

# Asian Journal of **Earth Sciences**

ISSN 1819-1886



www.academicjournals.com

Asian Journal of Earth Sciences 8 (4): 97-113, 2015 ISSN 1819-1886 / DOI: 10.3923/ajes.2015.97.113 © 2015 Academic Journals Inc.



## Assessment of Groundwater Quality Using GIS and Statistical Approaches

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#### ABSTRACT

Over groundwater exploitation owing to population, urbanization and industrialization make the groundwater unfavorable for living beings. This study deals with the assessment of groundwater quality in Gudiyattam and Vaniyambadi blocks of Vellore district, Tamil Nadu, India where groundwater is the major source of drinking due to deficiency in surface water. The significant physicochemical parameters such as pH, conductivity, total dissolved solids, chlorides, total alkalinity, calcium hardness, magnesium hardness and sulphate were assessed. Correlation matrix, box plot, multivariate statistical tools such as cluster analysis and principal component analysis were applied to groundwater quality analysis. The groundwater samples were assessed for its applicability in irrigation and drinking purposes and geographic information system techniques are used for mapping consequence. The parameters analyzed were compared with Bureau of Indian Standards (BIS) and WHO standards. Box plot analysis revealed that total dissolved solids and electrical conductivity was strongly correlated. Correlation analysis exhibits strong correlation ( $\mathbb{R}^2$ >0.7) between total dissolved solids and electrical conductivity, anions such as  $\mathbb{Ca}^{2+}$  and  $\mathbb{Mg}^{2^+}$  for both the study areas.

Key words: Physicochemical characteristics, mapping, correlation matrix, box plot, multivariate analysis

#### **INTRODUCTION**

In the present situation, in most of the cities in India, the daily water demand is met by groundwater utilization, as the surface water is either deficient or polluted. Groundwater is the main source that is commonly used for drinking and irrigation purposes in rural, urban and semi urban areas (Kumar *et al.*, 2013; Magesh and Chandrasekar, 2013). Generally, the analyses of physiochemical and biological parameters lead to assess the quality of groundwater (Fatombi *et al.*, 2012; Kulandaivel *et al.*, 2009; Senthilkumar and Meenambal, 2007). Hydro chemical characteristics of groundwater can also be analyzed for the groundwater assessment (Ranjan *et al.*, 2013). Geographic Information System (GIS) mapping technique is the best representative

tool in the assessment of groundwater quality and its utilization for irrigation, drinking and constructional needs (Ravikumar et al., 2013; Srinivasamoorthy et al., 2011) The better understanding of groundwater quality can be achieved by representing the data by ArcGIS Software (Thiyagarajan and Baskaran, 2013). There is a possibility of changes in groundwater quality due to hydrology and geologic conditions over a period of time (Pandey and Tiwari, 2009). Furthermore, improper disposal of waste or garbage are one among the primary factors for groundwater pollution (Abinandan et al., 2014). The present study was carried out in the Vellore district, located in the Northern part of Tamil Nadu, India in which the rivers Palar and Ponnaiar pass through. However, the major source of drinking water for the district is groundwater which is already contaminated due to industrial establishments. Vellore district receives less rainfall and the availability of ground water is major source for irrigation and drinking purposes. Hence, this study aims to assess the quality of groundwater in Gudiyattam and Vaniyambadi blocks of Vellore district. The datasets for the groundwater were compared with Bureau of Indian Standards (BIS) and World Health Organization (WHO) standards to ensure the quality of the water. In addition, the datasets were statistically analyzed with tools such as correlation matrix, box plots and multivariate analysis to reduce uncertainties associated with the parameters.

#### MATERIALS AND METHODS

**Study area:** Vellore district is the Northern most part of the state of Tamil Nadu in India. The District is bounded by two States in the Northern part by Andhra Pradesh and Western part by Karnataka. Vellore city is the capital for Vellore district and it is one of the upcoming cities in the state of Tamil Nadu, India as it lies in the mid of two South Indian state capitals Chennai and Bangalore. The Vellore district receives an average annual rainfall of 1099 mm and the mean daily minimum and maximum temperatures are 18.4-49.5°C, respectively. The district belongs to North Eastern Agro Climatic Zone consisting of either a red non-calcareous soil or black calcareous soil. Geologically, major part of the district covered by crystalline rock formations which includes charnockites, gneisses and granites. The groundwater occurs in weathered zone under phreatic condition and in the fractures in case of semi-confined condition all over the district. However, the quality of groundwater found to be moderate with high concentration of total hardness, nitrate and chlorides due to the litho units constituting the aquifers (Balakrishnan *et al.*, 2011).

The present study area, Gudiyattam and Vaniyambadi blocks of Vellore district (longitude-78°27'28" to 79°15'59" E, latitude-12°26'10" to 13°5'3" N) are located in Palar river basin with the total coverage of area is about 2115.6 Sq. km<sup>2</sup> and the elevation ranges from 220-656 m (from MSL). The present study intended to provide the snapshot of groundwater quality and distribution of selected region with the aid of Geographical Information System (GIS) and statistical approaches. The details of sampling points in the study area are depicted in Fig. 1.

**Sample collection and analysis:** The groundwater samples were collected from 28 different bore wells (Fig. 1) in pre-cleaned, sterilized polyethylene bottles and utmost care was taken to fill the bottles without air bubbles at each sampling site. The sampling locations in the study area (Vaniyambadi (VB) and Gudiyattam (GD)) along with their designation are shown in Table 1. The collected samples were labelled and transported to the laboratory using a refrigerator box. The reagents used in experimentation were prepared by using double distilled water. The samples were analyzed for eleven parameters such as pH, Electrical Conductivity (EC),



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Total Dissolved Solids (TDS), Total Alkalinity (TA), Total Hardness (TH), calcium hardness, magnesium hardness, chloride, sulphates, bicarbonate and carbonate. The physicochemical parameters are estimated by following standard procedure prescribed by American Public Health Association (APHA., 1995). Parameters such as pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS) were analyzed by employing Water Quality Analysis kit (Model No: PC650, Make: EUTECH Instruments). The analytical methods adopted for analysis of water quality parameters are presented in Table 2.

Fig. 1(a-c): Map of study area

$\frac{1 \text{ able 1. Sampling }}{C = 1 \text{ sampling }}$	points with their designa	111011	Variant adi (VD)					
Gudiyattam (GD)			vaniyanibadi (v.b)					
Sampling points	Locations	Designations	Sampling points	Locations	Designations			
1	Sethukkari	GD1	15	Alangayam	VB 1			
2	Parathirami	GD 2	16	Ambur	VB 2			
3	Melpatti	GD 3	17	Kavalur	<b>VB</b> 3			
4	Valathur	GD 4	18	Sekkumedu	VB 4			
5	Sempalli	GD 5	19	Vaniyambadi	VB 5			
6	Jittalappalli	GD 6	20	Ambur near bus stand	VB 6			
7	Madhanur	GD 7	21	Kamaraj nagar	VB 7			
8	Machampattu	GD 8	22	Thoothuppattu	VB 8			
9	Pugalur	GD 9	23	Karumboor	<b>VB 9</b>			
10	Kavasampattu	GD 10	24	Sengilikuppam	<b>VB</b> 10			
11	Aravatla	GD 11	25	Vinnamangalam	VB 11			
12	Pernampet	GD 12	26	Vadacheri	VB~12			
13	Lallapettai	GD 13	27	Vadaputhuppattu	VB 13			
14	Sayanagutta	GD 14	28	Mittur	VB 14			

Table 1: Sampling points with their designation

Table 2: Analytical method for analysis

<u>- a</u>		
Parameters	Abbreviations	Analytical method
pH	-	Potentiometry
Electrical conductivity (µS cm <sup>-1</sup> )	$\mathbf{EC}$	Potentiometry
Total dissolved solids (mg L <sup>-1</sup> )	TDS	Gravimetric
Sulphates (mg L <sup>-1</sup> )	$\mathrm{SO}_4{}^{2-}$	Nephelometry
Chlorides (mg L <sup>-1</sup> )	Cl-	Titrimetric
Calcium (mg $L^{-1}$ as CaCO <sub>3</sub> )	$\mathrm{Ca}^{2+}$	Titrimetric
Magnesium (mg L <sup>-1</sup> as CaCO <sub>3</sub> )	$\mathrm{Mg}^{2^+}$	Titrimetric
Carbonate (mg L <sup>-1</sup> )	$\mathrm{CO}_3{}^{2-}$	Titrimetric
Bicarbonate (mg L <sup>-1</sup> )	$\mathrm{HCO}_{3}^{-}$	Titrimetric
Total alkalinity (mg L <sup>-1</sup> )	ТА	Titrimetric
Total hardness (mg L <sup>-1</sup> )	TH	Titrimetric

Statistical analysis: The application of statistical tools helps in understanding the complex data matrices to know the water quality, also helps to identify the possible sources that influence water systems and offers valuable information for reliable management of water resources (Simeonov et al., 2004; Reghunath et al., 2002). In this study, the statistical analysis such as boxplot designs, multivariate statistical analysis (Principle component analysis, cluster analysis) were carried using Minitab software (Ver.14.0) and correlation matrix were carried out using SPSS (ver.16.0). Box plot were employed to assess and compare distributions. Cluster Analysis (CA) helps to delineate variables, observations based on its characteristics (Shrestha and Kazam, 2007). The Euclidean distance yields similarity between samples and a distance can be estimated by difference between analytical values of the samples. Principle Component Analysis (PCA) provides information on parameters of whole data set and elucidate the variances of large set of inter correlated variables and transforms to uncorrelated principal components. Correlation matrix between the parameters was carried out by Pearson's correlation. Variable representing with correlation coefficient  $(\mathbf{R}^2)$  and independent variables are the percentage of variance with dependent variable. A high correlation coefficient (near to 1 or -1) implies a good relationship between two variables and 0 implies there is no relationship between variables (Venkatramanan et al., 2013).

#### **RESULTS AND DISCUSSION**

The collected samples were analyzed for various physicochemical parameters and compared with BIS and WHO standards (Table 3) and the detailed values of all parameters are presented in Table 4 and 5.

	BIS (10500:2012)		Samples		
Parameters	Acceptable limit	Permissible limit	WHO (2011)	Gudiyattam	Vaniyambadi
pH	6.5 - 8.5		7.5 - 8.5	6.9-8.0	6.9-7.9
$EC (\mu S \text{ cm}^{-1})$		-	1500	718.5 - 3678	981.5-11930
$TDS (mg L^{-1})$	500	2000	500	726-5227	1204-9909
TH (mg $L^{-1}$ )	200	600	200	245 - 1635	225 - 3815
$TA (mg L^{-1})$	-	-	120	180-430	285 - 825
$CO_3^{2-}$ (mg L <sup>-1</sup> )	-	-	-	0-80	70-90
$HCO_{3}^{-}$ (mg L <sup>-1</sup> )	-	-	500	0-400	150-585
$Cl^{-}$ (mg $L^{-1}$ )	250	1000	250	90-1555	95-2035
$Ca^{2+}$ (mg L <sup>-1</sup> )	75	200	75	15 - 1155	55 - 1780
$Mg (mg L^{-1})$	30	No relaxation	50	116.5 - 2520.5	96-6604
${\rm SO_4^{\ 2-}}~({\rm mg~L^{-1}})$	200	400	250	1.28-16.17	0.2 - 25.3



EC: Electrical conductivity, TDS: Total dissolved solids, TH: Total hardness, TA: Total alkanity,  $CO_3^{2-}$ : Carbonate,  $HCO_3^{2-}$ : Bicarbonate,  $Cl^-$ : Chlorides,  $Ca^{2+}$ : Calcium,  $Mg^{2+}$ : Magnesium,  $SO_4^{2-}$ : Sulphate

Table 4: Physicochemical characteristics of Gudiyattam block

Sampling points	pН	EC	TH	TDS	TA	$CO_{3}^{2-}$	$HCO_3^-$	Ca <sup>2+</sup>	$Mg^{2+}$	Cl-	$SO_4^{2-}$
GD 1	7.4	3611.0	245.00	2669.0	270.0	40	210	215.0	30.00	340.3	16.20
GD 2	7.6	3611.0	320.00	1584.0	430.0	40	370	115.0	205.00	170.1	14.50
GD 3	7.1	2589.0	310.00	2611.0	400.0	50	325	275.0	35.00	372.2	9.30
GD 4	6.9	3678.0	285.00	3711.0	28.0	80	160	190.0	95.00	872.07	3.40
GD 5	7.2	718.1	305.00	726.0	380.0	50	305	240.0	65.00	116.9	10.50
GD 6	7.3	1989.0	390.00	2122.0	430.0	20	400	375.0	15.00	308.4	1.27
GD 7	7.9	1989.0	1265.00	3135.0	185.0	70	80	1010.0	255.00	345.6	1.40
GD 8	7.4	1405.0	610.00	1419.0	235.0	80	115	520.0	90.00	345.6	10.70
GD 9	7.0	2835.0	355.00	2863.0	325.0	40	265	340.0	15.00	345.6	1.80
GD 10	8.0	783.7	1245.00	790.5	180.0	30	135	90.0	1155.00	345.6	3.90
GD 11	7.7	613.5	505.00	618.8	215.0	BDL	BDL	325.0	180.00	138.2	8.20
GD 12	7.7	5187.0	1635.00	5227.0	335.0	70	230	1555.0	80.00	2520.5	7.60
GD 13	7.0	2617.0	1320.00	2638.0	425.0	BDL	BDL	595.0	725.00	808.2	4.70
GD 14	7.6	888.9	370.00	897.4	340.0	BDL	BDL	215.0	155.00	404.1	5.21
Minimum	6.9	718.1	245.00	726.2	180.0	BDL	BDL	90.0	15.00	116.5	1.28
Maximum	8.0	3678.0	1635.00	5227.0	430.0	80	400	1555.0	1155.00	2520.5	16.17
Mean	7.4	2214.5	654.29	2322.5	316.4	40.71	185.36	432.8	221.43	530.9	7.05

 $\overrightarrow{\text{EC: Electrical conductivity, TDS: Total dissolved solids, TH: Total hardness, TA: Total alkanity, CO_3^{2-}: Carbonate, HCO_3^{2-}: Bicarbonate, Cl^-: Chlorides, Ca^{2+}: Calcium, Mg^{2+}: Magnesium, SO_4^{2-}: Sulphate, BDL: Below detection limit$ 

Table 5: Physicochemical characteristics of Vaniyambadi block

Sampling points	pН	EC	TH	TDS	TA	$CO_{3}^{2-}$	HCO <sub>3</sub> -	$Ca^{2+}$	$\mathrm{Mg}^{2^+}$	Cl.	$SO_{4}^{2-}$
VB 1	7.3	2317.0	2342.0	370	400.0	0	0	200	170	319	15.8
VB 2	7.2	4528.0	4571.0	490	460.0	70	355	255	235	681	25.3
VB 3	7.4	1396.0	1409.0	190	295.0	70	190	95	95	117	11.6
VB 4	7.9	981.5	990.9	150	285.0	90	150	95	55	96	0.2
VB 5	7.2	3647.0	3647.0	225	720.0	90	585	45	180	409	22.6
VB 6	7.0	3549.0	3581.0	1710	340.0	BDL	BDL	715	995	1,723	1.2
VB 7	7.1	2324.0	2342.0	1005	695.0	BDL	BDL	415	590	782	2.1
VB 8	7.5	1484.0	1494.0	790	315.0	BDL	BDL	395	395	484	6.0
VB 9	6.9	5485.0	5530.0	1650	385.0	BDL	BDL	750	900	2,669	5.4
VB 10	7.0	4763.0	4804.0	1730	825.0	BDL	BDL	655	1075	1,819	0.4
VB 11	7.4	2639.0	2664.0	1115	820.0	BDL	BDL	350	765	851	10.2
VB 12	7.2	11930.0	1204.0	3815	415.0	BDL	BDL	2035	1780	6,604	1.0
VB 13	7.5	3955.0	3989.0	1460	505.0	BDL	BDL	650	810	1,574	1.4
VB 14	7.1	2788.0	2814.0	570	507.5	BDL	BDL	485	85	564	5.2
Minimum	6.9	981.5	1204.0	225	285.0	70	150	95	55	96	0.2
Maximum	7.9	11930.0	9909.0	3815	825.0	90	585	2035	1780	6604	25.3
Mean	7.3	2317.0	2342.0	370	400.0	0	0	200	170	319	15.8

EC: Electrical conductivity, TDS: Total dissolved solids, TH: Total hardness, TA: Total alkanity,  $CO_3^{2-}$ : Carbonate,  $HCO_3^{2-}$ : Bicarbonate,  $Cl^{-}$ : Chlorides,  $Ca^{2+}$ : Calcium,  $Mg^{2+}$ : Magnesium,  $SO_4^{2-}$ : Sulphate, BDL: Below detection limit



Fig. 2: Chlorinity index for GD and VB blocks

In order to assess the usability of groundwater for purposes such as drinking, irrigation etc., the results obtained were compared with Indian standards IS: 10500 (BIS., 2012) and World Health Organization standards (WHO., 2011). It is necessary that the consumption of water for drinking purposes should be free from physical parameters such as colour, odour etc. In this study, these physical parameters were below detectable limit and hence it is not reported in the Table 4 and 5. Also, in order to maintain proper irrigation practices, parameters such as water quality, soil types and cropping practices plays an important role as the excessive quantity of dissolved ions in water affects habitat such as plants, soil and thereby reduces the productivity. These effects lower the osmotic pressure in plants cells and decrease the rate of metabolic activity (Ravikumar and Somashekar, 2013).

Chlorinity index is measured for the study area in order to check the suitability of groundwater for irrigation as low tolerant crops are chloride sensitive. The chlorinity index for the study area is presented in Fig. 2. It can be observed from the figure that in both the study locations, sampling sites GD1, GD2, VB 6, VB 9, VB 10, VB 12 and VB 13 were exposed to high levels of chlorinity (>1,100 mg L<sup>-1</sup>) which cannot be used for irrigation. Similarly salinity index were developed using EC values obtained from both the study locations in order to ensure the suitability for irrigation purposes. It is reported that EC values in the range 750-2250 and >2250 ( $\mu$ S cm<sup>-1</sup>) are doubtful and unsuitable for irrigation purposes (Handa, 1969).

**Spatial distribution:** The spatial distribution of physicochemical analysis of groundwater samples collected form two blocks GD and VB are shown in Fig. 3-6. It can be observed that from Fig. 3a that the pH ranges between 6.9 and 8.0 for GD and, 6.9 and 7.9 for VB which are within the desirable limit as per the standards. From the parametric analysis, total alkalinity was in the range of 180-430 mg L<sup>-1</sup> for GD (12 locations exceeded the limits) and 285-825 mg L<sup>-1</sup> for VB (almost all places were exceeded the permissible limits) (Fig. 3b). Total hardness was in the range of 45-1635 mg L<sup>-1</sup> in GD and 150-3815 mg L<sup>-1</sup> in VB (Fig. 4a). In general, high level of hardness level makes water not potable and causes scaling problem. Most of the samples collected represents hard to very hard state (23 samples out of 28) and hence, exceeded the permissible limits as per the



Fig. 3(a-b): Spatial variation representation of physicochemical characteristics (a) pH and (b) Total alkalinity for GD and VB blocks



Fig. 4(a-b): Spatial variation representation of physicochemical characteristics (a) Total hardness and (b) Electrical conductivity for GD and VB blocks



Fig. 5(a-b): Spatial variation representation of physicochemical characteristics (a) Calcium and (b) Magnesium for GD and VB blocks



Fig. 6(a-b): Spatial variation representation of physicochemical characteristics (a) Chloride and (b) Sulphate for GD and VB blocks



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Fig. 7(a-b): Box plots for physicochemical characteristics (a) VB and (b) GD

BIS and WHO standards. Moreover, greater electrical conductivity indicates the presence of higher concentrations of total dissolved salts. Conductivity values varied from 613.5-3678  $\mu$ S cm<sup>-1</sup> for GD and 981.5-11930  $\mu$ S cm<sup>-1</sup> for VB (Fig. 4b).

Anionic concentrations such as calcium (Fig. 5a) were in the range of 90-1555 mg L<sup>-1</sup> for GD and 45-2035 mg L<sup>-1</sup> for VB which revealed that almost all the sampling points have been exceeded the desirable limit as the desirable limit of calcium is 75 mg L<sup>-1</sup> and the permissible limit is 200 mg L<sup>-1</sup> as per BIS standards. Similarly, magnesium (Fig. 5b) varied from 15-1155 mg L<sup>-1</sup> for GD and 55-1780 mg L<sup>-1</sup> for VB which reduces the soil quality and hence reducing the crops yield and also gives toxicity when it exceeds 50% of magnesium ratio (Ramkumar *et al.*, 2013). According to the BIS standard, the desirable limit for magnesium is 30 mg L<sup>-1</sup> and no relaxation for its permissible limit. Similarly, the desirable limit of chlorides is 250 mg L<sup>-1</sup> and permissible limit is 1000 mg L<sup>-1</sup> as per BIS standards. The chlorides for the study area ranged from 117-2520 mg L<sup>-1</sup> for GD block and 96-6604 mg L<sup>-1</sup> for VB (Fig. 6a). It can be noted that the chlorides content of 24 places (out of 28) were exceeded the prescribed limit. Likewise, sulphate concentrations were in the range of 5-9 mg L<sup>-1</sup> predominately in both the regions (Fig. 6b).

**Statistical analysis:** The box and whisker plots of the selected parameters of GD and VB are presented in Fig. 7. It can be observed that conductivity, TDS and total hardness were predominant factors and calcium, magnesium and chlorides were observed as major ions for GD sampling site.

Table 6: Correla	ation matr	ix for VB b	olock								
Parameters	$_{\rm pH}$	TDS	EC	TH	ТА	$CO_{3}^{2-}$	$HCO_3^-$	$Ca^{2+}$	$Mg^{2+}$	Cl-	$\mathrm{SO}_4^{2-}$
pН	1										
$TDS (mg L^{-1})$	-0.652*	1									
$EC (\mu S \text{ cm}^{-1})$	-0.407	0.155	1								
TH (mg $L^{-1}$ )	-0.36	0.071	0.885**	1							
$TA (mg L^{-1})$	-0.346	0.365	0.061	0.062	1						
$CO_3 (mg  L^{-1})$	0.429	-0.155	-0.263	-0.557*	-0.169	1					
$HCO_3 (mg L^{-1})$	0.055	0.117	-0.093	-0.459	0.105	$0.858^{**}$	1				
$Ca (mg L^{-1})$	-0.313	-0.034	0.909**	0.973**	-0.063	-0.513	-0.437	1			
$Mg (mg L^{-1})$	-0.387	0.172	0.814**	0.974**	0.182	-0.572*	-0.455	$0.895^{**}$	1		
$Cl (mg L^{-1})$	-0.32	0.021	0.957 * *	0.962**	-0.042	-0.391	-0.305	0.977 **	0.896**	1	
$SO_4^{2-}$ (mg L <sup>-1</sup> )	-0.088	0.192	-0.143	-0.511	0.099	0.526	0.756**	-0.482	-0.512	-0.38	1

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\*Correlation is significant at the 0.05 level, \*\*Correlation is significant at the 0.01 level, EC: Electrical conductivity, TDS: Total dissolved solids, TH: Total hardness, TA: Total alkanity, CO<sub>3</sub><sup>2-</sup>: Carbonate, HCO<sub>3</sub><sup>2-</sup>: Bicarbonate, Cl<sup>-</sup>: Chlorides, Ca<sup>2+</sup>: Calcium, Mg<sup>2+</sup>: Magnesium, SO<sub>4</sub><sup>2-</sup>: Sulphate

Table 7: Correlation matrix for GD block

Parameters	$_{\rm pH}$	TDS	EC	TH	TA	$CO_{3}^{2-}$	$HCO_3^-$	$Ca^{2+}$	$Mg^{2+}$	Cl.	$\mathrm{SO}_4^{2-}$
pН	1										
$TDS (mg L^{-1})$	-0.219	1									
$EC \ (\mu S \ cm^{-1})$	-0.238	0.871**	1								
$TH (mg L^{-1})$	0.487	0.396	0.177	1							
$TA (mg L^{-1})$	-0.526	0.101	0.295	-0.259	1						
${\rm CO_3^{\ 2-}}~({\rm mg}~{\rm L}^{-1})$	-0.066	0.514	0.424	0.08	-0.263	1					
${\rm HCO_{3}^{-1}} \ ({\rm mg \ L^{-1}})$	-0.227	0.167	0.358	-0.374	0.538*	0.304	1				
${\rm Ca}^{2^+} ({\rm mg} \ {\rm L}^{-1})$	0.278	0.693**	0.45	$0.747^{**}$	-0.089	0.354	-0.129	1			
${\rm Mg}^{2^+}~({\rm mg}~{\rm L}^{-1})$	0.385	-0.265	-0.291	0.571*	-0.277	-0.317	-0.399	-0.12	1		
$\mathrm{Cl^{-}}\ (\mathrm{mg}\ \mathrm{L^{-1}})$	0.063	$0.784^{**}$	$0.683^{**}$	$0.623^{*}$	0.08	0.312	-0.035	$0.783^{**}$	-0.037	1	
${SO_4^{\ 2-}} \ (mg \ L^{-1})$	0.044	-0.187	0.185	-0.332	0.133	0.098	0.218	-0.203	-0.244	-0.106	1

\*Correlation is significant at the 0.05 level, \*\*Correlation is significant at the 0.01 level, EC: Electrical conductivity, TDS: Total dissolved solids, TH: Total hardness, TA: Total alkanity, CO<sub>3</sub><sup>2-</sup>: Carbonate, HCO<sub>3</sub><sup>2-</sup>: Bicarbonate, Cl<sup>-</sup>: Chlorides, Ca<sup>2+</sup>: Calcium, Mg<sup>2+</sup>: Magnesium, SO<sub>4</sub><sup>2-</sup>: Sulphate

Likewise same trend in predominant factors were observed for VB, among them Ca<sup>2+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup> were found out to be the predominant ions for VB. These results indicate that factors distribution is same as the sampling sites were nearby; however, the distribution of ionic nature is slightly different which may be due to bedrock and its interaction with groundwater.

The correlation coefficient values in range of +1 or -1 explain strong relationship among variables and the value of zero indicates no relationship between the variables. Similarly, the geochemical parameters showing correlation coefficient  $R^{2}>0.7$  are considered to be strongly correlated; values between 0.5-0.7 show moderate correlation (Giridharan et al., 2008).

**Correlation matrix:** The correlation values obtained in the present study in VB and GD are presented in the Table 6 and 7, respectively. The TDS showed a strong correlation between conductivity, calcium and chloride (r>0.871, r>0.693, r>0.784) at GD, total hardness was moderately correlated with Ca, Mg,  $SO_4^{2-}$  (r>0.5) for GD samples, whereas, it exhibited strong correlation between Ca, Mg (r>0.97). The cation Ca strongly correlated with Cl for GD samples (r>0.78) and Mg for VB samples (r>0.89). The major concurrent decrease/increase among the ions in the groundwater of GD and VB may be due to the result of dissolution/precipitation reaction and concentration effects. Furthermore, the conductivity exhibited strong correlation (r>0.8) with TH, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup>. Likewise, TH followed strong correlation with Ca<sup>2+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup> and anions Ca<sup>2+</sup> and Mg<sup>2+</sup> were strongly correlated with Cl<sup>-</sup>.

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Table 8: Ionic relationship for GD and VB blocks

Ion relationship	Sample ID	Ions	Types of correlation
Highly competitive ion	GD	Ca <sup>2+</sup> with Mg <sup>2+</sup>	Negative correlation
		$HCO_3^-$ with $SO_4^{2-}$	Low positive correlation
	VB	$\mathrm{Ca}^{2^+}$ with $\mathrm{Mg}^{2^+}$	High positive correlation
		$\mathrm{HCO}_{3}^{-}$ with $\mathrm{SO}_{4}^{2-}$	Low negative correlation
Affinity ion relationship	GD	NA	NA
	VB	NA	NA
Noncompetitive ion relationship	$\operatorname{GD}$	HCO <sub>3</sub> <sup>-</sup> with Cl <sup>-</sup>	Negative correlation
		$\mathrm{CO_3}^{2-}$ with $\mathrm{SO_4}^{2-}$	Low positive correlation
	VB	HCO <sub>3</sub> <sup>-</sup> with Cl <sup>-</sup>	Low negative correlation
		$\mathrm{HCO}_{3}^{2-}$ with $\mathrm{SO}_{4}^{2-}$	Low positive correlation

GD: Gudiyatham, VB: Vaniyambadi

#### Table 9: PCA for VB and GD blocks

	Vaniyamba	di		Gudiyathan	Gudiyatham					
Parameters	PC1	PC2	PC3	PC1	PC2	PC3	PC4			
pН	-0.184	-0.473	-0.247	0.008	-0.399	-0.361	-0.408			
EC ( $\mu$ S cm <sup>-1</sup> )	0.352	0.191	-0.347	0.411	0.24	0.02	-0.177			
$TDS (mg L^{-1})$	0.053	0.521	0.288	0.481	0.105	0.075	0.162			
TH (mg $L^{-1}$ )	0.412	0.006	-0.121	0.308	-0.42	0.14	-0.182			
$TA (mg L^{-1})$	0.034	0.384	0.305	0.019	0.378	0.532	-0.347			
$CO_3^{2-}$ (mg L <sup>-1</sup> )	-0.285	0.098	-0.449	0.28	0.128	-0.538	0.312			
$HCO_{3}^{-}$ (mg L <sup>-1</sup> )	-0.285	0.098	-0.499	0.054	0.421	-0.065	-0.225			
$Ca^{2+}$ (mg L <sup>-1</sup> )	0.402	-0.041	-0.201	0.442	-0.167	-0.02	-0.028			
$Mg^{2+}$ (mg L <sup>-1</sup> )	0.401	0.053	-0.036	-0.085	-0.422	0.233	-0.238			
$\mathrm{Cl}^{-}$ (mg $\mathrm{L}^{-1}$ )	0.389	0.031	-0.285	0.465	-0.062	0.123	-0.141			
$SO_4^{2-}$ (mg L <sup>-1</sup> )	-0.237	0.031	-0.285	-0.069	0.224	-0.444	-0.631			
Eigen value	5.6773	2.1457	1.6359	3.7839	2.9831	1.3038	1.0107			
Var. (%)	51.60	19.50	14.90	34.00	27.10	11.90	9.20			
(%)	51.60	71.10	86.00	34.00	61.50	73.40	82.60			

GD: Gudiyatham, VB: Vaniyambadi, EC: Electrical conductivity, TDS: Total dissolved solids, TH: Total hardness, TA: Total alkanity,  $CO_3^{2-}$ : Carbonate,  $HCO_3^{2-}$ : Bicarbonate,  $Cl^{-}$ : Chlorides,  $Ca^{2+}$ : Calcium,  $Mg^{2+}$ : Magnesium,  $SO_4^{2-}$ : Sulphate, PCA: Principal component analysis

Barr and Newland (1977), proposed three different sets of strong relationship that exist between cations and anions in groundwater as follows:

- High competitive relationship between ions with same charge but different valence number (Ca<sup>2+</sup> and Na<sup>+</sup>)
- High affinity between ions with same valency but different charges (Na<sup>+</sup> and Cl<sup>-</sup>)
- Non-competitive relationship between ions with same valency and same charge ( $Ca^{2+}$  and  $Mg^{2+}$ )

Based on the hypothesis and from the results of correlation coefficient matrix, the groundwater samples correlations of ions are presented in Table 8.

**Multivariate analysis:** Multivariate analysis like clusters analysis and Principle Component Analysis (PCA) have been successfully employed for groundwater monitoring to reduce loss of information to manageable data set (Praus, 2005). The PCA was performed to examine different parameters and its association between them (Kuppusamy and Giridhar, 2006). Eigen values greater than 1 were taken as criterion for extraction of principle components required to explain the sources of variances in the data and are shown in Table 9. Liu *et al.* (2003), hypothesized the factor loadings as strong, moderate and weak based on the absolute loading values of >0.75, 0.75-0.50, 0.50-0.30, respectively. In this study, four principle components of each block showing eigen values >1 have been extracted that contributed to maximum loadings of each blocks. For VB block, component 1 show that parameters such as conductivity, TH, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup> exhibited





Fig. 8(a-b): Cluster analysis for physicochemical parameters (a) VB and (b) GD blocks

positive correlations with weak and moderate loadings. However, these parameters constituted one related group contributing 51.6% of total variance. Likewise, component 2 the factors such pH, TDS, alkalinity showed up loadings attributing to 19.5% of total variance. Similarly, for component 3 it can be noted that conductivity, alkalinity, bicarbonate and carbonate alone contributed to moderate and weak loading though some negative loadings contributing to 14.9% of total variance.

In the case of GD block, component 1 exhibited moderate loadings by the parameters conductivity, TDS, TH, Ca, Cl that attributed to 34% of total variance. Similarly, component 2 showed up TH, TA, bicarbonate and magnesium explains 27% of total variance observed. Likewise, component 3 the factors such as TA, carbonate and sulphates exhibits moderate relationship that attributes to 11.9% of total variances. This trend was similarly observed in component 4 but corresponds to 9.2 of total variance. Based on the results, of both study locations, the ionic composition may be due to effect of nature that influences groundwater especially weathering of carbonate contacting salts. Additionally, the contribution of factors such Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> ions indicate the significance of weathering of gypsum in the bed rock (Hellar-Kihampa *et al.*, 2013). Furthermore, the data from principle component analysis indicates that most of the variables are controlled by soil/rock mediated natural process.

Cluster analysis is generally used for grouping the cases based on the similarity of the responses to several variables. Based on the connecting distance between parameters and their positions of the dendrogram, clusters were demonstrated (Fig. 8). It can be noted from Fig. 8a that

cluster 1 comprises of conductivity, TDS, carbonate, TH, Ca<sup>2+</sup>, Cl<sup>-</sup>. Similarly, the second cluster comprises of Sulphates, Bicarbonate, alkalinity which may be resulted from natural precipitation/weathering process coupled with agricultural drainage (Kumarasamy *et al.*, 2014) and the third cluster comprise of pH and Mg. In the case of VB (Fig. 8b), it can be noted from the figure that cluster 1 comprises of pH, sulphates, bicarbonate and carbonate. Similarly cluster 2 consists of alkalinity and TDS. Likewise parameters such as chlorides, conductivity, total hardness, calcium and magnesium were in cluster 3. Based on the results, the groundwater aquifer receives ion charge from natural weathering carbonate contacting minerals (Livingstone, 1963).

#### CONCLUSION

In this study, a detailed analysis of various physicochemical parameters of samples collected from 28 bore wells revealed the presence of more chlorides, electrical conductivity, TDS, TH, Ca<sup>2+</sup>, Mg<sup>2+</sup> and also slightly alkaline especially in Vaniyambadi (VB) study location. Less in concentration of sulphates provided less possibility of contamination through agricultural practices. Statistical analysis in the study presents the need and its application of large complex datasets to obtain better information on the groundwater water quality. The values of correlation coefficients revealed that  $SO_4^{2-}$ ,  $HCO_3^{--}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  were found significant based on the groundwater ionic composition, predominantly  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Cl^-$  were high correlated (r<sup>2</sup>>0.9). Furthermore, the multivariate analysis viz., PCA and cluster analysis also possessed same trend with higher contribution of anions and cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$  and  $HCO_3^{--}$ ) to the groundwater.

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