

## **A Hydrogeochemical Elucidation of the Groundwater Composition for Drinking and Irrigation Usage in Virudhunagar District, Tamil Nadu, India**

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### **Abstract**

Hydrogeochemical analysis was carried out to survey the suitability of groundwater for the purpose of drinking, household, agriculture, and industries in Virudhunagar District, Tamil Nadu, India. Seventy-two groundwater samples were collected across the district during the southwest monsoon season (SWM) in 2021 and analyzed for electrical conductivity, total dissolved solids, cationic and anionic activity from Ca, Mg, Na, K, Cl, CO<sub>3</sub>, HCO<sub>3</sub>, SO<sub>4</sub>, and PO<sub>4</sub>. All analytical results were compared with the corresponding reference values from World Health Organization (WHO 2014). The abundance of these ions is in the following order: Na > K > Ca > Mg and Cl > HCO<sub>3</sub> > SO<sub>4</sub>. Na% and RSC results show that some of the groundwater samples are suitable for agriculture Purpose. Wilcox sample ratings indicating that the samples show low alkali hazard to high hazard. The results of the analysis were understood with the geology; the ion concentration in the groundwater varies temporally and spatially. Interpretation of the analytical data shows the dominant facies of Na- Cl, mixed Ca- Mg-Cl, mixed Ca-Na-HCO<sub>3</sub>. Weathering, salt leaching, and anthropogenic activities have been identified as dominant factors in the groundwater chemistry of this region.

**Keywords:** Virudhunagar, Ground water, Hard rock aquifer, Hydrogeochemical

### **Introduction**

The nature of the groundwater quality is variously varying by the physical, chemical, biological activities of natural and anthropogenic factors. The physical parameters of water quality parameter are the temperature, turbidity, color, taste and odor. Properties of groundwater is generally colorless, odorless, and has no specific taste. Groundwater naturally contains dissolved ions that are slowly extracted from soil particles, sediments and rocks as they pass through the unsaturated zone, and in mineral surfaces of pores or aquifer structures. The main decisions regarding the available freshwater resources will determine the future, economic and political environment of any region of the world (Sivakumar et al. 2016; Ramachandran et al. 2020). The earth's water sources have been classified as groundwater and surface water, with groundwater, being the primary source of freshwater for drinking, household, agricultural, and industrial purposes. (Anitha et al., 2011; Prabakaran et al., 2020). Therefore, it has a direct and serious impact on the country's economic growth and social wealth (Milovanovic 2007). The chemical properties of groundwater are mainly influenced by natural and anthropogenic factors (Garcia et al. 2001; Nur et al. 2011; Fakir et al. 2002; Kim et al. 2005). Recent researchers are more concerned with hydrogeochemical studies (Chidambaram et al.

2011, Thilagavathi et al. 2012, Thilagavathi et al. 2016 Tatawat and Singh 2008; Panda et al. 2017; Semwal and Jangwan 2009; Dinesh and Singh 2010; Biswajeet and Saied 2011; Senthil et al. 2014; Devaraj et al. 2018) The quality of the groundwater and its movements depend on the properties of the nearby lithology and also on the various human activities (Jayaalakshmi et al. 2012). Activity, in addition to the processes that control the interaction of the groundwater (Panda et al. 2017; Chidambaram et al. 2012). Groundwater quality and geochemistry also play an important role in groundwater protection and quality management. It is more important to assess the groundwater quality for current and future use (Kori et al., 2006). Many researchers have recommended a different methodology for analyzing groundwater quality (Bassam and Rumikhani 2003; Hameed et al. 2010, Selvam 2017, Singaraja et al. 2015) The groundwater quality of the Virudhunagar district and its slopes was determined by Nageswari et al. (2007), Magesh et al. (2013) Udayanapillai et al. (2016), Muthulakshmi et al. (2009, 2010), Ponmanickam et al. (2007) Senthilkumar et al. (2021). The content of heavy metals in groundwater and its health risk were determined by Raja et al. (2021). Therefore it is a great need to assess the current state of groundwater quality and its suitability for consumption and irrigation. Agriculture is a major practice in Virudhunagar as it is the main source of food for the majority of the population. The area of study also relies primarily on the agricultural and small to large fireworks industries, printing plants, ginning factories, oil and spinning mills, hand and weaving machine industries, and cement industries. Since it is more important to study groundwater quality and factors, monitoring the variation in hydrochemical parameters has proven beneficial in solving many groundwater quality problems and is used as a powerful tool by hydrologists. The suitability of the groundwater for irrigation and also for drinking and its spatial variation is essential. Therefore, the present study attempts to assess the suitability of groundwater for drinking and irrigation. In addition, the study describes the processes involved in controlling the geochemistry of the groundwater in this region.

### **Study Area**

The Virudhunagar District was branched off from the Ramanathapuram District in Tamil Nadu. The city of Virudhunagar serves as the district headquarters. The investigation area lies between the latitude  $9^{\circ} 24'27.85''$  N to  $9^{\circ} 11'10.19''$  N and the longitude  $78^{\circ} 24'9.55''$  E to  $78^{\circ} 5'24.45''$  E (Figure.1). The study area extends over an area of 4234 square kilometers. The Virudhunagar District consists of taluks with an average altitude of 102 m above the previous mean sea level. This district has a total population of 19,42,288 (2011) Census. The Vaippar, Gundar, and Arjunanadi are the three main rivers that flow from northwest to southeast of the district. The annual temperature ranges from  $23.78^{\circ}\text{C}$  to  $33.95^{\circ}\text{C}$ . The most important soil types in the district are red and Black cotton soil. The study area is mainly covered by the physiographic units of plains, highlands, hills and valleys and waters. Geologically, the entire district Virudhunagar can be roughly divided into hard rock and alluvial and tertiary sedimentary formations. Most of the district is of gneiss rock group including feldspar gneiss, Charnokite and Pink granite. In the eastern part of the district tertiary formation is observed. The typical water level during the pre-monsoons is 12 m below the surface (bgl) and 8 m bgl during the post-monsoon period. The availability of groundwater was observed in both porous, sedimentary and rugged, hard rock formations. The study region is known for the matchbox, fireworks, and printing industries.

A Hydrogeochemical Elucidation of the Groundwater Composition for Drinking and Irrigation Usage in Virudhunagar District, Tamil Nadu, India

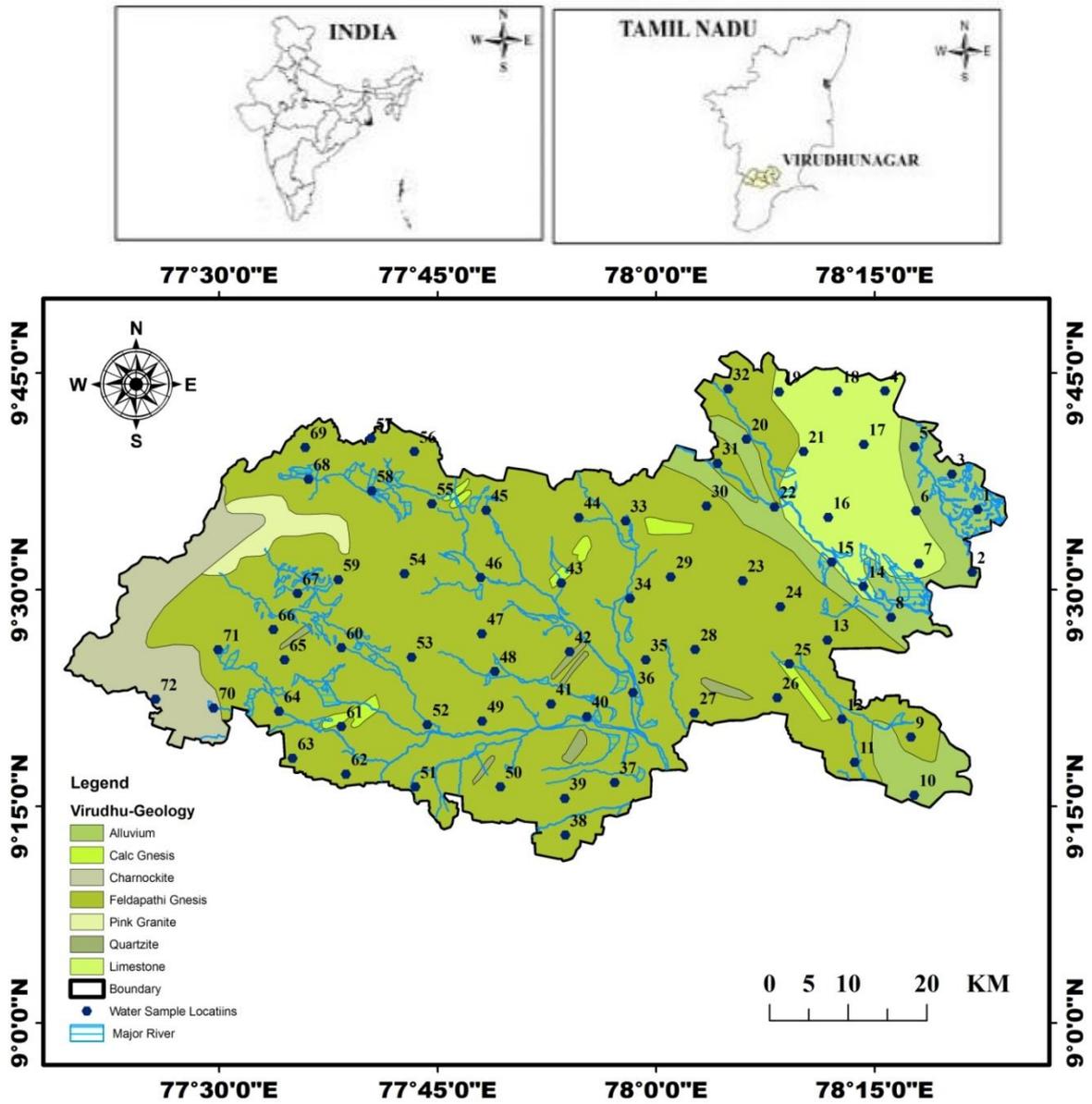


Figure 1: Geology map of the study area with sample location

Flow chart for Methodology Figure.2.Methodology

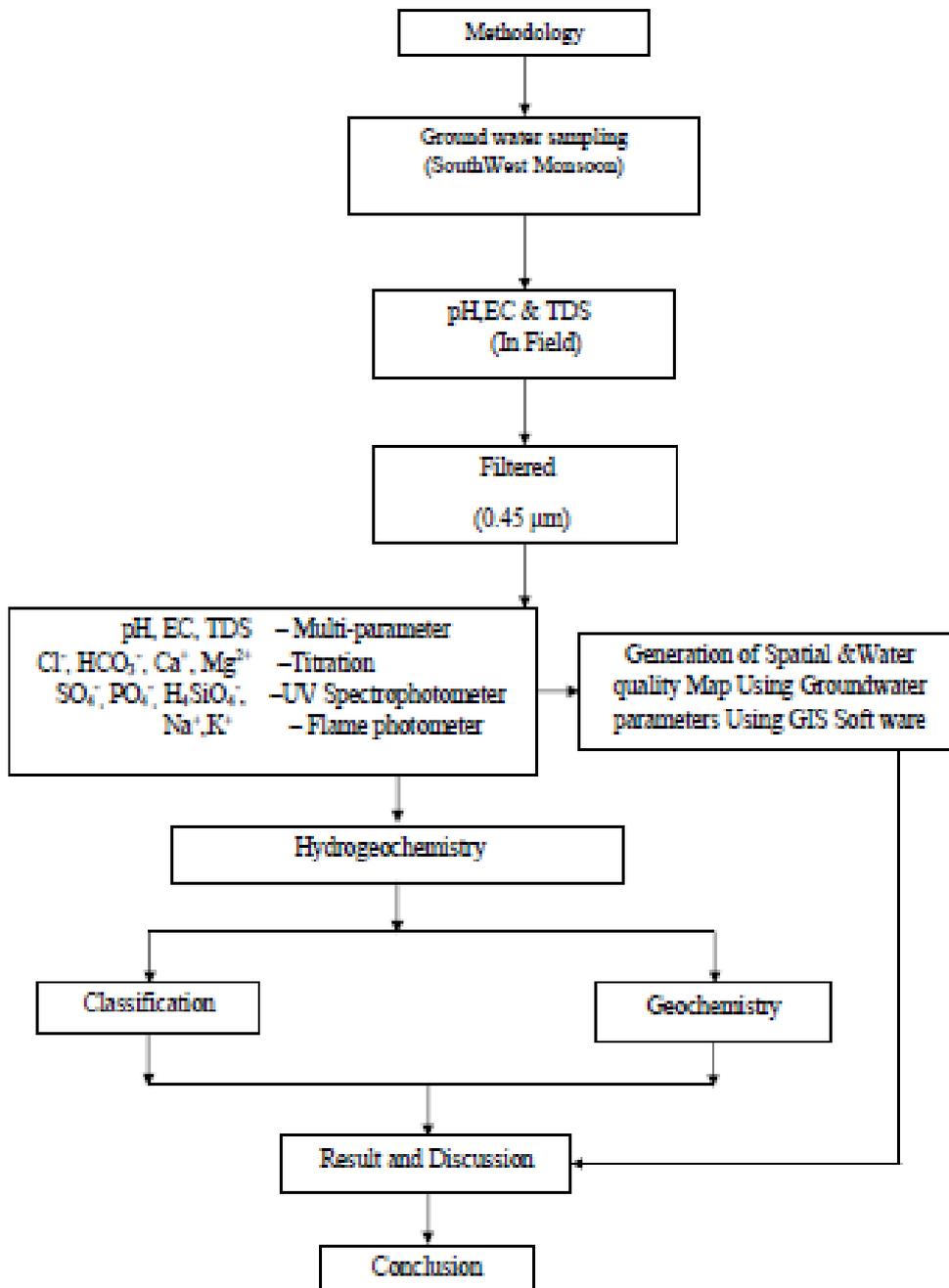


Figure. 2. Flow chart for Methodology

A Hydrogeochemical Elucidation of the Groundwater Composition for Drinking and Irrigation Usage in Virudhunagar District, Tamil Nadu, India

Groundwater samples were taken from bore wells and hand pumps during South west monsoon(SWM). A total of 72, groundwater samples were taken and analyzed for cations and anions using standard methods. physical parameters (EC, pH, TDS) were analyzed using the field multiparameter (PCSTestr<sup>TM</sup> 35). The main cations such as Ca and Mg were determined by the titration method. Na and K were analyzed with a flame photometer (Elico CL 378). The Major anions (Cl & HCO<sub>3</sub>) were analyzed using Titration method. SO<sub>4</sub>, PO<sub>4</sub>, and SiO<sub>2</sub> were analyzed with an instrument spectrophotometer (UV 1800 spec). The data obtained by analyzing the samples served as input for the calculation of the various indices to determine suitability for various purposes using. The Sodium Adsorption Ratio (SAR) (meq)  $= \text{Na}/(\sqrt{\text{Ca}+\text{Mg}/2})$ , Sodium Adsorption Ratio (SAR) (meq)  $= \text{Na}/(\sqrt{\text{Ca}+\text{Mg}/2})$ , Residual Sodium Carbonate (RSC) (meq)  $= (\text{CO}_3+\text{HCO}_3) - (\text{Ca}+\text{Mg})$ , Sodium percentage Na% (meq)  $= \text{Na}+\text{K} / (\text{Ca}+\text{Mg}+\text{Na}+\text{K}) \times 100$ , Magnesium Hazard (MH) (meq)  $= \text{Mg}/\text{Ca}+\text{Mg} \times 100$ , Kelly Ratio (KR) (meq)  $= \text{Na}/\text{Ca}+\text{Mg} \times 100$ .

**Watclast software used for Suitability of groundwater for drinking and irrigation**

The classification of groundwater for irrigation purposes is determined from the values of the sodium adsorption ratio (alkali hazard) and the electrical conductivity of the groundwater (salinity hazard), which are plotted in the USSL and SAR diagrams.

**Table: 1 Maximum, minimum and average values for the analytical results of groundwater**

Parameters	Max	Min	Avg	WHO 2014	% of samples >WHO 2014
Ca (mg/L)	272.0	28.0	74.79	200.0	3%
Mg (mg/L)	156.0	4.8	50.58	150.0	1%
Na (mg/L)	1341.0	3.3	466.25	200.0	76%
K (mg/L)	699.4	4.7	51.05	10.0	54%
Cl (mg/L)	1984.3	88.625	634.66	600.0	38%
HCO <sub>3</sub> (mg/L)	987.2	134.2	405.89	500.0	20%
PO <sub>4</sub> (mg/L)	1.6	0.83	0.87	NG	Nil
SO <sub>4</sub> (mg/L)	16.73	8.5	10.21	400.0	Nil
SiO <sub>2</sub> (mg/L)	32.8	15.26	23.79	NG	Nil
pH	8.37	7.05	7.59	6.5-8.5	Nil
EC $\mu\text{s}/\text{cm}$	7210.0	174.0	1879.63	1500.0	45%
TDS (mg/L)	5120.0	122.0	1338.47	1500.0	29%

samples

**Table.2 Suitability of groundwater for drinking and irrigation (Results from CHIDAM software, Chidambaram et al 2020)**

Category	Range	Number of Samples	Percentage of Samples	Category	Range	Number of Samples	Percentage of Samples
<b>Na% (Wilcox,1955)</b>				<b>Indices of Base Exchange (IBE) Schoeller (1965)</b>			
Excellent	0-20	3	4%	Exchange between Na and K in rock with Mg or Ca in groundwater		54	75%
Good	20-40	5	7%	Exchange between Na and K in groundwater with Mg or Ca in rock		18	25%
Permissible	40-60	13	18%	<b>TDS Classification (USSl 1954)</b>			
Doubtful	60-80	36	50%	<200		1	1%
Unsuitable	>80	15	20%	200-500		13	18%
<b>Na% (Eaton,1950)</b>				500-1500		36	50%
Safe	<60	21	29%	1500-3000		16	22%
Unsafe	>60	51	71%	>3000		6	8%
<b>Kelly Ratio,(Kelly,1946)</b>				<b>Chloride Classification (Stufzand 1989c)</b>			
Safe	<1	13	18%	Extremely Fresh	<0.141	0	
Unsafe	>1	59	82%	Very Fresh	0.141-0.846	0	
<b>Magnesium Adsorption Ratio (Lloyd &amp; Heathcoat (1985))</b>				Fresh	0.846-4.231	6	8%
Safe	<50	32	44%	Fresh Brackish	4.231-8.462	12	17%
Unsafe	>50	40	56%	Brackish	8.462-28.206	45	62%
<b>Sodium Adsorption Ratio (Richards 1954)</b>				Brackish salt	28.206-282.064	9	12%
Excellent	0-10	41	57%	Salt	282.064-564.127	0	
Good	18-Oct	19	26%	Hyperhaline	>564.127	0	
Fair	18-26	8	11%	<b>CATION FACIES</b>			

A Hydrogeochemical Elucidation of the Groundwater Composition for Drinking and Irrigation  
Usage in Virudhunagar District, Tamil Nadu, India

Poor	>26	4	6%	Calcium-Magnesium Facies		3	4%
<b>Residual Sodium Carbonate (Richards,1954)</b>				Calcium-Sodium Facies		67	93%
Good	<1.25	59	82%	Sodium-Calcium Facies		2	3%
Medium	1.25-2.5	5	7%	Sodium Facies		0	
Bad	>2.5	8	11%				
<b>Electrical Conductivity (Wilcox,1955)</b>				<b>ANION FACIES</b>			
Excellent	<250	1	1	Bicarbonate Facies		0	
Good	250-750	17	24	Bicarbonate-Chloride-Sulfate Facies		0	
Permissible	750-2250	36	50	Chloride-Sulfate-Bicarbonate Facies		50	69%
Doubtful	2250-5000	15	21	Chloride Facies		22	31%
Unsuitable	>5000	3	4				
<b>Sawyer and McCarty Hardness</b>							
Soft	<75	0					
Slightly Hard	75-150	2	3%				
Moderately Hard	150-300	28	39%				
Very Hard	>300	42	58%				

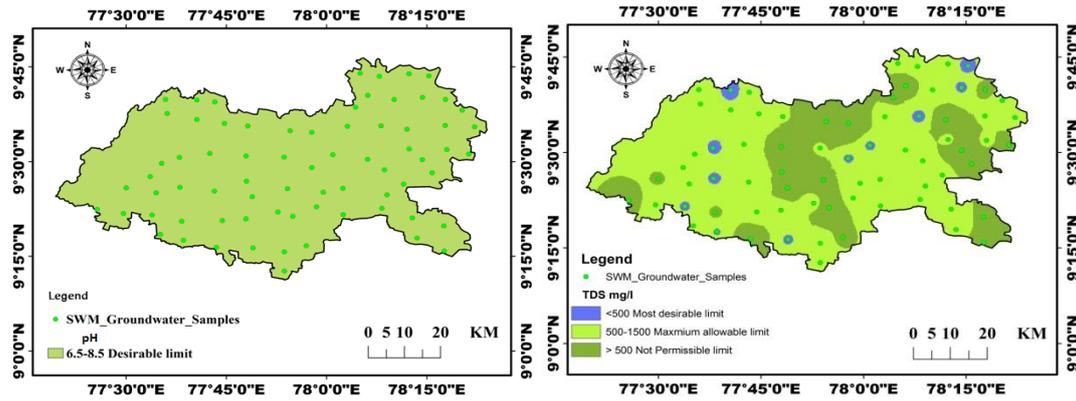
### Result and discussion

The ground water samples analysis result in given in the table.2

#### Physico chemical parameters

Hydrogen ion activity (pH)

The maximum, minimum, and average pH values in the southeast monsoon are 8.37, 7.05, and 7.59(Table.1) in the study area Concentration of pH is excellentcategory(Fig.3a).



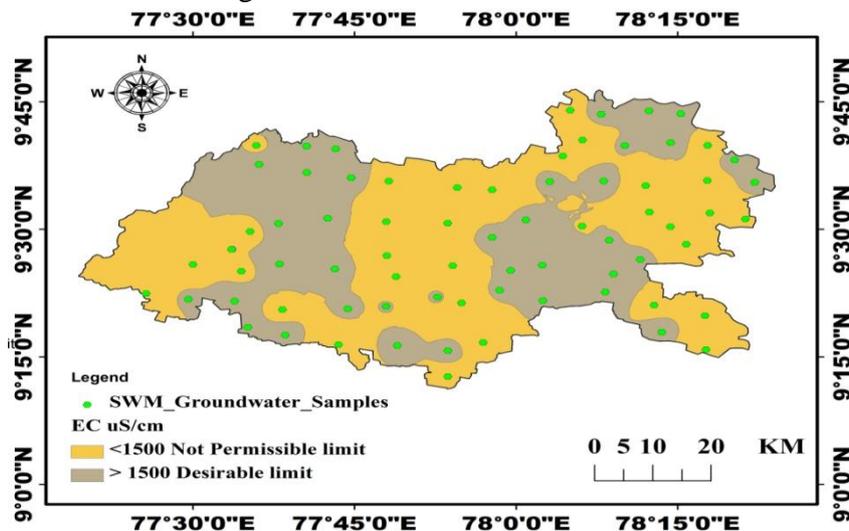
**Fig 3(a) (b): Spatial distribution of pH& TDS in groundwater samples**

### Total Dissolved Solids(TDS)

Total dissolved solids  $>1500$  mg / L is not a permissible limit, these values are not recommended for drinking, and TDS values above  $2000$  mg / L are generally a problem for irrigation. TDS calculate the amount of all minerals dissolved in water. TDS in the study region is in the range between  $122$  and  $5120$  mg / L and  $29\%$ (Table.1) of the samples from the center of the north, and some isolated part from the south and eastern part of the studied region is not suitable for the drinking purpose(Fig.3b)

### Electrical Conductivity(EC)

Electrical conductivity generally shows the total concentration of natural water. It is closely related to the sum of cations and anions determined by chemical analysis and correlates well with the value of the dissolved solids. The EC values range from  $174 \mu\text{S} / \text{cm}$  to  $7210 \mu\text{S} / \text{cm}$  and the mean EC value is  $1879.63 \mu\text{S} / \text{cm}$ (Table.1).According to the EC Values the suitable region are the North Western and South Eastern part of the study area(Fig.4).About  $45\%$  of the samples which is not permissible for the drinking purpose. Most of the central and less portion of the west and east part of study area representing the higher level of EC. The dissolution of minerals from the aquifer medium through re-enrichment of rainwater increases the dissolved solids content in the groundwater, which leads to an increase in the EC during the southwest monsoon

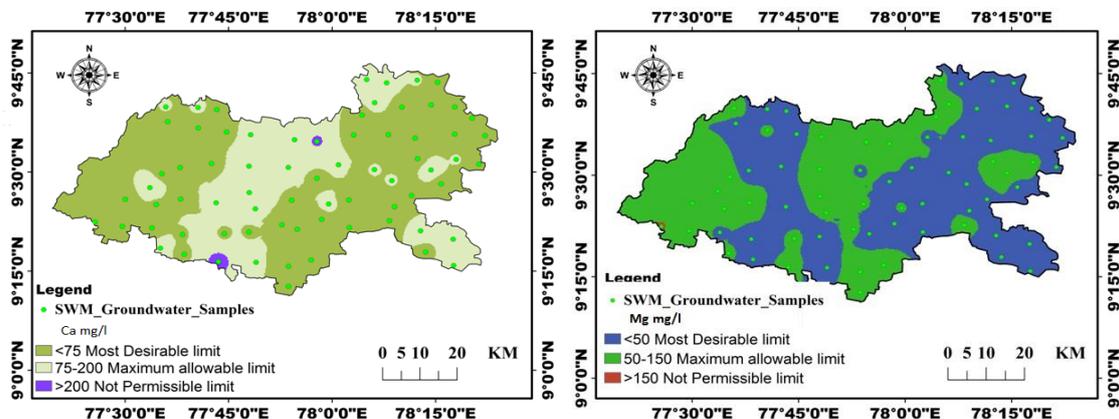


**Fig.4: Spatial distribution of EC uS/cm in groundwater samples**

# A Hydrogeochemical Elucidation of the Groundwater Composition for Drinking and Irrigation Usage in Virudhunagar District, Tamil Nadu, India

## Calcium (Ca)

Calcium is the most common ion in groundwater. Ca concentration fluctuates between 28 and 272 mg /l(Table.1). In the study area, only very (3%) few groundwater samples are affected by Ca pollution (Fig.5a).



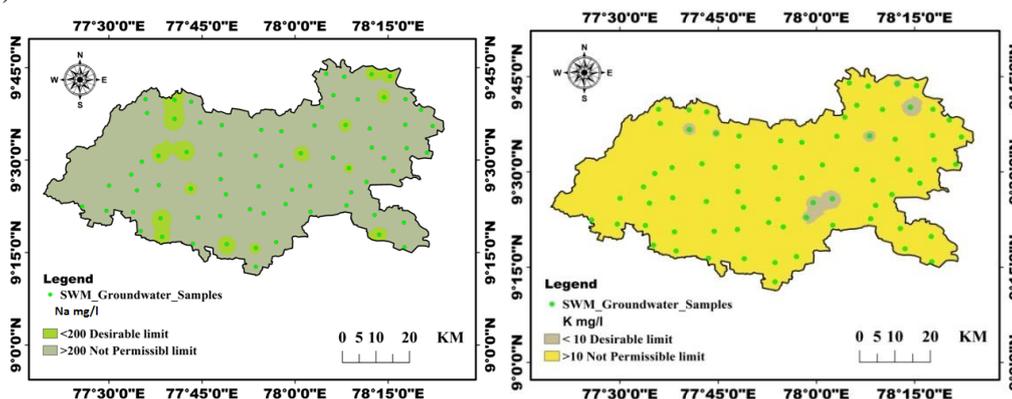
**Fig.5(a)(b): Spatial distribution of Ca& Mg in groundwater samples**

## Magnesium (Mg)

Magnesium range in the study area fluctuates between 4.8 and 156 mg/l (Table 1). The magnesium range in the study area falls under the most desirable and the maximum allowable limit value. (Fig.5b).

## Sodium (Na)

The sodium concentration varies between 3.3 and 1341 mg/l (Table.2). A high sodium concentration was observed in the study area. Most of the 76% samples were not permissible for drinking. Most of the area's agricultural land and fertilizers are used so that may be enriched with sodium in the study area (Fig.6a).



**Fig.6 (a) (b): Spatial distribution of Na & K in groundwater samples**

## Potassium (K)

The potassium concentration ranges from 4.7 to 699.4 mg/l (Table.1). Most of the 54% samples present in not permissible limit. The study area is mainly occupied by feldspathic gneiss (Fig.6b). The wells closest to the quarries also show increasing K values in the groundwater, the pollutants penetrating the groundwater.

### Chloride(Cl)

The maximum and minimum concentrations of Cl range from 1984.3 and 88.625 mg/l, respectively. The concentration is above the permissible limit value of the WHO drinking water standards (Table.1 and Figure.7a). Anthropogenic wastes such as agricultural fertilizers, animal waste, municipal as well as small and large cracker industries that enter the groundwater lead to a higher concentration of Cl.

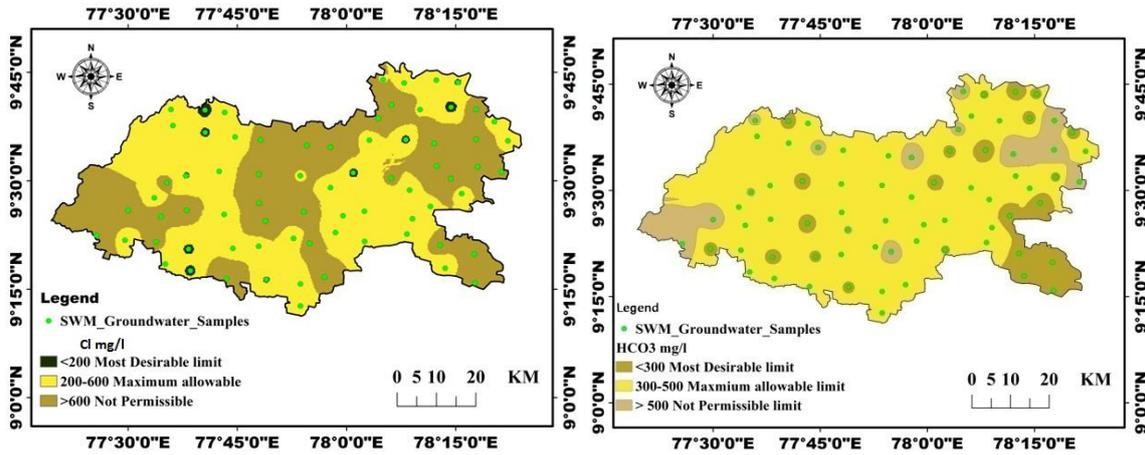


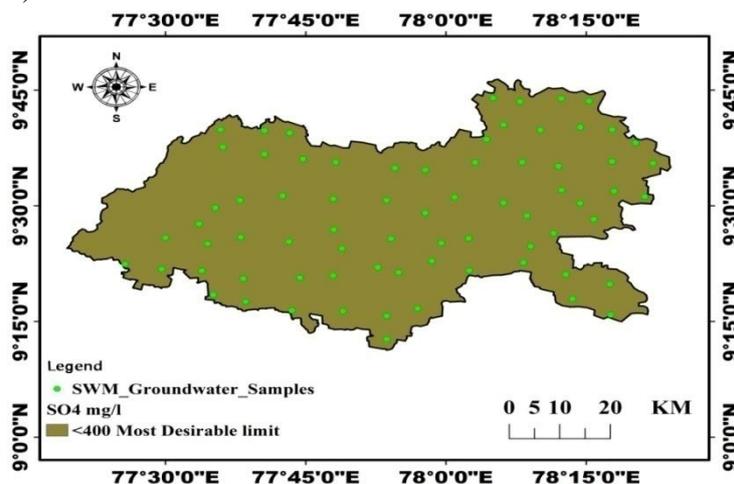
Fig.7 (a) (b): Spatial distribution of Cl & HCO<sub>3</sub> in groundwater samples

### Bicarbonate HCO<sub>3</sub>

The maximum and minimum concentration of HCO<sub>3</sub> is between 987.2 and 134.2 mg/l (Table.1) respectively the spatial pattern of the HCO<sub>3</sub> concentration shows that most of the study area is an excellent category (Fig.7b).

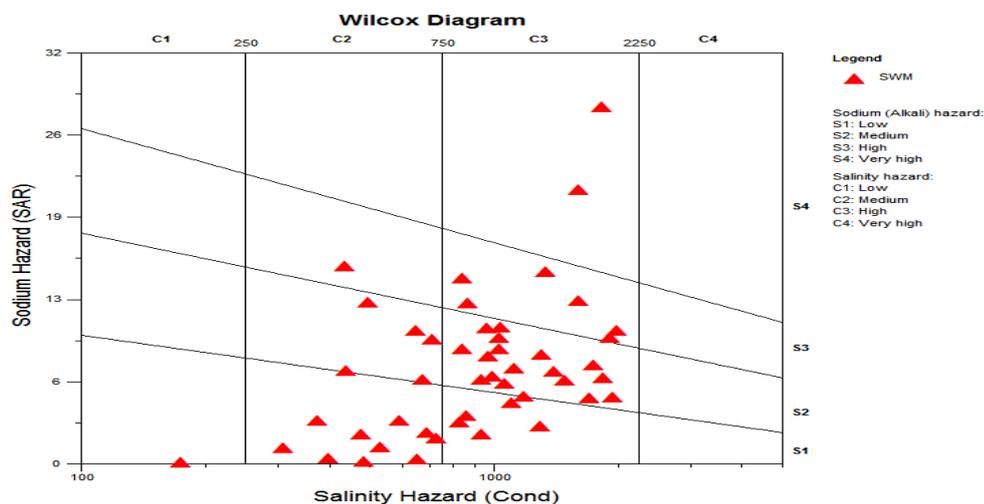
### Sulfate SO<sub>4</sub>

The maximum and minimum concentration of SO<sub>4</sub> ranges between 16.73 and 8.5 mg/l (Table.1). The spatial pattern of SO<sub>4</sub> concentration shows that all values the study area is an excellent category for drinking purpose (Fig.8).



**Suitability of Irrigation quality:**

The suitability of groundwater for irrigation purposes is examined using the sodium adsorption index (SAR) and salinity. The variation in SAR and EC values (Chidambaram et al., 2020) was identified from the Wilcox plot. A high SAR value reflects the vulnerability of sodium, which replaces calcium and magnesium in the soil and affects its permeability, soil fertility and agricultural activities (Tahmasebi et al., 2018).



**Figure.9 Wilcox Diagram**

Most of the samples fall into the category good to excellent based on their SAR value, which means that irrigation water has a low sodium risk. Low-sodium groundwater can be used for agriculture (Jeon et al 2020). The Wilcox plot shows that 10% of the samples are high sodium and are in the low salinity hazard area of S1-C2, followed by 40% of the high salinity groundwater samples and the risk of S2-C3 category medium sodium. 10% of the samples fall into the S1-C3 risk class for low sodium content and medium salinity and 30 % of the samples fall into the S3-C3 risk class with high salt content and fall into the high sodium S4-C3 very high sodium hazard to high salinity hazard. According to the Wilcox classification, all samples have a medium to very high salt content with a low sodium hazard, which means that the maximum of the samples is suitable for irrigation purposes of crops with high salt tolerance (Zhu 2002).

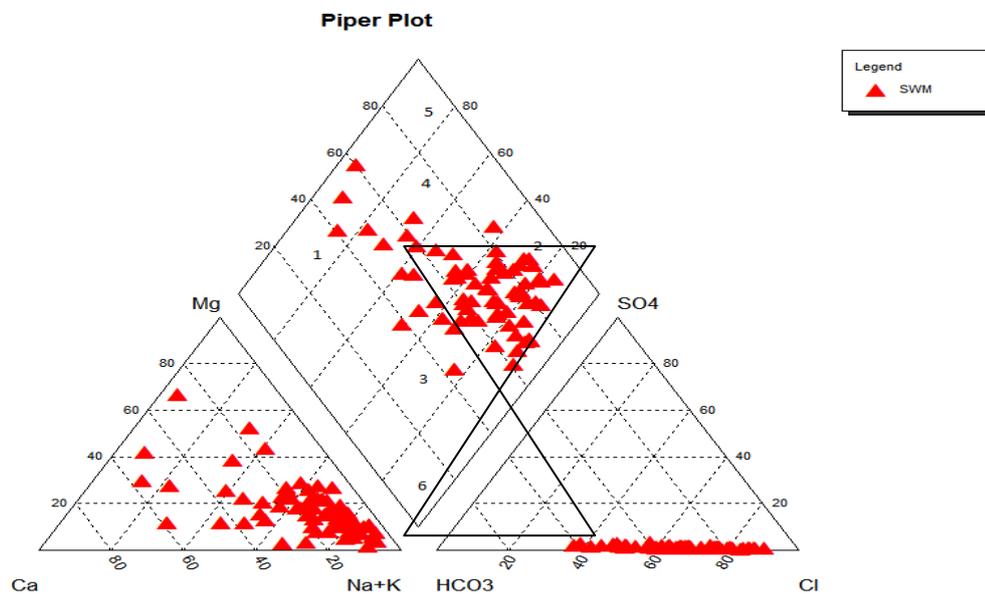
The % Na also helps in assessing the suitability of groundwater for irrigation purposes. The percentage of Na in groundwater samples is excellent (4%), good (7%), permissible (18%), insufficient (20%), doubtful (50%). Most of the samples are unsuitable for irrigation. Various minerals and the use of highly chemical fertilizers lead to a high proportion of Na (Rao, 2002; Bhat, 2016). Some samples are presented in a category from acceptable to excellent, which indicates the suitability of the groundwater for irrigation (Table 2).

Residual Sodium Carbonate (RSC) is the sum of the excess of CO<sub>3</sub> and HCO<sub>3</sub> over the sum of Ca and Mg, which affects the quality of the irrigation water (Eaton, 1950) and (Richards, 1954). Table 3 shows that 82% of the samples are suitable for agricultural use, 7% of the samples fall into the medium category, and 11% of the groundwater samples are unsafe for agricultural use (Toumi et al., 2015; Ramesh and Elango 2012).

An increase in the Ca and Mg content in the groundwater increases the pH value in the soil and reduces the quality of the soil infiltration, which has a direct effect on plant growth. which makes up 46% of the samples are unsafe for irrigation and 54% of the samples are in the safe category (Table 2).

The assessment of the irrigation suitability of groundwater samples proposed by Kelley (1940) and Paliwal (1967) depends on the value of Ca and Mg with Na. The Kelly ratio of <1 not suitable for irrigation. Approximately 18% of the samples are in a safe area for irrigation and the remaining 82% of the samples are in an unsafe area for groundwater sampling.

Approximately 8% of the samples are fresh, 17% of the samples are fresh brackish, 62% of the samples are brackish, and 12% of the samples belong to the brackish salt category based on the classification of Cl (Table 2) Long residence time and infiltration of anthropogenic pollutants (Subba Rao et, 2007) are the main sources of higher chloride levels in groundwater samples from the study area.



**Figure.10Piper facies diagram**

### Hydro chemical facies

The Piper diagram (Piper 1953) is created by plotting the proportions (in equivalents) of the main cations ( $\text{Ca}_2^+$ ,  $\text{Mg}_2^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) in a triangular diagram, the proportions of the main anions ( $\text{CO}_3$ ,  $\text{HCO}_3$ ,  $\text{Cl}$ ,  $\text{SO}_4^{2-}$ ) in another and combines the information from the two triangles into a square. The position of this diagram shows the relative composition of the groundwater in relation to the cation-anion pairs, which correspond to four corner points of the field understood from Piper's diagram (Fig. 10), which has been divided into six subfields, viz. 1 (Ca- $\text{HCO}_3$  type); 2 (Na-Cl type); 3 (Ca-Na- $\text{HCO}_3$  mixed type); 4 (Ca-Mg-Cl mixed type); 5 (Ca-Cl type) and 6 (Na- $\text{HCO}_3$  type). The groundwater samples position of the data represents the major type of sample to the Present Na-Cl Type and mixed Ca-Mg-Cl-type. The groundwater samples position of the data represents the major type of sample to the Present Na- $\text{HCO}_3$ -type. Most of the samples are concentrated in the Na-Cl-type (Fig.10), which indicates the salty character of the groundwater (Prasanna et al., 2010). The

## A Hydrogeochemical Elucidation of the Groundwater Composition for Drinking and Irrigation Usage in Virudhunagar District, Tamil Nadu, India

water type Ca-Mg-Cl, which indicates that calcium and magnesium are the main cations and chloride are the main anions. These two facies indicate that groundwater samples are associated with alkaline earth ions such as the strongly acidic cations of calcium and magnesium. Reverse ion-exchange Ca-Mg-Cl type of water. Ca-Na-HCO<sub>3</sub> indicates alkalinity. The entire hydrochemistry of the study area is dominated by strong acids and alkalis.

### Gibbs diagram

The Gibbs diagram (1970) shows the mechanism for controlling water quality based on the process of evaporation, precipitation, and the interaction of water from the rock. According to the Gibbs diagram Fig (11), the rock-water interaction is the main control factor for the groundwater quality in the study area. Carbonate minerals in the study area indicate that Ca and Mg mainly originate from silicate weathering. However, the concentration of Na and K in the study area also shows hard rock weathering.

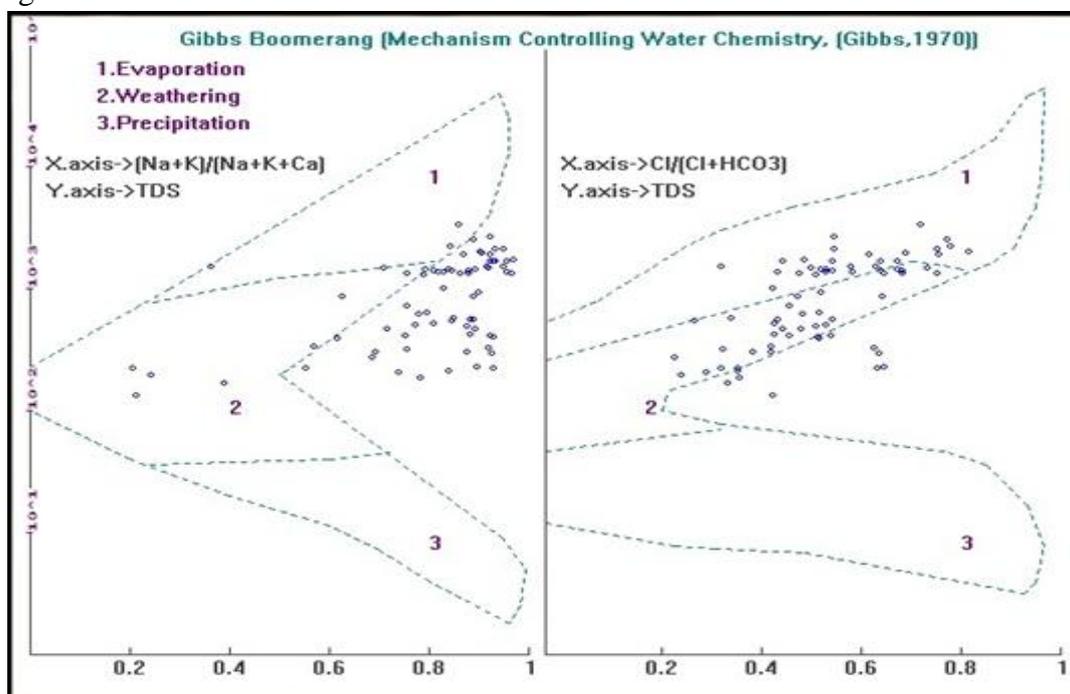


Fig 11: Gibbs plot to identify the mechanism of groundwater chemistry (after Gibbs et al.,1970)

### CONCLUSION

The result of the analysis is compared with the reference values of drinking water, the TDS ranges from 122 to 5120 mg / l and the EC ranges from 174 to 7210 uS / cm, which show that the most of the groundwater in the study area is suitable for drinking. According to the SAR% Na, and RSC show that most groundwater samples are suitable for irrigation. The SAR % shows about 83% of the samples are good for agriculture. The RSC 82% of the samples are suitable for agriculture. Na% shows that 29% and 71% of samples are safe. The strong acids are found as the dominant facies and alkaline earth as the dominant followed by mixed water facies. The few samples not suitable for domestic use in some areas and some parts of the region have good quality groundwater for agriculture, drinking water, household, and industrial use. According to pH and TDS results, the water quality is suitable for home use and irrigation throughout the district.

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A Hydrogeochemical Elucidation of the Groundwater Composition for Drinking and Irrigation  
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