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Seasonal variations of Physiochemical Characteristics of Groundwater Quality from Nambiyar River Basin, Tirunelveli District, Tamil Nadu, India

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Abstract: The present study was carried out to analyse and evaluate the groundwater quality for two different seasons in Nambiyar river basin of Tirunelveli district, Tamil Nadu, India. The parameters studied were pH, Electrical Conductivity, Total Dissolved Solids, Total Hardness, Calcium, Magnesium, Chloride, Sodium, Potassium, Nitrate, Fluoride, Sulphate and Bicarbonate. Correlation coefficient studies have been carried among all possible pairs of 13 physiochemical parameters. Correlation coefficients were determined to identify the highly correlated and interrelated water quality parameters. Regression equations were formulated for highly correlated water quality parameters. Piper and Multi-rectangular diagram have been used to identify the water type of the study area. The water type in the study area was found to be mixed Ca^{2+}–Mg^{2+}–Cl^- in both monsoon and summer seasons. However, in summer season some samples have shown mixed Na^+–HCO_3^- type.

Keywords: *Groundwater, Chemical classification, Piper diagram, Correlation, Regression, Tirunelveli, Tamil Nadu*

1. Introduction

Water is an elixir of life. In recent decades it has become evident in many countries of the world that groundwater is one of the most important natural resources. The chemical composition of groundwater is controlled by many factors which include composition of precipitation, geological structure and mineralogy of aquifers and geochemical processes within the aquifer [1]. The quality of water for drinking and irrigation purposes is affected by the presence of various soluble salts [2]. Groundwater quality is an important water resources issue due to rapid increase of population, rapid industrialization and intense application of fertilizers and pesticides in agriculture field [3]. The major problem with the groundwater is that once contaminated, it is difficult to restore its quality. Contamination of groundwater results in worsening drinking water quality, high clean-up cost, health problems and high costs for alternative water supplies [4].

The literature is available regarding the analysis of groundwater quality data using regression techniques for prediction purposes in different parts of India [5, 6]. The developed regression equations for the parameters having significant correlation coefficient can be effectively used to determine the concentration of other constituents [7]. The correlation and regression coefficients study for the water quality parameters not only helps to determine the overall water quality but also to quantify relative concentration of various pollutants in water [8].

There are many trilinear diagrams for representing the water types. The piper diagram [9] is the most popular form of graphical representation of water chemistry. The Multi-Rectangular Diagram (MRD) is a new method which has been applied successfully to groundwater [10]. In this study, the MRD and Piper diagrams were used to assess the chemical compositions of groundwater. The correlation coefficients were determined to identify the highly correlated water quality parameters and the regression equations were also formulated for these highly correlated water quality parameters.

2. Study Area Description

The present study was conducted in Nambiyar river basin in Tirunelveli district, Tamil Nadu, India. In Tamil Nadu 34 river basins were identified by Tamil Nadu Public Works Department (TNPWD). Nambiar basin is one of them. Nambiyar river basin is situated in the Southernmost part of south India and is located between latitudes of 8°08’-8°33’ N and longitudes 77°28’-78°6’ E. The total area of the basin is 2084 km^2. Nambiyar basin spreads over Tirunelveli and Thoothukudi districts of Tamil Nadu and it has Tamirabarani basin on north, Pachayar and Valliyoor basins on the West, Bay of Bengal on the east and Indian Ocean on the South. The economy of Tirunelveli district is chiefly agrarian in nature and people are engaged in the cultivation of banana, pulses, groundnut, coconut and cotton. The district receives rain under the influence of both southwest and northeast monsoons. The northeast monsoon chiefly contributes to the rainfall in the district. The normal annual rainfall over the district is 879 mm. The district enjoys a sub-tropical climate. The period from May to June is generally hot and dry. The weather is pleasant during the period from December to January. The relative humidity is, on an average, varies between 79 and 84%. The minimum temperature is 22.9°C and maximum daily temperature is 34°C. Major soil types in Tirunelveli are arid desert soil, deep red soil, black cotton soil, red sandy soil, saline coastal alluvium and river alluvium. In the study area mostly arid desert soil is found and this soil is infertile. The study area and sample location maps are shown in Figures.1 and 2 respectively.

3. Materials and Methods

3.1 Groundwater Sampling and Analytical Techniques

A total of 35 water samples were collected from the study area during September 2012 (monsoon) and March 2013 (summer) after a detailed well inventory survey. The location of the samples were marked using a handheld global positioning system (GPS).

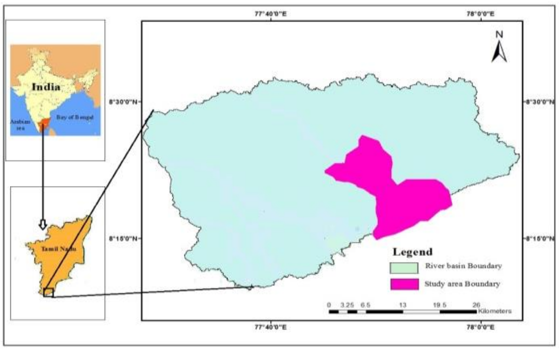

***Figure 1:** Study area map*

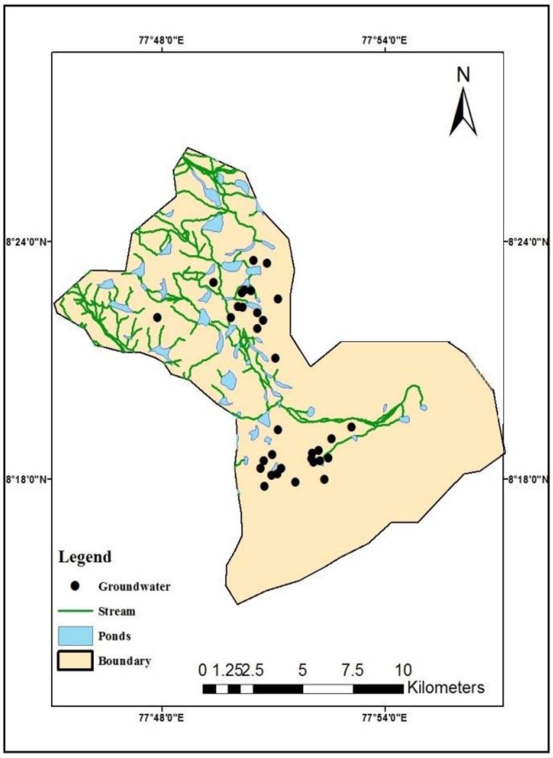

***Figure 2:** Sample location map*

The selected wells are used for domestic and agricultural purposes. River Nambiyar is an ephemeral river, as the water flows only during monsoon season. After collection, the bottles were sealed and labelled. The chemical analyses were carried out for the major ion concentrations of the water samples collected from different locations using the standard procedures as per

***Table 1:** Percent of total dissolved ion concentration*

Sample No.	%Ca	%Mg	%(Na+K)	%(CO_3+HCO_3)	%SO_4	%Cl	water type
Monsoon season							
1	35.0	23.1	42	37.8	10.9	50.8	sodium chloride
5	25	32.8	42.3	22.7	10.5	66	sodium chloride
8	25.6	16.8	58.2	46.2	6.8	43.4	sodium bicarbonate
14	45	30	25.4	8.9	2.3	88.7	calcium chloride
20	38.8	19	42.5	22.7	13.1	64.2	sodium chloride
26	28.8	39.8	38.3	36.1	8.7	52	magnesium chloride
35	34	21.7	44.5	30.3	13.5	56.5	sodium chloride
Summer season							
Sample No.	%Ca	%Mg	%(Na+K)	%(CO_3+HCO_3)	%SO_4	%Cl	water type
1	23	30	47	25	11	63	sodium chloride
5	26	31	70	23	9	83	sodium chloride
8	30	21	74	61	14	58	sodium bicarbonate
14	94	66	69	32	7	90	calcium chloride
20	51	24	58	30	10	95	sodium chloride
26	15	32	86	22	18	61	sodium chloride
35	30	16	46	39	15	51	sodium chloride

APHA (American Public Health Association) standard methods [11]. Chemical constituents such as calcium (Ca^{2+}), magnesium (Mg^{2+}),sodium (Na^{+}), potassium (K^{+}), chloride (Cl^{-}), bicarbonate (HCO_3^{-}),

In the sodium chloride content, all samples show a dominance of chloride and half of the sample show dominance of sodium. The majority of the water samples plot within the sodium chloride rectangle. For in the summer season, the water classified similar to the monsoon as sodium chloride, calcium chloride and sodium bicarbonate type. The numbers of samples in these rectangles are 23, 7, and 3 respectively.

Table 2: *Correlation coefficients among various water quality parameters for monsoon season*

Parameter	pH	EC	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	TH	TA	NO_3^-	F^-
pH	1.000												
EC	-0.414	1.000											
Cl^-	-0.378	0.985	1.000										
SO^{2-}_4	-0.226	0.440	0.420	1.000									
HCO_3^-	-0.396	0.193	0.149	0.370	1.000								
Ca^{2+}	-0.394	0.940	0.954	0.193	0.072	1.000							
Mg^{2+}	-0.325	0.854	0.863	0.223	0.131	0.862	1.000						
Na^+	-0.329	0.819	0.800	0.742	0.414	0.635	0.576	1.000					
K^+	0.120	0.258	0.256	0.161	0.103	0.226	0.173	0.368	1.000				
TH	-0.385	0.943	0.955	0.208	0.092	0.988	0.930	0.638	0.217	1.000			
TA	-0.282	0.173	0.130	0.351	0.968	0.038	0.088	0.424	0.152	-0.054	1.000		
NO^-_3	-0. 226	-0.018	-0.090	0.159	0.279	-0.128	-0.008	0.116	0.089	-0.095	0.251	1.000	
F^-	0.516	-0.304	-0.341	0.077	0.089	-0.382	-0.410	-0.041	0.163	-0.401	0.126	0.240	1.000

Table 3: *Correlation coefficients among various water quality parameters for summer season*

Parameter	pH	EC	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	TH	TA	NO_3^-	F^-
pH	1.000												
EC	-0.433	1.000											
Cl^-	-0.406	0.388	1.000										
SO^{2-}_4	-0.237	0.490	0.578	1.000									
HCO_3^-	-0.175	0.215	-0.050	0.255	1.000								
Ca^{2+}	-0.370	0.194	**0.960**	0.465	-0.076	1.000							
Mg^{2+}	-0.405	0.222	**0.968**	0.520	-0.115	**0.954**	1.000						
Na^+	-0.424	**0.698**	**0.726**	0.704	0.025	0.563	0.649	1.000					
K^+	0.188	0.185	0.261	0.372	-0.081	0.177	0.255	0.393	1.000				
TH	-0.385	0.208	**0.974**	0.492	0.088	**0.994**	**0.980**	0.601	0.211	1.000			
TA	-0.175	0.213	-0.052	0.252	**0.978**	-0.077	-0.115	0.025	-0.182	-0.089	1.000		
NO^-_3	-0.159	0.220	-0.062	0.295	0.246	-0.113	-0.107	0.138	0.279	-0.108	0.242	1.000	
F^-	0.018	0.126	-0.162	0.311	0.385	-0.169	-0.198	0.005	-0.128	-0.178	0.383	0.318	1.000

The correlation coefficients (r) among various water quality parameters of groundwater of the study area in monsoon and summer were evaluated and the values of correlation coefficients are given in table 2 and 3 respectively.

In relationship between two variables is the correlation coefficient (r) which shows how one variable predicts other. A high correlation coefficient value nearly 1 or -1 indicate a good relationship between two variables and the two variables have no relationship when correlation coefficient is around zero [13]. Positive values of r indicate a positive relationship while negative value means an inverse relationship.

From Table 2, it is evident that distribution of chloride, calcium, magnesium, sodium and total hardness are significantly positively correlated with EC in majority of the area. This indicates that the conductivity of ground water is due to the presence of Ca^{2+}, Mg^{2+} and Cl^-. EC is weakly correlated with Total Alkalinity (TA), HCO_3^-, and K^+ and negatively correlated with NO_3^-, F^- and pH. Cl^- has positive significant correlation with Ca^{2+}, Mg^{2+}, Na^+ and Total Hardness (TH), weak correlation with HCO_3^-, K^+, and TA and negative correlation with NO_3^- and F^-. Ca^{2+} shows a positive correlation with Mg^{2+} (0.862), TH (0.988), EC (0.940) and Cl^- (0.954), negative correlation with NO_3^- (-0.128) and F^- (-0.382). Mg^{2+} has positive correlation with TH (0.930), EC (0.854) and Cl^- (0.863). K^+ does not have good correlation with any of the parameters. NO_3^- and F^- have a negative correlation with most of the water quality parameter in both the seasons.

For summer season (Table 3), EC is weakly correlated with other parameter. Distribution of Na^+ only shows the high positive correlation (0.698) with EC. EC has weak correlation with K^+, Ca^{2+}, Mg^{2+}, F^-, HCO_3^-,

NO_3^- and Mg^{2+}. SO_4^{2-} has positively correlated with Na^+ (0.704) and poorly correlated with HCO_3^- (0.255), NO_3^- (0.295) and TA (0.252). Cl^- gives good alignment between Ca^{2+} (0.960) and Mg^{2+} (0.968). Ca^{2+} and Mg^{2+} have shown a negatively correlation with TA, NO_3^- and F^-.

To determine the straight linear regression, following equation of straight line was used:

$$y = ax + b \qquad (1)$$

Where, y and x are the dependent and independent variable respectively. a is the slope of line, b is intercept on y-axis. The slope, a and y-intercept, b can be determined using the following equation.

$$a = \frac{n\sum(xy) - \sum x \sum y}{n\sum(x^2) - (\sum x)^2} \qquad (2) \quad \text{and}$$

$$b = \frac{\sum y - a\sum x}{n} \qquad (3)$$

The linear regression equation to predict the concentration of various constituents present in the groundwater for two seasons is given in Table 4. Regression equation based on observed groundwater quality parameters facilitated the evaluation of many parameters without experimental determination. One can be able to find many parameters if one or two are analysed.

5. Conclusion

Electrical conductivity, chloride and sodium were correlated with most of the water parameters. So it can be concluded that these parameters are considered important physicochemical parameters of water quality. Calcium and Magnesium were highly correlated with EC and Chloride in Monsoon season. However in summer season, Ca^{2+} and Mg^{2+} were correlated only with Cl^-. The linear regression equations were developed for the constituents having strong correlation coefficient. These equations were used for calculating the concentrations of other constituents in groundwater in monsoon and summer season. The developed regression equation reduces analysis cost as well as time. Mixed Ca^{2+}-Mg^{2+}-Cl^- type of water was identified by using Piper diagram in both seasons. However, in summer season some samples have shown mixed Na^+-HCO_3^- type. The majority of the water samples fall within the sodium chloride rectangle in both seasons using multi rectangular triangle.

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Table 4: *Linear correlation coefficient and regression equation for some pairs of parameters which have significant value of correlation*

Y(Dependent)	X(Independent)	Correlation	a	b	Regression equation
Monsoon season					
EC	Cl	0.985	2.5	682	EC=2.5(Cl^-) + 682
EC	Ca^{2+}	0.940	12	727	EC=12(Ca^{2+})+727
EC	TH	0.943	3.4	474	EC=3.4(TH)+ 474
Cl^-	Ca^{2+}	0.954	4.7	18	Cl^- =4.7(Ca^{2+})+ 18
Cl^-	TH	0.955	1.4	-81	Cl^- =1.4(TH)-81
SO_4^{2-}	Na^+	0.742	0.30	24	SO_4^{2-}= 0.30(Na^+)+24
HCO_3^-	TA	0.968	1.0	-7	HCO_3^- =1.0(TA) -7
Ca^{2+}	Mg^{2+}	0.862	3.3	36	Ca^{2+}=3.3(Mg^{2+})+36
Ca^{2+}	TH	0.988	0.29	-19.6	Ca^{2+} =0.286(TH) -19.6
Summer season					
Y(Dependent)	X(Independent)	Correlation	a	b	Regression equation
Cl^-	Ca^{2+}	0.960	4.5	3.6	Cl^- = 4.5(Ca^{2+})+3.6
Cl^-	Mg^{2+}	0.968	13	5	Cl^- = 13(Mg^{2+})+5
Cl^-	Na^+	0.726	1.7	266	Cl^- =1.7(Na^+)+266
Cl^-	TH	0.974	1.2	-4.7	Cl^- =1.2(TH) -4.7
SO_4^{2-}	Na^+	0.704	0.30	27	SO_4^{2-} =0.30(Na^+)+27
HCO_3^-	TA	0.978	-0.1	202	HCO_3^-=-0.1(TA)+202
Ca^{2+}	Mg^{2+}	0.954	2.7	6.5	Ca^{2+} =2.7($Mg^{2+)}$ +6.5
Ca^{2+}	TH	0.994	0.25	0.45	Ca^{2+} =0.25(TH)+0.4

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