



Assessment of Hydrogeochemical and Quality studies in groundwater of Villupuram District, Tamilnadu, India

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Abstract

Groundwater plays a vital role in supplying water all over the world. The qualitative and quantitative assessment of water for drinking purpose is done by understanding its physico-chemical and bacteriological properties. A study on hydrogeochemistry is done to understand the utilization of groundwater for various purposes. A total of 170 groundwater samples were collected from the Villupuram district and they are measured for major ions during premonsoon. The measured ions taken into consideration, to understand the suitability of groundwater for consumption, cultivation and household purpose and also to identify the hydrogeochemical processes. The study implies that most of the groundwater samples are suitable for agricultural purpose and unsuitable for domestic and drinking purpose. The study also identifies that hydrogeochemistry of the region is mainly influenced by weathering processes.

Keywords: Groundwater quality, Hydro geochemistry, Weathering, Ion Exchange..

Introduction

Ground water is the most important source of consumption water in our country and essential source of our life. Water is an important and vital component of our life support system. Its quality depends on the recharged water, atmospheric precipitation, inland surface water and subsurface geochemical processes¹.

Hydrogeochemistry helps in understanding the suitable water quality needed for household, cultivation and build up purposes. A number of studies on water quality and its utility for consumption, cultivation and house hold purposes are there²⁻⁸. Groundwater quality changes due to several factors, but chemistry is one of the important aspects. Rock water interaction and human activities influence the quality of groundwater which can be determined by hydrochemical studies^{9,10}.

Hence, physico-chemical analysis of water is essential to evaluate the groundwater quality. That influences the suitability of water for household irrigation, and built-up needs¹¹. Several studies have highlighted the role of weathering in groundwater chemistry, regulating the concentration of dissolved ions in groundwater¹²⁻¹⁴. Various groundwater contaminants have been carried out in various parts of the world¹⁵⁻¹⁷.

An attempt on the concise of quality and hydrogeochemical studies in groundwater of Villupuram district is lacking. The study gains its importance as it falls in both hard and

sedimentary rocks. Hence an attempt has been made to study the quality and identify the hydrogeochemical processes that control the ion chemistry in groundwater of Villupuram district of Tamilnadu.

Study area: Villupuram district forms the eastern part of Tamil Nadu state surrounded by Cuddalore District in the East and South, Salem and Dharmapuri districts on the West, and Thiruvannamalai and Kanchipuram districts on the North, covering an area of about 7.223 sq km. It is located between north Latitude of 11°49' and 12°47' and East Longitude of 78°61' and 80°03'.

The climate is sub-tropical and the temperature varies from 26.1 to 35.2°C in the district. The relative humidity varies from 20 to 70% and is high during PRM monsoon.

The water level depth varies from 76 to 450 m below ground level. It receives 111.8mm rainfall (1902-1980) annually and highest in coastal region. The development of the groundwater in this region is through dug wells and bore wells¹⁸. And granular rock bodies overlies on the crystalline sedimentary contact regions where wells of 40 to 60 mbgl depth, having 7 to 10 lps discharge capacity are found.

The study area is represented by Hornblende-biotite gneiss, Charnockite, Clay and sandstone, Laterite, pegmatite, Granite, Limestone with calcareous shale and argillaceous with hard sandstone lithologies (Figure-1).

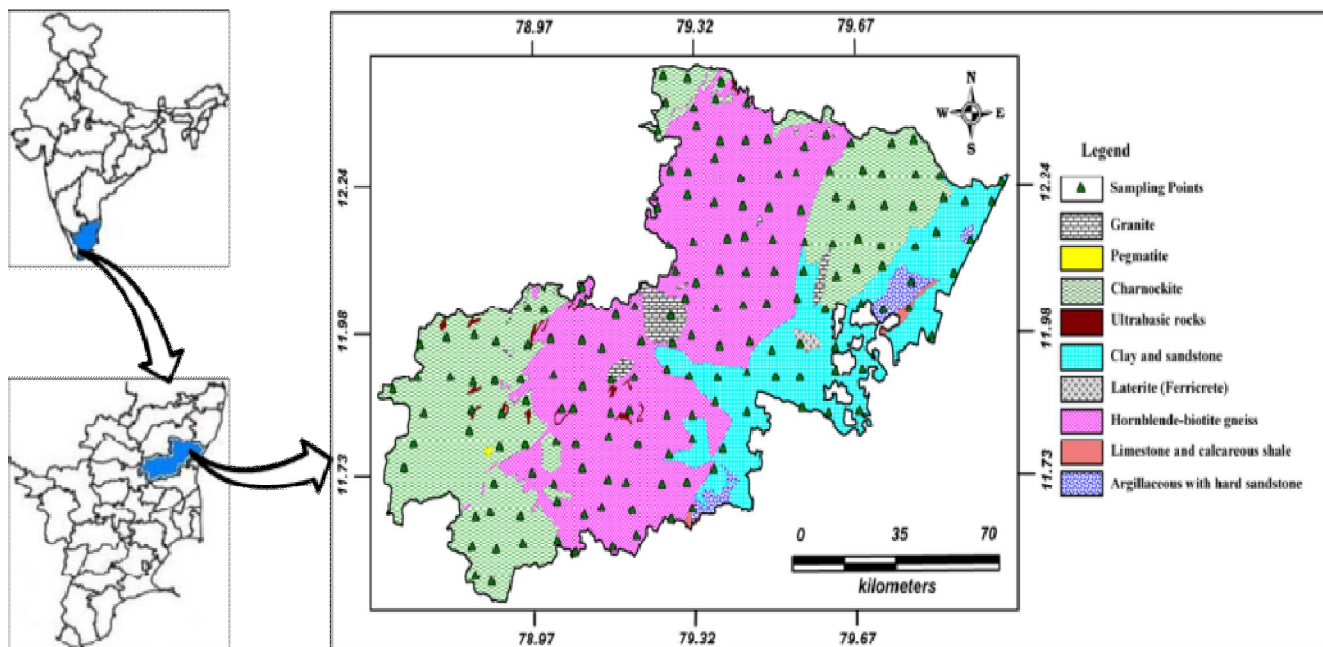


Figure-1
Lithology and sampling points of the study area

Table-1
The maximum, minimum and average chemical constituent's of Groundwater
(All values are in mg/l except pH and Electrical conductivity (EC) in μ S/cm)

Parameter	Minimum	Maximum	Average
Ca	6	256	76.89
Mg	2.4	123.6	34.89
Na	4.9	762	90.20
K	BDL	116.8	10.95
Cl	35.45	1807.95	273.35
HCO ₃	30	426	196.71
NO ₃	BDL	267.54	28.56
PO ₄	BDL	4.09	0.22
SO ₄	0.06	7.74	1.06
H ₄ SiO ₄	24	500	118.62
F	0.04	3	0.55
pH	6.15	8.23	7.41
EC	252	7360	1542.89
TDS	108.2	1810	627.49

Methodology

170 water samples were taken from different hand pumps covering throughout the study area during Pre monsoon (PRM). Parameters like pH, TDS, Temperature and conductivity were analysed in field itself by using water analysis kit. Sampling and analysis was carried out using standard¹⁹⁻²¹. Uranium was analyzed by the Laser fluorimeter. The collected sample were measured for major ions like Ca²⁺, Mg²⁺, by titrimetric; Na⁺, K⁺ by flame photometry (CL 378); Cl, HCO₃⁻ by titrimetric; and SO₄²⁻, PO₄⁻, NO₃⁻ and H₄SiO₄ by Using spectrophotometer (DR 6000, HACH). The Ionic balance of groundwater. Samples ranges of 5-10 %^{22, 23}. The software Aquachem 4.0 was used for piper plot²⁴. A computer program WATCLAST in C++ was used for calculation and graphical representations²⁵.

Results and Discussion

pH values ranges from 6.15 to 8.23 which shows the alkaline nature of groundwater.. EC ranges from 252 to 7360 µs/cm with an average of 1542.89 µs/cm. Total Dissolved Solids (TDS), is the sum total of dissolved ions which ranges between 108.2 to 1810mg/l. (Table-1). The dominance of cations and anions are as follows
 Na > Ca > Mg > K = Cl > H₄SiO₄ > HCO₃ > NO₃ > SO₄ > PO₄ > F

A higher value of EC was noted in the southern part nearby Gomuki River and it may be due to the infiltration of sewage effluents along the river^{6, 26}. A lower value of EC was observed

in the north eastern part (Figure-2). In majority of the groundwater samples EC were varies from 252 and 7360 µs/cm.

Groundwater Quality studies: Drinking water quality: The result of analysed parameter compared with the WHO,²⁷ BIS²⁸ and ISI²⁹ standards for drinking water. The hydrogeochemistry shows that some groundwater in this region the chemically potable and suitable for household purposes. Incaution concentrations 24, 22, 6 and 14% of the Ca, Mg, Na and K respectively exceeds the permissible limit of all standards. The anion concentrations shows that 9, 49, 16, and 3% of the F, Cl, NO₃ and HCO₃ concentrations respectively exceed the permissible limit and SO₄ concentrations are within the limit (Table-2).

Classification for Agricultural purpose (Irrigation quality)

Residual sodium carbonate: The Carbonate and Bicarbonate rich water which covers the alkaline earth mainly having Ca and Mg in excess of allowable limits affects agriculture unfavorably³⁰.

$$RSC = (CO_3 + HCO_3) - (Ca + Mg)$$

The alkaline earth helps in determining whether the water is suitable for irrigation or not. The precipitation of Ca and Mg become more which results the excess of sodium in the form of sodium carbonate. The RSC can be divided as good, medium and bad categories³⁰. 93% of the groundwater samples of the study area fall in Good category, 7% falls in medium category and 3% in the bad categories (Table-3).

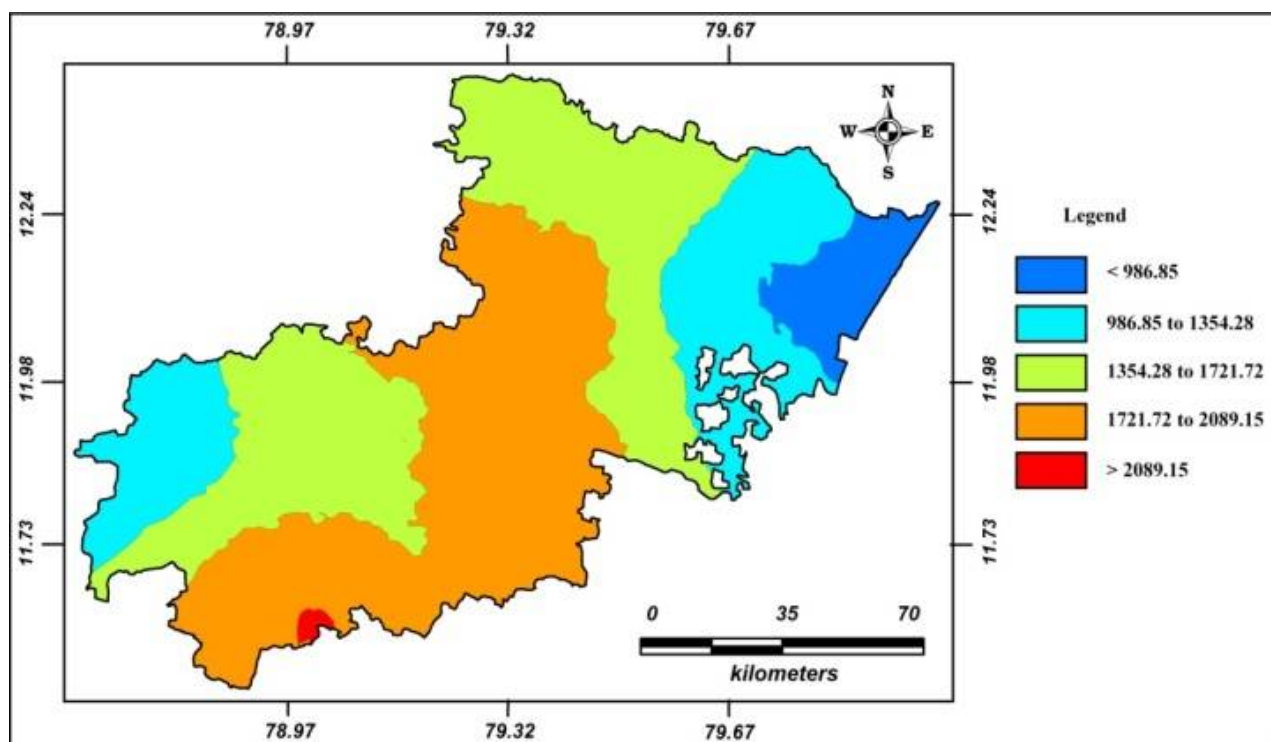


Figure-2
 Spatial Distribution of Electrical Conductivity of groundwater samples

Sodium absorption ratio: Salinity and SAR helps in determining whether the water is suitable for the agricultural purpose. The permeability of soil and drainage system of an area gets affected by the concentration of Na and HCO_3 ^{32,33}. SAR can be defined as the relative ratio of total concentration of sodium in water to the amount can be absorbed by soil .Which can be expressed as; $\text{SAR} = \text{Na}^+ / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}$

The distribution of SAR was calculated using³⁰ and only excellent and good categories are found. 99% of samples the falls under excellent category and 1% percentage fall under good class (Table-3).

Permeability Index (PI): The PI influences the utility of groundwater for irrigation. Irrigation water is classify on the basis of permeability index by³⁴.
 $\text{PI} = \text{Na}^+ + \sqrt{\text{HCO}_3^-} / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+) \times 100$

Water belongs to Class I and II having 75% or more permeability is consider as good and suitable for irrigation. Water belongs to Class III have 25% permeability is not suitable for irrigation. All most 98% of samples belongs to Class I and Class II and is also suitable for irrigation. (Figure-3) (Table-3).

Table-2
Comparison of Groundwater Samples with (WHO 2004) Standards (BIS 2014) and (ISI 1995) for PRM season (all values (mg/L) all values are in mg/l except pH).

Parameter s	WHO (2004)	BIS (2014)	ISI (2012)	PRM	Polluted Samples
pH	6.5-8.5	6.5-8.5	6.5-8.5	6.15-8.23	-
TDS	500-1000	500	500	108.2-1810	4,28,46,53,59,89,96,126,146,151, 153,155,156,158, 161,162
Ca	100	75	75	6-256	1,4,6,10,16,17,19,23,26-28,44-46, 50,51,65,68,72,73,77,89,91,93,96,100-102,107,117,119,121,125,128,144, 153 - 156,163
Mg	50	30	30	2.4-123.6	10-14,22,24,26-28,32,46,49,53,57, 59,66,77,83,86,87,89,92,96,103, 107,113,117,120,126,128,129,151, 155, 158, 166,168,169
Na	200	200		4.9-762.2	10,48,49,51,54,57,59,60,61,63
K	20	-		116.8	8,14,16,18,42,49,52,53,63,93,96, 101,107,108,110,111,112,114, 130,138,139,142,155,161
F	1	1.0	1.0	0.04-3	11,13,22,28,38,42,50,59,62,72,84, 85,103,113,124,158
Cl	250	200	250	35.45-1807.95	7,6,7,10,11-13,16-19,22-28,32,42, 44-46,48-54,57-61,63-66,68, 72-77,82,83,88,89,91-103,160, 107,111,113-115,117,118,120, 121,126,128,129,146,153,155,156,161,168,169
NO₃	50	45	45	267.54	16,18,22,28,42,49,59,61,63,64,67,68,73,89,94,96,98,108,110, 119,124, 141,143,152,153,157
SO₄	250	200	200	0.06-7.74	-
HCO₃	125-350	-	-	30-426	18,49,54,151,161

Table-3
Summary of Geochemical classification by WATCLAST Program for PRM seasons (Chidambaram 2000)³¹.

Category	Grade	PRM	Category	Grade	PRM	Category	PRM
Na% Wilcox (1955)			USGS Hardness			TDS Classification(USSL,1954)	
Excellent	0-20	28	Soft	<75	1	<200	3
Good	20-40	78	Slightly Hard	75-150	20	200-500	57
Permissible	40-60	50	Moderately Hard	150-300	62	500-1500	107
Doubtful	60-80	13	Very Hard	>300	87	1500-3000	3
Unsuitable	>80	1	IBE Schoeller (1965)			CationFacies	
Na% Eaton (1950)			(Na+k)rock->Ca/Mg g.w.		12	Ca-Mg Facies	28
Safe	<60	156	(Na+k)g.w.->Ca/Mg rock		158	Ca-Na Facies	141
Unsafe	>60	14	Schoeller Classification (1967)			Na-CaFacies	1
S.A.R. Richards (1954)			Type I		170	Na Facies	0
Excellent	0-10	168	Type II		0	Anion facies	
Good	Oct-18	1	Type III		0	HCO3 Facies	0
Fair	18-26	1	Type IV		0	HCO3-Cl-SO4 Facies	0
Poor	>26	0	Corrosivity Ratio (1990)			Cl-SO4-HCO3 Facies	149
R.S.C. Richards(1954)			Safe	<1	149	Cl- Facies	21
Good	<1.25	165	Unsafe	>1	21	Hardness Classification (Handa,1964)	
Medium	1.25-2.5	4	Chloride Classification (Stuyfzand,1989)			Permanent Hardness (NCH)	
Bad	>2.5	1	Extremely fresh	0		A1	9
EC Wilcox (1955)			Very fresh	0		A2	130
Excellent	<250	1	Fresh	41		A3	19
Good	250-750	25	Fresh Brackish	64		Temporary Hardness (CH)	
Permissible	750-2250	115	Brackish	64		B1	3
Doubtful	2250-5000	28	Brackish-salt	1		B2	1
Unsuitable	>5000	1	Salt	0		B3	8
			Hyperhaline	0			

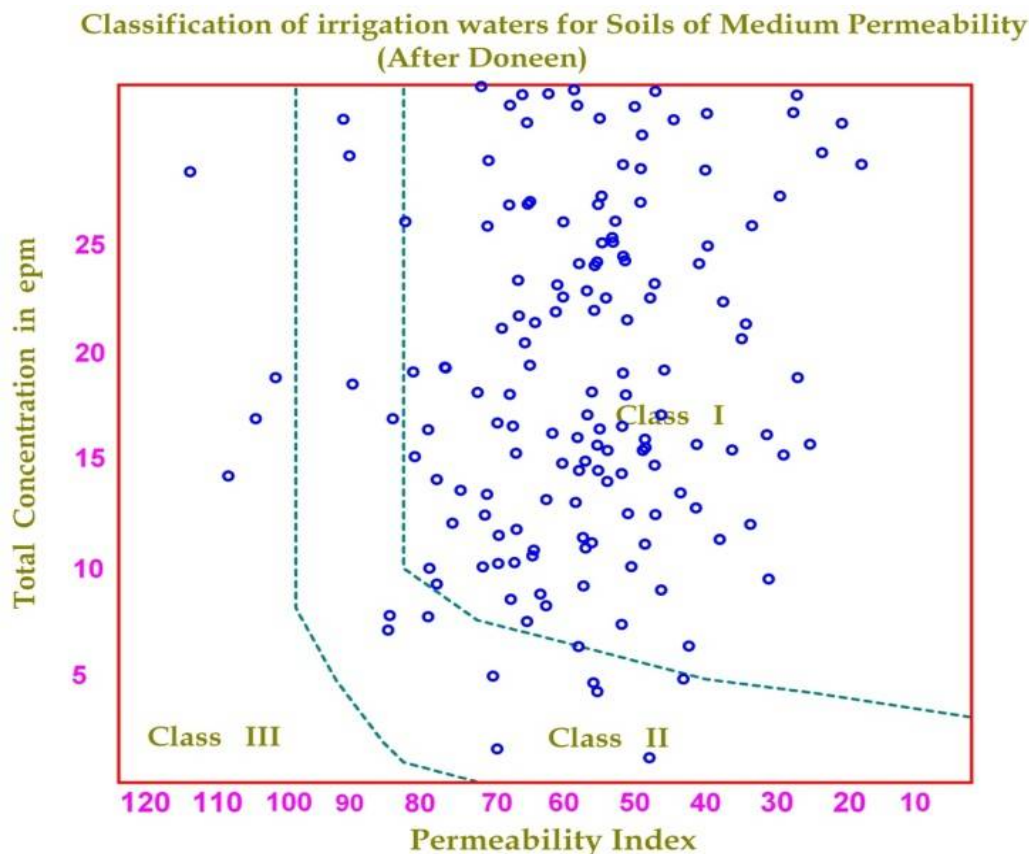


Figure-3
Doneen plot for classification of irrigation purpose.

Sodium percentage: Na%³⁵ helps to classify the suitability of groundwater for irrigation calculated as

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

Alkaline soil Composed of Na and CO₃ but saline soils composed of Na and Cl. Both alkaline and saline soils are unsuitable for plant growth. Groundwater having maximum 60% sodium is suitable for agricultural purpose³⁶. 17% of the samples fall in excellent category in study area. The Good category is represented by 46% (Table.3). The permissible category is represented by 28% and 8% of the samples fall in doubtful region whereas 1% in unsuitable category.

Classification for domestic purpose: Hardness: It is related to its reaction with soap and to the scale of incrustation accumulating in containers (or) conducts where water is heated or transported. Since soap is precipitated by Ca and Mg ion. Hardness increases by metallic ion dissolved in water. Hardness is classified as soft, slightly hard, moderately hard and very Hard by USGS Hardness³⁷. Very hard water leads to scaling problems in air conditioning plants³⁸ have hardness of more than 180 mg/L. The soft category is represented by 1%, slightly hard

is represented by 12%. 36% of samples are represented by moderately hard and 51% in very hard category.

Chloro-Alkaline Indices: The chemical reactions in which ion exchange between the groundwater and aquifer environment occurs during the periods of residence and movement may be understood through study of Chloro – Alkaline Indices³⁹.

$$\text{CA I} = \text{Cl} - (\text{Na} + \text{K}) / \text{Cl}$$

$$\text{CA II} = (\text{Na} + \text{K}) / (\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3)$$

³⁹ proposed a measure called “Index of Base Exchange” (IBE) to describe the metasomatism taking place in groundwater. There are certain minerals (clay minerals, glauconitic, zeolites and organic substances) which can absorb and exchange their cations with cations present in the water. Cation exchange plays an important role in the chemistry of Na and K. 7% of samples are represented as Ca-Mg by Na- K and the exchange of Na- K by Ca-Mg is represented in 93% of samples.

Hydro geochemical processes: In piper plot the concentration of major cations(Ca, Mg, Na,K) and anions (CO₃ + HCO₃, Cl, SO₄) are plotted on two separate triangular diagrams and its combined information on a quadrilateral. The position of diagrams signifies the composition of groundwater.. The geochemical evolution can be understood from the Piper plot, (Ca-Mg-Cl mixed type), (Na-Cl type), (Ca- HCO₃).

number of samples have Ca-Mg-Cl and Na-Cl water type corresponding to mixed water type, may be due to anthropogenic impact⁴⁰. Some Na-Cl type water samples are also found in coastal region may be due to seawater infiltration into the aquifer^{11,5}. Above diagram shows that the alkali (Na) exceeds the alkaline earth (Ca and Mg) and strong acids Cl exceed the weak acids (HCO₃ and SO₄). Some Samples having Ca-HCO₃ water type signifies the predominance of infiltration of freshwater into the aquifer⁶. Higher Ca and Mg occurring in groundwater may be due to weathering of primary mineral sources of rock- water interaction⁴¹ (Figure-4).

The hydro chemical studies describe the source and distribution of dissolved ions and also explains about the parameter responsible for hydro chemistry. According to⁴², the main natural process which controls the surface and groundwater chemistry are (1) atmospheric precipitation (ii) Rock weathering and (iii) evaporation and fractional crystallization. A boomerang shaped diagram resulted when Gibbs plotted the ratio of three major cations as (Na+K)/(Na+Ca+K), versus TDS. In the study area, the ratios of (Na+K) / (Na+Ca+K) of the groundwater samples have been plotted against TDS. Similarly the ratio of Cl (Cl + HCO₃) has been plotted against TDS and is shown in (Figure-5). Figure 5 illustrates that most of the groundwater samples fall in the weathering field may be due to rock water

interaction processes and few samples plotted on evaporation zone. The samples falls outside the plot indicates that they are affected by the anthropogenic activities⁴³.

Conclusion

The following inferences are arrived out of the above study:
 i. Groundwater flowing in this region is neutral to alkaline innature. ii. The order of dominance of major cations and anions are Na > Ca > Mg > K = Cl > H₄SiO₄ > HCO₃ > NO₃ > SO₄ > PO₄ > F. iii. Higher EC values are noted along the southern part of the study area nearby Gomuki River and it may be due to the infiltration of sewage effluents. iv. Water of this region is not suitable for human consumption²⁷. v. Classification on Irrigation quality based on residual sodium carbonate, sodium percentage and permeability index suggests that the water can be utilized for irrigation. vi. Classification based on hardness and chloroalkaline index most of the samples are unsuitable for domestic purpose. vii. The chemical composition of the groundwater in the study areashows that Na and H₄SiO₄ are the dominant ions. viii. weathering, ion exchange processes and saline water intrusion are the mechanism which controls the hydro chemistry of this area. Amo0ng which weathering of rocks mainly responsible for the major ion chemistry of water.

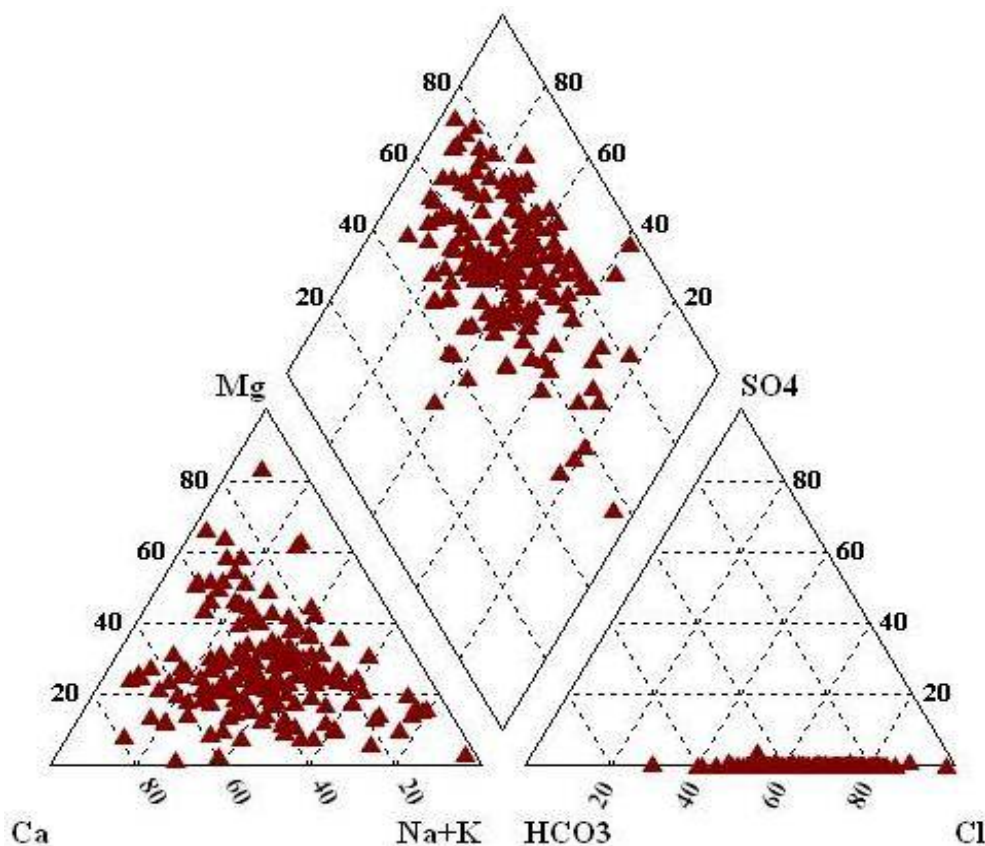


Figure-4
 Piper diagram for identify the geochemical processes in groundwater

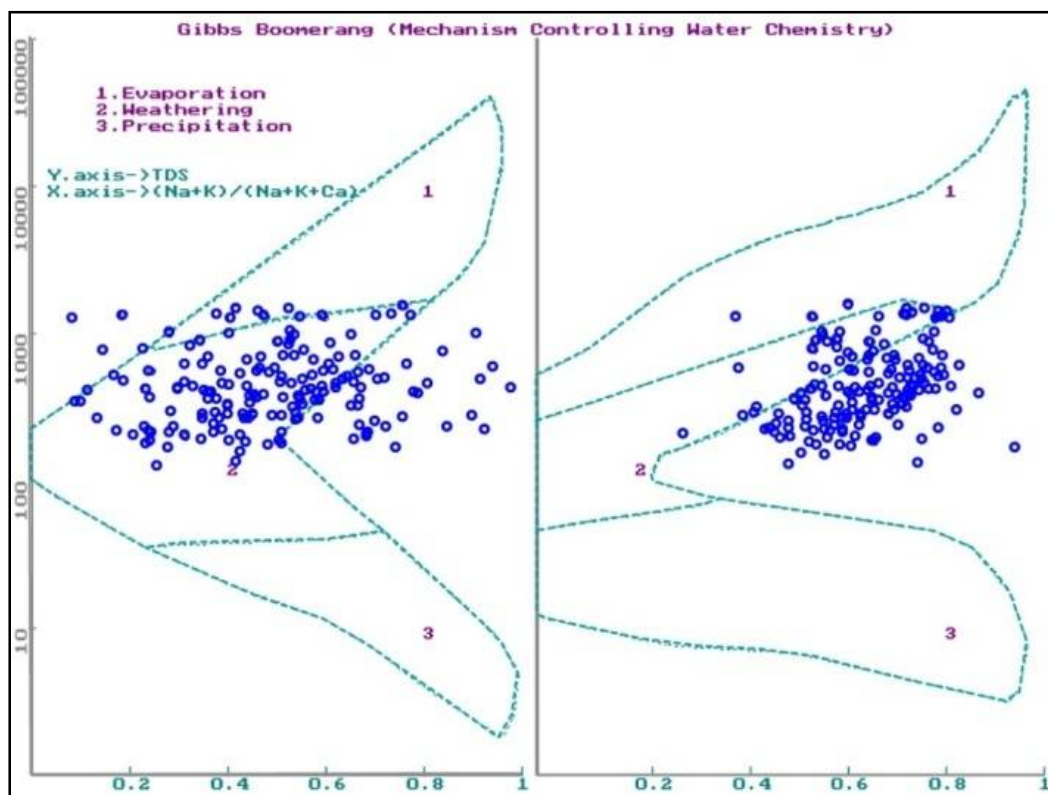


Figure-5

Gibbs Plot for groundwater samples

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