Assessment of seasonal groundwater quality using CHIDAM software in Virudhunagar district of Tamil Nadu.

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Abstract: Hard rock aquifer is the most predominant in the southern peninsula exclusively in Tamil Nadu, India. Virudhunagar district is situated in the South west part of Tamil Nadu, mostly of hard rock topography. Groundwater plays a major role in this area contributing to domestic, irrigation and industrial practices. Running down of groundwater by extreme consumption and less recharge in the study area has reduced the level of groundwater. On the other hand, intensive domestic, agriculture and industrial practices impacts the quality of quality of groundwater as well. Hydro geochemistry plays an important role in evaluation of suitability of groundwater for its usage in several purposes. A total of 72 samples from North East Monsoon (NEM) and Post Monsoon (POM) has been analyzed hydrochemically. The irrigation quality parameters such as sodium adsorption ratio (SAR), %Na, Residual Sodium Carbonate (RSC), Kelley’s index and Magnesium hazard were calculated using CHIDAM software 2020 in conjunction with USSL and Doneen diagrams. During NEM, EC and TDS ranges from 273 to 5869 mg/L and 194 to 4159 mg/L and during POM is from 235 to 6850 mg/L and 233.8 to 6916 mg/L. The hydrogeochemical facies represents that Ca-HCO\(_3\) and mixed Ca-Mg-Cl facies are predominant during NEM and Na-Cl and mixed Ca-Mg-Cl are predominant during POM. The higher concentration of TDS and EC in the samples reflects the unsuitability of groundwater in both seasons.

Keywords: CHIDAM software, Virudhunagar Groundwater, Seasonal Groundwater, Hydrogeochemical
Introduction

The economic growth of the region has resulted in an increased demand for water; for potable supplies, for irrigation and industry. Groundwater is generally of tremendous microbiological feature and suitable of chemical quality for both irrigation and drinking purposes. Still, groundwater quality is one of the challenging features because of anthropogenic pollution, saline Intrusion and also by naturally-occurring contamination, associated to hydrogeochemical evolution in certain types of aquifers. The significance of water quality in social health has recently intent vast deal of awareness. Increasing population and industries have led to a prompt decline in groundwater level due to over-exploitation and also caused in quality falls. The water resources available in India are not adequate to achieve the needs of the entire population [1] Numerous studies have been conducted by various researchers in different parts of the world on groundwater quality [2-5]. The water quality will also help us to obtain information regarding the environments through which the water has circulated [6-11]. The relationship between the regional lithology, groundwater quality, characteristics of the soil and rock masses present along the pathway of groundwater and its saturation zone has been studied by many researches [12-24]. The association of geo-physical approach to determine the lithological contact and groundwater quality has been studied by [25-27]. There are various complications for the accessibility of groundwater in hard rock [28,29]. The current study area Virudhunagar district is predominated by agriculture-based population, predominant with gneissic group of rocks which include feldspathic gneiss and Charnokite. The foremost objective of the current work is to make a groundwater quality assessment for utility like drinking, domestic, and irrigation using CHIDAM software, based on the available physicochemical data for North East Monsoon and Post monsoon seasons for Virudunagar district.

Study area

Virudhunagar district was bifurcated from Ramanathapuram district, Tamil Nadu. Virudhunagar town serves as the district Headquarters. The study area is located between the latitude 9°24’27.85” N to 9°11’10.19” N and longitude of 78°24’9.55” E to 78°5’24.45” E (Figure 1). The study area spread over an area of 4234 sq. km. The Virudhunagar district is comprised of 8 Taluks with an average elevation is of 102 m of the above mean sea level. This district has a total population of 17, 51,301. The Vaippar, The Gundar, and The Arjunanadi are the three major rivers flowing along the northwest to south east of the district. The annual temperature varies from 23.78°C to 33.95°C. The major soil types in the district are Red soil, Black Cotton soil and Red sandy soil. The study region is mostly covered by the physiographic units of plains, uplands, hills and valleys. The landuse of the study area is comprised of built-up land, agricultural land, forest, wastelands, and water bodies [30]. Geologically the entire Virudhunagar district can be broadly classified into hard rock and sedimentary formation of alluvium and tertiary. The major part of the district is covered by a gneissic group of rocks.
which include feldspatic gneiss, Charnokite and the pink granite. Tertiary formation is observed in the eastern part of the district. The typical water level during pre-monsoon is 12m below ground level (bgl) and 8m bgl during post monsoon. The groundwater is observed in both the porous, sedimentary and fissured, hardrock formations. The study region is known for the match box industries, fireworks and printing press.

Figure 1. Groundwater sampling location and drainage map of the Study area

Materials and Methods

Groundwater samples were collected from bore wells and hand pumps during North East Monsoon (NEM) and Post Monsoon (POM). A total of 144 groundwater samples were collected and analyzed for major cations and anions by using the standard procedures [31]. The physical parameters (EC, pH, TDS) were analyzed by using the field multi-parameter (PCSTestr™ 3.5). The major cations like Ca and Mg were determined by used titration method. Na and K was analyzed using Flame photometer (Elico CL 378). The major anions like Cl and HCO₃ were analyzed titration Methods. SO₄, PO₄, and SiO₂ were analyzed used instrument spectrophotometer (UV 1800 spec). The data obtained by the analysis of the samples served as
an input to calculate the different indices to determine the suitability for different purpose using [32].

**Results and Discussion**

The general geochemical characters of the analyzed parameters like minimum, maximum and average of physio-chemical parameters, major ion concentrations are tabulated in Table 1. The ionic dominance in the groundwater during NEM for cations is in the following order Na>Ca>Mg>K and anions are Cl>HCO3>SO4>PO4. The POM shows that the cation is in the following order Na>K>Ca>Mg and that of anion is Cl>HCO3>PO4>SO4. Table 2 explains that Calcium-Sodium and Calcium-Magnesium Facies is the dominant cation facies during NEM and Calcium-Sodium facies is the predominant facies during POM. The Anion facies during NEM shows Chloride-Sulfate-Bicarbonate facies and in POM shows Chloride–Sulfate-Bicarbonate facies and Chloride facies.

**Classification for Drinking Water Purpose**

Groundwater samples were classified for the drinking purpose based on the standards of [33]. Table 1 exhibits the range of ionic concentration in groundwater of the study area and compared with the prescribed limits of [33]. Groundwater shows near acidic to alkaline nature with the pH level of 6.8 to 8.4 during NEM and 7.5 to 8.9 in POM and the level of pH during NEM is within the permissible limit of WHO. 5.5% of samples during POM show the exceeding level of pH.

Figure 2. Spatial distribution of TDS (mg/L) in groundwater samples with respect to North East Monsoon (NEM) and Post Monsoon (POM) seasons.

pH greater than permissible limit indicates the higher cation concentration. Total Dissolved Solids of the samples during NEM ranges between 194 and 4160 mg/L and during POM ranges from 234 to 6916 mg/L. Groundwater samples shows that 21% and 29% of the sample during NEM and POM are exceeding the permissible limit. The higher level of TDS is due to the effect of anthropogenic activities like the of impact of limestone tailings from...
quarries, cement and firework industries. During NEM higher TDS is noted at isolated patches of Northern, Eastern and Central part of the study region (Figure 2) and during POM higher TDS is noted in Central and Eastern part of the study area.

**Table 1.** Maximum, minimum and average values of the hydrochemical parameters in groundwater samples. (all the values are in mg/L except pH and EC in µS/cm)

|        | Ca  | Mg  | Na  | K   | Cl  | HCO₃⁻ | PO₄³⁻ | SO₄²⁻ | SiO₂ | pH  | EC  | TDS  |
|--------|-----|-----|-----|-----|-----|-------|-------|-------|------|-----|-----|------|
| NEM    |     |     |     |     |     |       |       |       |      |     |     |      |
| Maximum| 892 | 450 | 944 | 296 | 2980| 1198  | 22.7  | 35    | 84.2 | 8.4 | 5870.0 | 4160.0 |
| Minimum| 20  | 4.8 | 9.1 | 2.8 | 53.2| 134   | 5.5   | 3.7   | 9.9  | 6.8 | 273.0 | 194.0 |
| Average| 153 | 90.7| 151 | 16.6| 441 | 539   | 7.1   | 19.5  | 49.6 | 7.5 | 1593.0 | 1136.0 |
| POM    |     |     |     |     |     |       |       |       |      |     |     |      |
| Maximum| 252 | 230 | 1201| 325 | 1987| 783   | 25    | 17    | 32.3 | 8.9 | 6850.0 | 6916.0 |
| Minimum| 16  | 7.2 | 3.4 | 1.9 | 70.9| 73.2  | 0.1   | BDL   | 5.8  | 7.5 | 235.0 | 233.8 |
| Average| 58.1| 65.1| 274 | 23  | 467 | 286   | 2.1   | 1.6   | 23.5 | 8.1 | 1621.4| 1585.4 |
| WHO (2014)| 200 | 150 | 200 | 10  | 600 | 500   | -     | 400   | NG   | 6.5-8.5 | 1500.0 | 1500.0 |

NEM | Percent of Samples exceeding WHO standard | 22% | 11% | 24% | 17% | 19% | 35% | BDL | 36% | 21% |
POM | Percent of Samples exceeding WHO standard | 6%  | 7%  | 57% | 17% | 40% | 4% | BDL | 5.50% | 38% | 29% |

**Figure 3a.** Classification of ground water samples for irrigation adopting salinity and sodim hazard during NEM.
Most of the samples from NEM and POM are within the permissible limit of the major cation like Ca, Mg, Na and K, but the samples during NEM shows that 22%, 11%, 24% and 17% are above the permissible limit of cations. During POM 6%, 7%, 57% and 17% of samples (Table 1) exceeds the permissible limit of Ca, Mg, Na and K. The anions like SO$_4$ and PO$_4$ in both the seasons are within the permissible limit of all the groundwater samples but the Cl and HCO$_3$ shows that 19% and 35%, of the samples during NEM and 40% and 4% of samples during POM are exceeding the permissible limit of drinking water quality of WHO (2014) [33] (Table 1).

**Irrigation purpose**

The classification of groundwater for the irrigation purpose is determined from the values of Sodium Adsorption Ratio (Alkali hazard) and groundwater Electrical Conductivity (Salinity hazard) which is plotted in USSL diagram. SAR values ranges between 0-18 which represents the good to excellent category in NEM and during POM the samples falls between 0 to >26

![Figure 3b. Classification of ground water samples for irrigation adopting salinity and sodim hazard during POM.](image)

indicating that 95% of samples are good to excellent category and 5 % of samples are fall under poor to fair zone of Sodium Adsorption Ratio (Table 2).
Table 2: Suitability of groundwater for drinking and irrigation based on the results from CHIDAM software (Chidambaran et al., 2020)

| Category | Range | Percentage of Samples (NEM) | Percentage of Sample (FISD) | Category | Range | Percentage of Samples (NEM) | Percentage of Sample (FISD) |
|----------|-------|-----------------------------|-----------------------------|----------|-------|-----------------------------|-----------------------------|
| Excellent | 0-50 | 42% | 7% | Exchange between Na and K in rock with Mg or Ca in groundwater | 24% | 46% |
| Good     | 51-100 | 38% | 10% | Exchange between Na and K in groundwater with Mg or Ca in rock | 76% | 24% |
| Permissible | 101-200 | 17% | 22% | TDS Classification (USSI 1994) | 1% | |
| Doubtful | 201-300 | 3% | 45% | <200 | 21% | 8% |
| Unsuitable | >300 | <1% | 5% | 200-500 | 54% | 28% |
| Na (%) (Eaton, 1950) | | | | | 50% | 35% |
| Safe     | <60 | 96% | 50% | 500-1600 | 8% | 17% |
| Unsafe   | >60 | 4% | 50% | >1600 | 8% | 17% |

Kelly Ratio (Kelly, 1946)

| Chloride classification (Stayman, 1979) |
|----------------------------------------|
| Safe | <0.14 | 0 |
| Unsafe | >0.14 | 0 |

Maganesium Adsorption Ratio (Lloyd & Heavnes, 1965)

| Fresh | 100% | 100% |
| Fresh Brackish | 4.211-8.492 | 7% |
| Brackish | 1462-2220 | 20% |
| Hard | >2220 | 0% |

Sodium Adsorption Ratio (Richards, 1954)

| Sodium-Sodium Chloride | 100% | 100% |
| Sodium-Chloride-Sulfate | 0% |
| Chloride-Sulfate-Bicarbonate | 0% |

Electrical Conductivity (Wilson, 1955)

| Anion Faciex | Bicarbonate-Facies | 0 |
| Calcium-Facies | 0 | 0 |
| Magnesium-Facies | 0 |

Sawyer and McCarty Hardness

| Carboxylic Ratio greater than 1 | Unsafe | 20% | 76% |
| Carboxylic Ratio less than 1 | Safe | 80% | |

Temporary Hardness (CAH)

| Hardness Classification (USSI 1994) |
|-----------------------------------|
| Safe | 28% | 42% |
| Unsafe | 42% | 8% |

| Sodium, Chloride, and Sulfate in Water |
|---------------------------------------|
| Type I | 100% | 100% |
| Type II | 0% |
| Type III | 0% |
| Type IV | 0% |

| Hardness Classification (USSI 1994) |
|-----------------------------------|
| Safe | 28% | 42% |
| Unsafe | 42% | 8% |

| Hardness Classification (USSI 1994) |
|-----------------------------------|
| Safe | 28% | 42% |
| Unsafe | 42% | 8% |

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| Hardness Classification (USSI 1994) |
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| Safe | 28% | 42% |
| Unsafe | 42% | 8% |
Electrical conductivity classification by Wilcox (1955) [34] for the NEM samples shows the category of Good to Unsuitable, 25% samples are of Good (Table 2), 54% of permissible, 17% of Doubtful and 4% of Unsuitable category. During POM 1% samples fall in Excellent category, 29% of Good, 60% of permissible, 14% of Doubtful and 4% of samples are in Unsuitable zone. According to the groundwater samples during NEM most of the samples fall in the low sodium hazards and high salinity hazard (Figure 3a) zone where the less sodium hazard samples are mostly useful for the irrigation purposes which have high salt tolerant crops [35,36]. During POM, Majority of samples during this season fall under C2S1, C3S1, C3S1, and few samples present in the C3S3, C4S3, C4S4 Categories (Figure 3b). About 18% of samples shows the high salinity and medium sodium hazard. It is observed that 8.3% of samples during POM are not suitable for the irrigation which shows the high sodic and salinity hazard category.

![Figure 4. Doneens Permeability Index for the groundwater samples during (a) NEM and (b)POM](image)

Doneen (1964) [37] suggested classification of the groundwater samples based on accumulation calcium, magnesium, sodium and bicarbonate of the soil. The samples plotted in Doneen plot represents that during NEM majority of the groundwater samples (97%) falls in Class I (Fig 4a). During POM, 80% of the samples falls in the Class I, 17.3% of the samples falls in the Class II, and 2.7% of samples falls in the Class III (Fig 4b) represents the larger permeability index is connected with groundwater systemic features, which facilitate widespread pollution of groundwater [38]. As per the PI ranges, the groundwater sample fall in Classes I and class II excellent to good category, Class III unsuitable for the irrigation. Comparing both the season NEM samples is more suitable for the irrigation.

The Na% is also considered to calculate the fitness of groundwater for agriculture purpose. Table 2 shows that the Na% (Wilcox 1955) in 43% groundwater samples during NEM is of excellent category, 38% of good,15% of permissible, 3% of doubtful and 1% of
unsuitable category. During POM, 7%, 18%, 25%, 43% and 7% of samples falls in excellent, good, permissible, doubtful and unsuitable category respectively. Most of POM samples represent doubtful to unsuitable category. Dissolution and weathering of different minerals and extensive application of chemical fertilisers leads to high Na% in groundwater \[39,40\]. Most of the NEM samples are represented in permissible to excellent category which signifies the suitability of groundwater for irrigation (Table 2). According to Na% (Eaton 1950) NEM samples are in safe category for irrigation purpose but during POM 50% of the samples are unsafe for the agriculture activities (Table 2).

Residual Sodium Carbonate (RSC) is governed by the CO\(_3\) and HCO\(_3\) and their relationship to Ca and Mg which controls the irrigation quality of water \[41\]. Table 2 represents, during NEM, 79% of samples are good, 10% of samples are medium and 11% of bad Category. During POM, 83%, 10% and 7% of samples are from good, medium and bad category respectively. Most of the samples are in good category for both seasons representing lesser dominance of carbonate than the alkaline earth. Higher RSC decreases the permeability of soil and reduces the yield \[1\].

Kelly proposed the ratio based on Ca, Mg and Na for the suitability of agriculture activities of the groundwater. According to the Kelly ratio samples with value <1 is not suitable for the irrigation. During NEM about 92% (Table 2) of samples are safe for irrigation and remaining 8% of samples are unsafe. During POM only 39% of samples are in safe zone and 61% of samples are unsafe.

Magnesium in groundwater significantly affects the harvest of crops \[38\]. The magnesium hazard value > 50 is assumed to be inappropriate for the irrigation purpose, however in the study area, NEM and POM samples reveals that 58% and 61% of groundwater are not suitable for the irrigation purposes (Table 2).

Index of base exchange (IBE) was proposed by Schoeller (1965) to delineate the metamorphic responses in groundwater. There is an exchange of Na and K in groundwater during more in both the seasons with Mg or Ca in rock, 76% and 54% respectively (Table 2). Few of the groundwater samples in both the seasons represents that the Na and K in mainly derived from the ion exchange process i.e Ca or Mg in groundwater is exchanged for Na and K in the rock matrix with a percentage of 22% and 46%.

In Stuyvesant (1989c) \[42\] chloride classification, both the NEM and POM samples were classified between fresh and brackish salt category. During NEM about 39% of samples are fresh, 17% of samples are fresh to brackish, 36% of samples are brackish and 8% of samples are from Brackish salt category (Table 2). During POM, 18% of samples are fresh, 25% of samples are fresh to brackish, 50% of samples are brackish and 11% of samples are from brackish salt. Maximum number of samples from POM shows the brackish nature of groundwater. Long residence time and anthropogenic pollutants infiltration are the foremost source for higher chloride level in the groundwater samples.
Domestic Purpose

Water hardness is the amount of dissolved calcium and magnesium in the water \([43]\). Hard water is high in dissolved ions largely calcium and magnesium. Depending on the hardness of the water, soap develops a film of residue left on the skin. In hard water, soap reacts with the calcium (which is relatively high in hard water) to form soap scum. When using hard water, more soap or detergent is needed for cleaning \([44,45]\). Based on Sawyer and McCarthy’s classification of groundwater hardness (Table 2) represents that 85% of samples of NEM represent very hard water and 15% of samples are moderately hard and during POM, 63% of samples are very hard, 33% of samples are moderately hard and 4% of samples are slightly hard. According to \([46]\), the hardness can be classified into permanent and temporary hardness. During NEM, 70% of the samples are represented in permanent hardness category (Table 2), 30% of the samples shows the temporary hardness and during POM. Similarly, 73% and 27% of samples are in permanent and temporary hardness category. Maximum samples represent Non-Carbonate Hardness (NCH) indicating dominance of Ca and Na facies due to rock-water interaction \([47]\).

The suitability of water quality for the transportation is influenced by the corrosive nature of the sample. This can be measured by means of the corrosivity ratio (CR) proposed by \([48]\). The groundwater shows that 61% of samples are in safe category i.e., corrosivity ratio less than one during NEM and 26% of samples during POM (Table 2). Since POM 74% of samples have value greater than one indicating that they are unsafe for the storage and transportation purpose.

Conclusion

This study categorizes the groundwater samples collected from the study area conferring the quality and utility for two different seasons during North east monsoon and the post monsoon periods, using CHIDAM software. The results suggest that the TDS in groundwater is found higher in POM than NEM is due to the influence of the precipitation. During NEM, Ca and Mg is the dominant cation and during POM, Ca and Na is the dominant cation, considering the anion Cl and HCO\(_3\) is predominant in both the seasons. Based on WHO comparison, most of the major ion concentration suggests that predominant samples from NEM belong to the suitable category for drinking and domestic purposes then the POM. The irrigation water quality parameters indicated that the majority of the water samples are suitable for irrigation purposes in NEM. Most of samples from POM are brackish to brackish salt nature. An overall seasonal observation on the geochemistry of the groundwater samples shows that NEM samples are more suitable for drinking and irrigation than the POM.

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