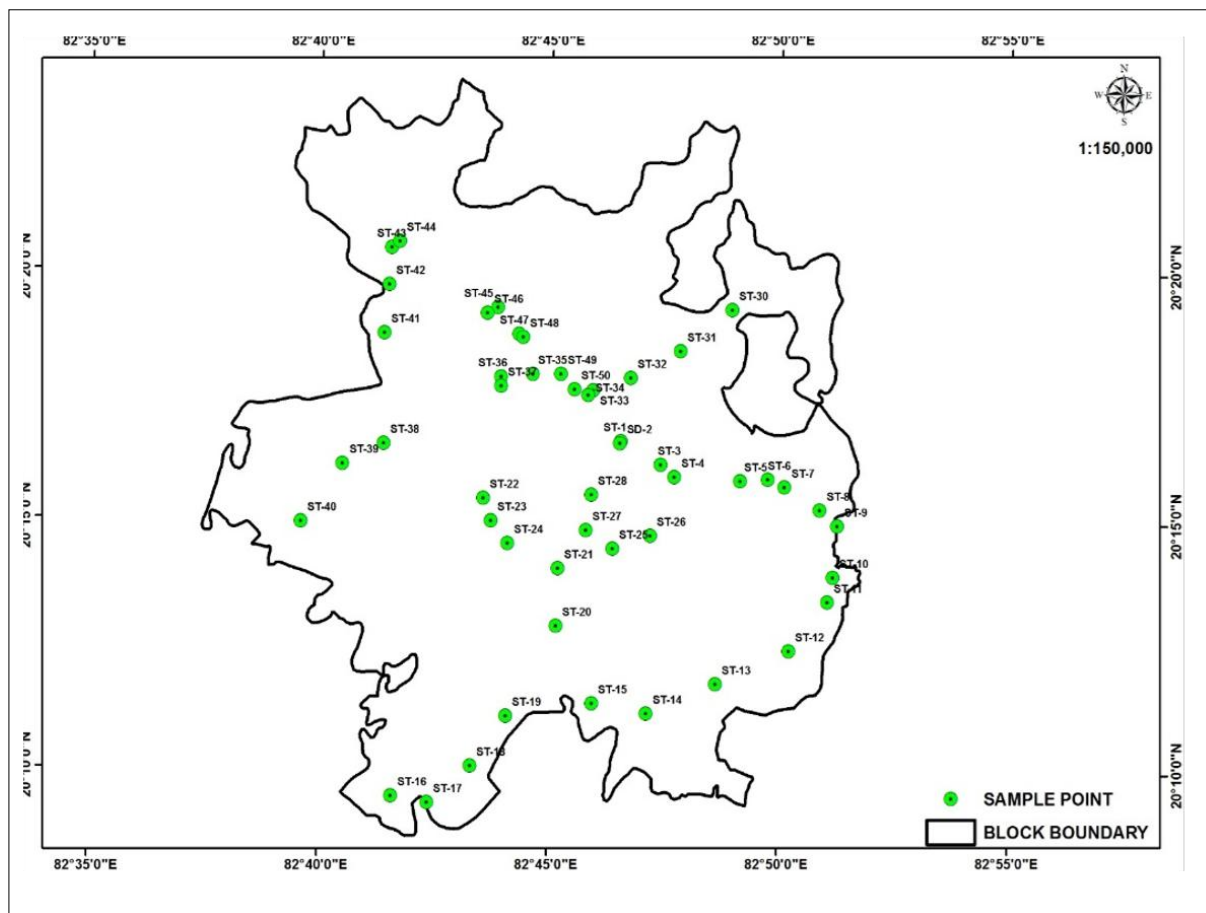


Fig 2: Sample Location map of the study area.

2.2 Sample collection and physiochemical analysis

Various types of data were utilized to evaluate the groundwater quality of Khariar Block, Nuapada, Odisha. The study area uses the Universal Transverse Mercator (UTM) projection, zone 44N, with the WGS 1984 datum. The research involved both fieldwork and laboratory investigations, including the collection of groundwater samples from hand pumps and dug wells at different locations. A total of 50 groundwater samples were collected following the standard procedures outlined by APHA (1995). The sampling locations were recorded using a Global Positioning System (GPS) and mapped on a geo-referenced map (Fig. 2). The collected samples were analyzed for fifteen key water quality parameters according to APHA (1995) standards, and the statistical analysis of these parameters is presented in Table 1.

Groundwater samples were collected from 50 locations in Khariar Block, Nuapada District, Odisha, during the pre-monsoon season. The samples were preserved in pre-cleaned, one-litre high-density polyethylene (HDPE) bottles to maintain their integrity for analysis. (Dupont *et al.*, 2020; Liu *et al.*, 2021) [11, 15]. Subsequently, the collected samples were transported to the laboratory for chemical analysis.

All chemical parameters were analyzed using the standard methods recommended by the American Public Health Association (APHA, 2012). Sulfate (SO_4^{2-}) and nitrate (NO_3^-) concentrations were determined using a UV-visible spectrophotometer, while chloride (Cl^-) was measured by the AgNO_3 titration method. Magnesium (Mg^{2+}) was calculated using the formula: Magnesium Hardness (MgH) = Total Hardness (TH) - Calcium Hardness (CaH) Mg^{2+} (mg/L) = $\text{MgH} \times \text{Equivalent weight of } \text{Mg}^{2+} \times \text{Normality}$

of EDTA. The total hardness (TH as CaCO_3) and calcium (Ca^{2+}) were estimated by EDTA titration method.

Total hardness (TH as CaCO_3) and calcium (Ca^{2+}) were determined using the EDTA titration method, and sodium (Na^+) and potassium (K^+) concentrations were measured with a Systronics flame photometer.

A standard method using sulfuric acid (H_2SO_4) and methyl orange indicator was employed to determine bicarbonate (HCO_3^-). Fluoride (F^-) was measured using the ion-selective electrode technique, specifically an Orion fluoride electrode connected to an Orion electrometer (Ali *et al.*, 2016; Rena *et al.*, 2022). Calibration standards of fluoride (0.1-10 mg/L) were prepared from a 100 mg/L sodium fluoride stock solution. For measurement, 2 mL of total ionic strength adjustment buffer (TISAB III) was added to 20 mL of each sample as required for the analysis.

2.3 Statistical Method

Assessing the chemical quality of groundwater for irrigation purposes involves several statistical methods to analyse and interpret water quality data. Here's an overview of key steps and methods; Collect groundwater samples from various locations and depths. Determine key chemical parameters including pH, electrical conductivity (EC), total dissolved solids (TDS), major ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^-), and heavy metals. Calculate mean, standard deviation, minimum, and maximum for each parameter. Assess relationships between different chemical parameters (e.g., Na^+ vs. EC) using correlation coefficient. Based on statistical analysis, provide recommendations for irrigation practices or necessary interventions. Employing these statistical methods allows for a comprehensive assessment

of groundwater quality for irrigation purposes, ensuring that agricultural practices are sustainable and safe. It's essential to adapt the methods based on local conditions and specific research goals.

3. Result and Discussion

3.1 Hydrochemical results

The Hydrochemical analysis are given in Table-1, which shows pH concentration of the study area varies from 6.49-7.64 and average value is 7.24, that indicates the water is slightly alkaline. TDS varies from 143-1090 mg/l. and Average value is 546.5 mg/l, which indicates fresh water. Electrical conductivity is the measure of dissolved ion and salinity. EC value in water is high due to leaching of aquifer material. The EC value of the area varies from 255-1710 $\mu\text{mho/cm}$ and average value is 871 $\mu\text{mho/cm}$. Total Hardness of the area varies from 92.07-696.56 mg/l and Average value is 349.43 mg/l, it shows the water is very hard. The fluoride concentration in the study area ranges from 0.1 to 3.04 mg/L, with an average of 0.88 mg/L, primarily originating from granite formations. Nitrate levels vary between 0.08 and 142 mg/L, averaging 50.77 mg/L, largely resulting from the overuse of fertilizers in agricultural fields.

Table 1: Statistical analysis of the data

Parameter	Min	Max	Mean	Std.dev
pH	6.49	7.64	7.24	0.24
EC	255	1710	871	347.26
F ⁻	0.1	3.04	0.88	0.57
TH	92.07	696.56	349.43	146.21
Ca ²⁺	24.05	200.4	78.06	35.93
Mg ²⁺	5.83	108.86	37.13	24.87
CO ₃ ²⁻	0	0	0	0
HCO ₃ ⁻	48	540	327.52	109.14
TA	48	540	326.56	109.79
Cl ⁻	12.00	339.89	78.46	69.82
SO ₄ ²⁻	2.69	102.86	29.98	25.59
Na ⁺	6.49	219.63	54.13	35.63
K ⁺	0.04	55.74	1.75	7.88
Fe	0.006	2.36	0.36	0.49
NO ₃ ⁻	0.08	142	50.77	42.4
TDS	143	1090	546.5	209.98

All the samples are expressed in mg/l except pH and EC

3.2 Sodium Adsorption Ratio (SAR)

The Sodium Adsorption Ratio (SAR) is an important parameter for evaluating water suitability for irrigation, as it reflects the balance of sodium relative to calcium and magnesium in the water. It helps predict the potential for sodium to affect soil structure and permeability (Mahanta *et al.*, 2016, Mahanta *et al.*, 2020, Mahanta *et al.*, 2020) [16, 17, 18]. From the analysis it is found that all 50 samples are fall in to excellent category. That means the water is suitable for irrigation.

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

All values are expressed in meq/L.

US Salinity diagram is mostly used for irrigation of water. In this diagram SAR is plotted against EC (fig10). From this diagram it is observed that 15% samples belong to C1S1 class, 55% sample belongs to C2S1 class, 22% sample

belongs to C3S1 class and 8% sample belongs to C4S1 class. This indicates that all the samples are of good quality.

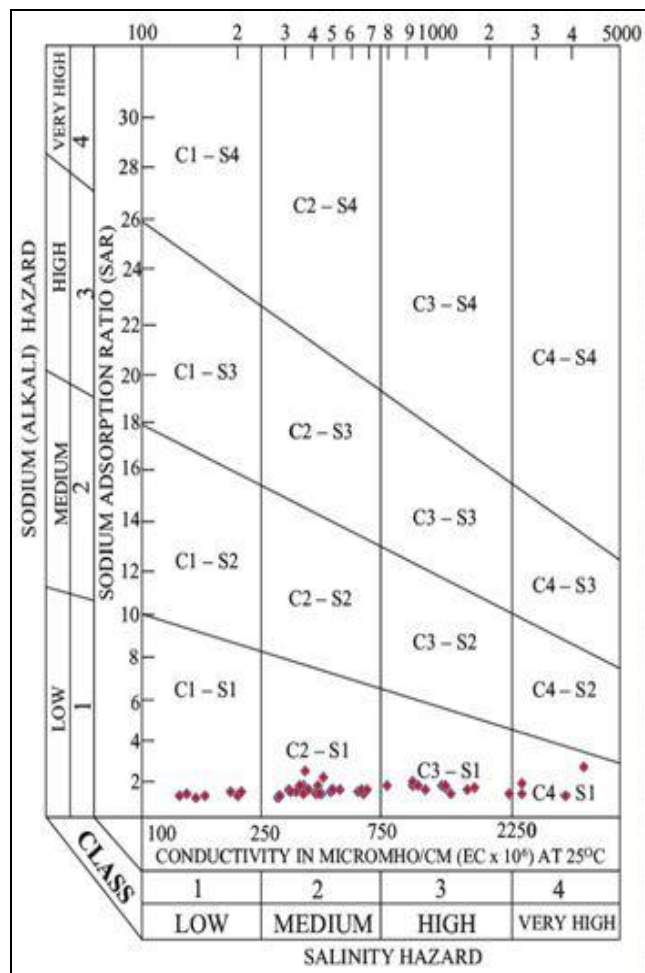


Fig 3: US salinity diagram of the sample

3.3 Percent Sodium (%Na)

Percent Sodium (%Na) is a crucial parameter for assessing irrigation water quality, representing the proportion of sodium relative to the total cations in the water. This measure helps determine the potential effects of sodium on soil structure and crop yield. In the present study (Mahanta *et al.*, 2020) [17], the results show that 18% of the samples are classified as excellent, 46% as good, 28% as permissible, and 8% as doubtful.

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

All values are expressed in meq/L.

The Wilcox (1948) [26] diagram elucidates percent sodium and electrical conductivity to classify groundwater (Fig.4), can be divided into five divisions (excellent to good, good to permissible, permissible to doubtful, doubtful to unsuitable and unsuitable). A high sodium ratio can indicate potential soil dispersion, reducing water infiltration and harming plant growth. Monitoring Na% helps in making informed decisions about water use in agriculture (Mahanta *et al.*, 2020) [17]. The diagram shows that 8% of the samples fall within the excellent to good category, 54% within good to permissible, 22% within doubtful to unsuitable, and 2% within permissible to doubtful.

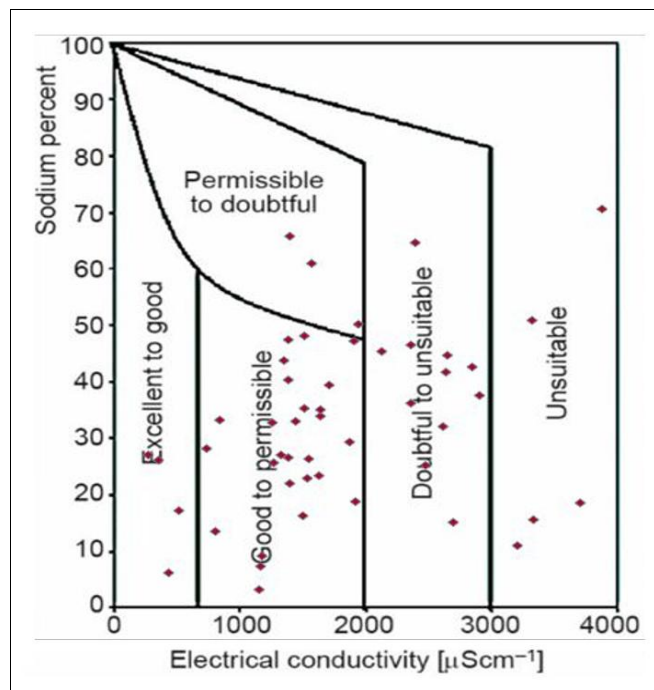


Fig 4: Wilcox diagram of the sample

3.4 Permeability index (PI)

The Permeability Index (PI) is used to assess the effect of irrigation water on soil permeability and to predict the potential for soil degradation, particularly in terms of sodium impact on soil structure. From the data analysis, it is found that 46% samples belong to suitable class and 54% samples belongs to good class.

$$PI = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+} \times 100$$

Here all values are in meq/l.

Doneen (1964) [9] irrigation water was categorized according to the Permeability Index (PI). (Fig.12). it shows that all the samples belong to class -1 type, which is good for irrigation. The soil permeability is affected by the extensive use of irrigation water as it is influenced by Na^+ , Ca^{2+} , Mg^{2+} and HCO_3^- .

Monitoring the Permeability Index is crucial for sustainable agricultural practices. High values can indicate that the water may negatively impact soil structure, reducing water infiltration and increasing runoff, which can adversely affect crop growth.

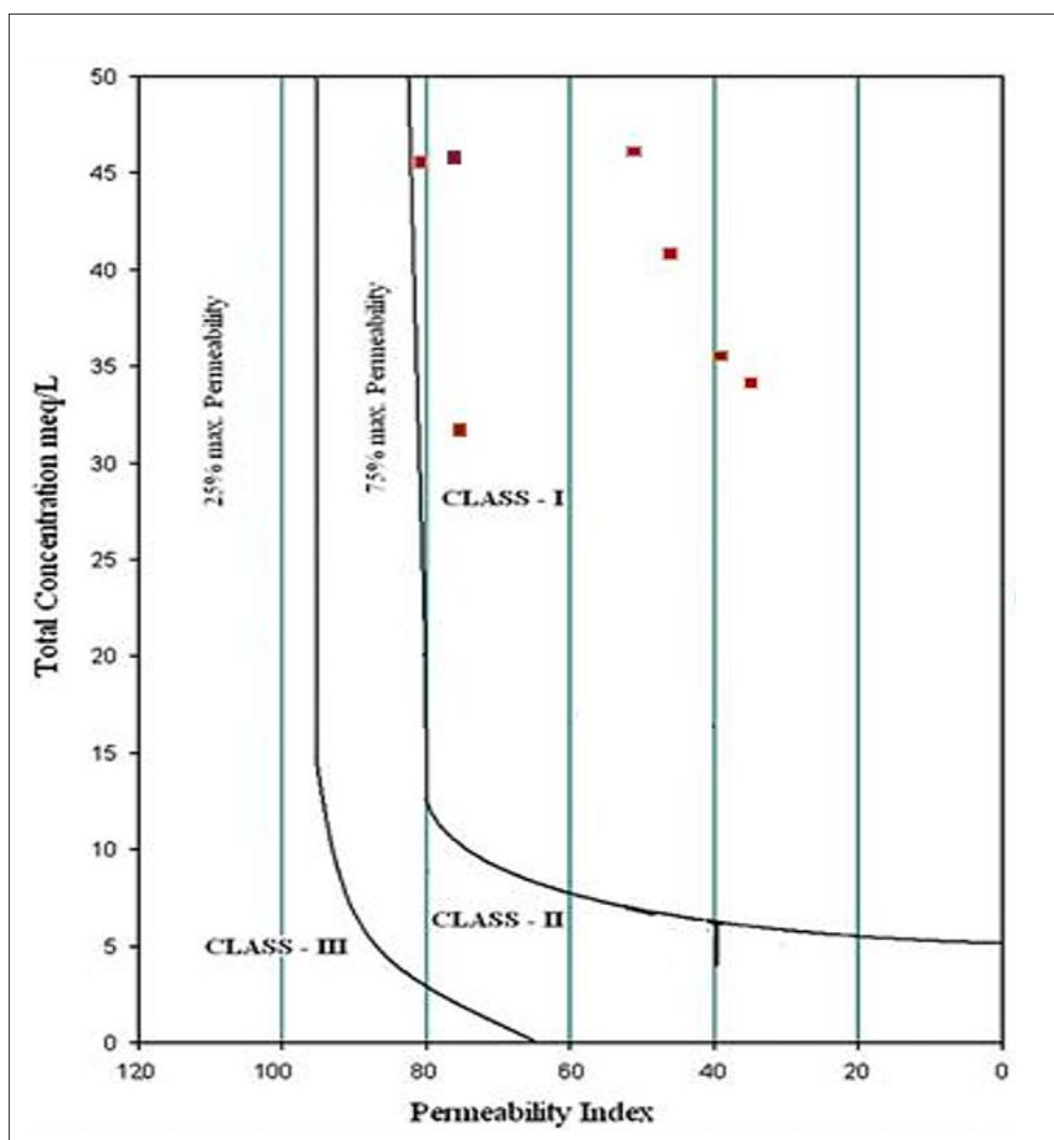


Fig 5: permeability index diagram of the sample

3.5 Residual sodium carbonate (RSC)

Residual Sodium Carbonate (RSC) is an important parameter for assessing irrigation water quality, reflecting the potential for sodium and carbonate accumulation in the soil, which may impact soil structure and crop health. RSC is calculated based on the concentrations of sodium, calcium, and magnesium in the water. Elevated RSC values indicate a higher risk of sodium toxicity and soil dispersion, making it a critical factor in evaluating water for irrigation purposes.

The formula of RSC is given below;

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

All values are reported in meq/L.

50% of the samples fall below <1.25, making them suitable for irrigation purposes. In contrast, 18% of the samples fall 1.25-2.5 range, which is moderate for irrigation and 32% of the sample >2.5, which is unsuitable for irrigation, (Table 2).

Table 2: Residual Sodium Carbonate (RSC)

Classification of Groundwater Based on RSC		
RSC	Category	No of Samples
< 1.25	Suitable	25
1.25-2.5	Marginal	9
> 2.5	Unsuitable	16

3.6 Kelly's Ratio (KR)

Kelly's Ratio (KR) It is a parameter used to evaluate irrigation water suitability based on the sodium and calcium content, calculated using the following formula:

$$\text{KR} = \frac{\text{Na}^+}{\text{Ca}^{2+} + \text{Mg}^{2+}}$$

Here all values are in meq/l.

Here, Na^+ represents the concentration of sodium ions, while Ca^{2+} and Mg^{2+} denote the concentrations of calcium and magnesium ions, respectively.

KR value of less than 1 suggests that the water is suitable for irrigation, as it indicates a lower proportion of sodium relative to calcium and magnesium. A KR value greater than 1 may indicate a higher risk of sodium accumulation in the soil, which can lead to soil dispersion and reduced crop yields. This ratio is an important factor in assessing the potential impact of irrigation water on soil health. Eighty-four percent of the samples fall below <1.0, making them suitable for irrigation purposes. In contrast, 16% of the samples exceed >1 which is unsuitable for irrigation, (Table 3).

Table 3: Kelly's Ratio (KR)

Classification of groundwater based on KR		
KR	Category	No of Samples
< 1	Good	42
> 1	Unsuitable	8

3.7 Potential Soil Salinity (PS)

Potential Soil Salinity (PS) indicates the estimated concentration of soluble salts in the soil, which can influence crop growth and soil fertility. Its levels are affected by irrigation practices, rainfall distribution, and

evaporation rates. PS is often measured in terms of electrical conductivity (EC), with higher values indicating higher salinity levels. Elevated salinity can lead to issues such as reduced water uptake by plants, nutrient imbalances, and toxicity. Managing PS is crucial for sustainable agriculture, as it helps in determining suitable crops for specific soils and guiding irrigation practices to minimize salinity build-

$$\text{PS} = \text{Cl}^- + \frac{1}{2} \text{SO}_4^{2-}$$

All values are given in meq/L.

88% percent of the samples fall below <5 which fall under excellent to good category. In contrast, 14% of the samples fall 5-10 range which is good to injurious for irrigation (Table 4).

Table 4: Potential Soil Salinity (PS)

Classification of groundwater based on PS		
PS	Category	No of Samples
< 5	Excellent to Good	44
5-10	Good to Injurious	6
> 10	Injurious to Unsatisfactory	nil

3.8 Magnesium ration (MR)

Elevated magnesium levels indicate that groundwater may pose a risk for irrigation, as reflected by the Magnesium Ratio (MR). The MR is a key parameter for assessing groundwater suitability for agricultural use and is important in agriculture for several reasons: MR helps assess soil fertility and nutrient balance, influencing plant growth and yield. A high MR can indicate potential toxicity in groundwater, affecting crop health and productivity. Understanding MR allows farmers to choose suitable crops that can tolerate specific magnesium level. It aids in developing effective fertilization strategies, ensuring plants receive the right nutrients. Monitoring MR can help prevent soil degradation and maintain sustainable farming practices. Farmers can adjust their irrigation methods based on MR findings to optimize water use and minimize salinity issues.

$$\text{MR} = \left[\frac{\text{Mg}^{2+}}{\text{Mg}^{2+} + \text{Ca}^{2+}} \right] \times 100$$

All values are expressed in meq/L.

Seventy percent of the samples fall below 50, making them suitable for irrigation purposes. In contrast, 30% of the samples exceed 50, rendering them unsuitable for irrigation (Table 5).

Table 5: Magnesium ratio (MR)

Classification of groundwater based on MR		
MR	Category	No of Samples
< 50	Suitable	35
> 50	Unsuitable	15

Gibbs Diagram (Mechanism controlling groundwater quality)

The Gibbs diagram (Gibbs, 1970) is widely employed to examine the relationship between water chemistry and the lithological characteristics of aquifers. As illustrated in Fig. 6, the diagram is divided into three distinct zones: evaporation-crystallization, weathering or rock-water

interaction, and precipitation dominance. (Mahanta & Sahoo, 2016) [16]. In this research work it is concluded that

all sample under the rock dominance category.

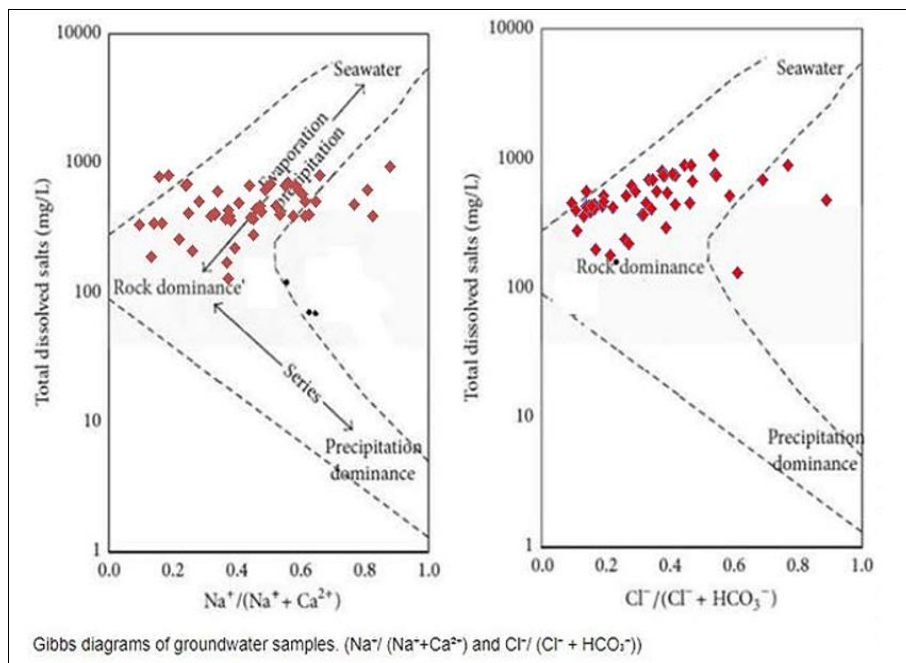


Fig 6: Gibbs Diagram of the study area.

Piper Diagram (Geochemical evaluation of groundwater)

The Piper Diagram (Piper, 1944) for the study area classifies groundwater based on the distribution of cations and anions, as shown in Fig. 7. The diagram is divided into six fields: (1) $\text{Ca}^{2+}\text{-HCO}_3^-$ type, (2) $\text{Na}^+\text{-Cl}^-$ type, (3) $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-$ type, (4) $\text{Ca}^{2+}\text{-Na}^+\text{-HCO}_3^-$ type, (5) $\text{Ca}^{2+}\text{-Cl}^-$ type, and (6) $\text{Na}^+\text{-HCO}_3^-$ type. Most samples fall in field 1, indicating that alkaline earths ($\text{Ca}^{2+} + \text{Mg}^{2+}$) exceed alkalis

($\text{Na}^+ + \text{K}^+$), and in field 3, where weak acids ($\text{HCO}_3^- + \text{CO}_3^{2-}$) exceed strong acids ($\text{SO}_4^{2-} + \text{Cl}^-$). Field 5 represents the $\text{Mg}\text{-HCO}_3^-$ type, followed by field 6, which corresponds to the $\text{Na}^+\text{-HCO}_3^-$ type. Overall, the dominant hydrochemical facies in the study area are of the $\text{Ca}^{2+}\text{-Cl}^-$ type, followed by the $\text{Na}^+\text{-Cl}^-$ type, with groundwater chemistry primarily characterized as calcium-magnesium bicarbonate-chloride, alongside a presence of sodium chloride type.

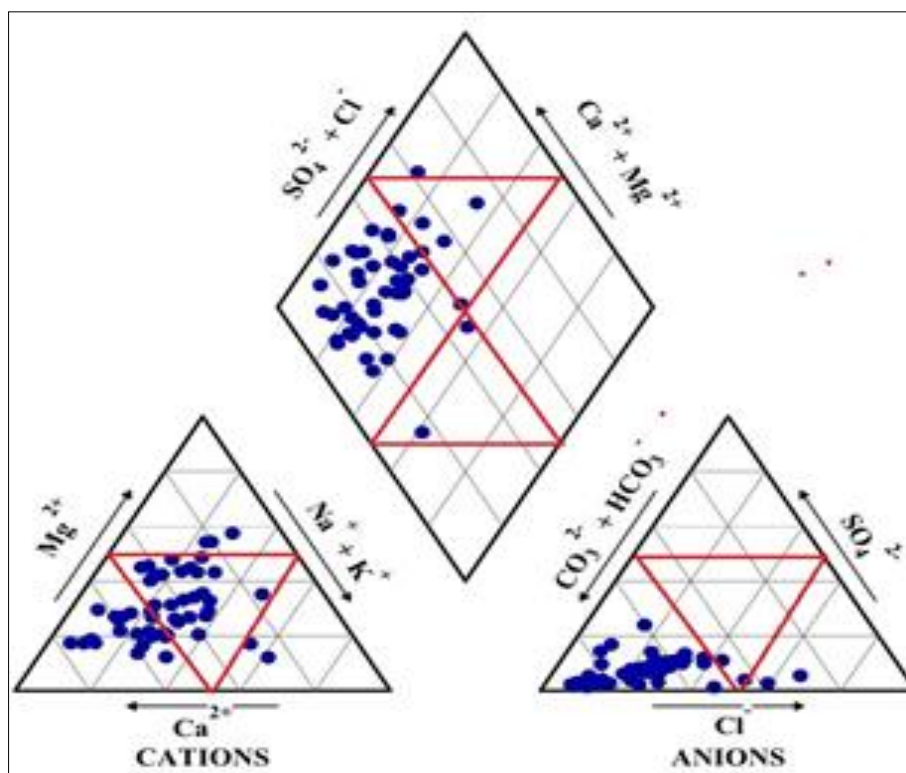


Fig 7: Gibbs Diagram of the study area

3.9 Correlation

Correlation of water quality involves analyzing relationships between various chemical constituents in water to understand their interactions and impacts on overall water quality. This analysis can help identify potential sources of contamination, predict water behaviour, and assess suitability for various uses, including agriculture. Correlation between SAR, PI, PS, KR, % Na and MR shown in Table 6. SAR has high positive correlation between KR ($r = 0.92$) and % Na ($r = 0.89$). KR has strong positive correlation with % Na ($r = 0.93$). PI has negative correlation with PS ($r = -0.11$). RSC has negative correlation with PS ($r = -0.1$).

Table 6: Correlation of water quality

	SAR	PI	RSC	KR	%Na	PS	MR
SAR	1						
PI	0.637742	1					
RSC	0.586124	0.913852	1				
KR	0.924191	0.758303	0.684576	1			
%Na	0.893881	0.864034	0.798439	0.933208	1		
PS	0.315408	-0.11296	-0.10154	0.240468	0.213799	1	
MAR	0.351598	0.616427	0.7492	0.547886	0.609316	0.137741	1

4. Conclusion

The recent groundwater study has highlighted the dynamics of fluoride in the area, which significantly affect the health of humans, and animals, among other factors. Analyses using Piper and Gibbs diagrams, correlation studies, statistical methods. The key conclusions are summarized as follows.

- From piper diagram, The dominant hydrochemical facies are $\text{Ca}^{2+}\text{-Cl}^-$ type followed by $\text{Na}^+\text{-Cl}^-$ type
- Average value of pH is 7.24, which shows the water is alkaline in nature. Average value of Total Hardness is 349.43mg/l, most of sample comes under moderate to hard type. Fluoride concentrations range from 0.01 to 3.24 mg/l, with enriched zones noted in the the far western and central regions of the study area. According to BIS ^[7] standards, 8% sample exceed the permissible limit of 1.5 mg/l, placing them in the high-risk zone.
- In permeability index diagram all samples comes under Class I type, which is very suitable for agricultural system.
- The statistical analysis shows SAR has high positive correlation between KR and % Na KR has strong positive correlation with % Na PI has negative correlation with PS). RSC has negative correlation with PS.
- From Gibbs diagram it concluded that all samples belong to rock dominance type.
- The area primarily consists of Khandalite, gneiss, and gabbro, along with small patches of Charnockite and quaternary sediments. It features diverse geomorphology, including pediments, structural hills, denudational hills, and valley fills. Fluoride dissolution in this region is significantly influenced by the interaction between rock and water.

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