



## A study on groundwater quality and its characteristics in Tuticorin coastal region using geo-statistical approaches, Tamil Nadu, India

G Sakthivel<sup>†</sup> & R Manjula<sup>§</sup>

Department of Civil Engineering, National Institute of Technology, Tiruchirappalli, Tamil Nadu – 620 015, India

[E-mail: <sup>†</sup>403114054@nitt.edu; <sup>§</sup>manju@nitt.edu]

*Received 01 November 2019; revised 14 August 2020*

The aim of the present research is to identify the factors and processes to manage groundwater susceptibility using geostatistical techniques. Shortage of freshwater and drinking water are the major problems in the southeast coast of Tuticorin district, Tamil Nadu, India. Due to the different landscape and geological frame work across the coastal area, ever increasing population and manmade activities there is a necessity to check the groundwater quality in drinking and domestic water supply. Geostatistical analysis has been carried out through the field samples (24 nos) which were analyzed and visually interpreted in a graphical representation. The quality characteristics of the samples analysed using multivariate statistical analysis in the study area have been identified to be abnormal (EC, TDS, Cl and Na). The values are approximately 3 times exceeding the WHO standard for the villages of Sahupuram, Kayalpattinam, Arumuganeri, Vaalagamuthram and Arasadi spread over 300 km<sup>2</sup>. Principle Component Analysis (PCA) indicates that the field of groundwater quality is predominantly associated with geogenic (rock-water interaction) and anthropogenic sources and domestic sewage. Findings of factors, cluster analysis (CA) and correlation matrix (CM) were also found to be consistent with the PCA results. It has been evident from the statistical analysis that the major groundwater quality is significantly influenced by EC, TDS, Cl and Na due to the inland salinity caused by seawater intrusion. Results of the study are expected to provide insights into taking effective action for groundwater quality protection by decision-makers on the Tuticorin coast of southern Tamil Nadu.

**[Keywords:** Groundwater quality, Groundwater vulnerability, Multivariate statistical analysis, Seawater intrusion, Tuticorin coastal region]

### Introduction

Freshwater sources in the present study area *i.e.* the groundwater is the major water source for agriculture, domestic and industrial use. Thus, in the coastal areas, groundwater quality and quantity plays a major role since it is important for a valuable component of human life, social and economic growth of a sustainable ecosystem and is also susceptible to natural and human factors<sup>1</sup>. In the event of rainfall excess than required by the crops, high evapotranspiration causes transportation of the salts by infiltration of water from vadose zone to water table, thereby elevating the salt content in groundwater and decreasing the salt content in top soil layers<sup>2,3</sup>. In addition, the quality of groundwater is superior to the surface water as far as microbial contamination is considered, due to the soil matrix that act as a filter. The above groundwater quality is a function of natural process influenced by physico-chemical parameters such as intermixing of different water zones, hydrogeochemistry of the recharge area, dark

slope and chemical rock weathering<sup>1,4-7</sup> (Fig. 1). Hence, in coastal regions, major issues are the seawater intrusion and the solidity of water, directly or indirectly associated with hydrogeological formation, climatic conditions, recharge capacity of lithology, and land use and land cover pattern. Further, the quality of groundwater is affected by the natural activities like groundwater recharge, discharge of rainfall and chemical weathering of rock forming minerals<sup>8-11</sup>. Once groundwater is contaminated, it takes long time to nullify the contamination effect because of the low flow rate in the aquifers<sup>1,4,12,13</sup>. The important aspects of the coastal areas of Tuticorin are large population, urbanization and increased industrial activity. Manmade activities import huge pressure on the fragile coastal ecosystem. Coastal pollution in Tuticorin has vastly affected the mankind and livestock, commercial and recreational uses of coastal areas and the overall integrity of the coastal and marine ecosystems. Studies on seawater intrusion have been performed with various methods such as

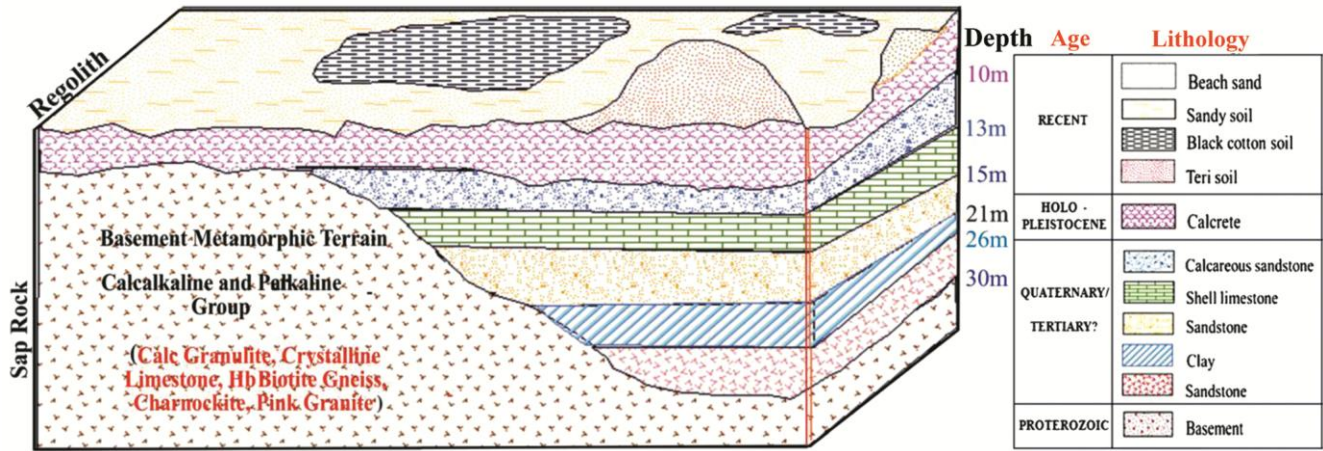


Fig. 1 — Schematic sequential stratigraphy of the study area (Perumal Velmayil 2020)

multivariate statistical analysis<sup>1,14,15</sup> and geochemical modeling<sup>1,7,16</sup> to investigate geochemical analysis and the hydrochemical process controlling geochemical characteristics. Multivariate analysis of geochemical data is based on the idea that each aquifer has its respective groundwater quality indicator, which is affected by the chemical parameters of surrounding sediments. Hence the present study attempts a geochemical analysis using ionic ratio and statistical analysis to assess water quality parameters in the Tuticorin coastal region.

**Materials and Methods**

**Study area**

*Geological and General settings of the area*

Study area (latitude: 8°19'35.09" N to 9°3'46.13" N and 77°57'42.88" E to 78°21'52.82" E longitude) extends between Vembar to Kulasekarapattinam for about 98 km. The range of altitude above MSL (Mean Sea Level) of the coast varies from 1.5 to 68 m and has distinct eastward slope of gentle nature. The area is prominent with numerous beach plains, isolated sandy beaches, marine terraces, sand dunes, and estuary. In addition, among the important drainage networks in the study area are the Thamirabarani river in the centre of the area under study and Vaippar river towards the north of the study area which flows eastward from the western ghats making an estuary and backwater at the river mouth (Fig. 2). Study area experiences annual rainfall of 621 mm and temperature is 29.2 °C.

**Industries**

Tuticorin comprises of various manufacturing industries like using AlF<sub>3</sub>, carbamide, NH<sub>4</sub>Cl, NaOH, Cu, aquaculture, refinery, chemicals and fertilizers,

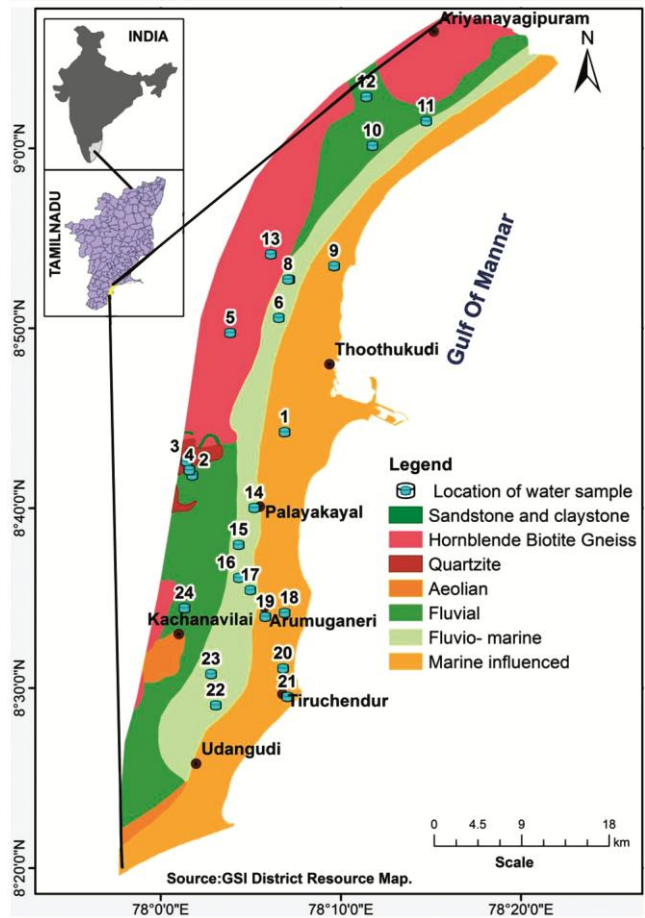


Fig. 2 — Map showing the study area, sample locations and geology of Tuticorin coastal region, southern Tamil Nadu

and a thermal power plant on the Tuticorin coast (Table S1). As a result of domestic activities, the town releases sewage of 17.5 MLD (million litres per day), which is untreated due to the lack of treatment facilities which is then disposed of in canals that finally reach the sea.

### Geology

The geology map has been prepared using the information of a District Resource Map of scale 1:250,000 obtained from Geological Survey of India. The study area comprises of different types of geological settings like the marine, fluvial marine, aeolian, sandstone, claystone, hornblende biotite gneiss and quartzite. Among them, sand, silt, and clay are widely seen in the near and back shore areas, whereas coarse sandy clay is spotted in the northern parts of the area under study (Fig. 2). The area within the coastline between Tuticorin and Tiruchendur is covered by coarse gravelly terrace soils and deposits with thickness ranging from 1.5 to 7.0 m. Owing to this formation composed of coarse and reddish brown sandy material the permeability of surface water into the aquifer is influenced. Towards the north of the Vaippar river the formations are mainly of clayey sand and sandy clay surface. The coast from Tiruchendur to Tuticorin has coarse sandy soils added with minerals like garnet, illmenite, and monazite which are evacuated by placer mining.

There are various types of land use and land cover patterns observed in the study area including rural and urban settlements, sandy deposits, agricultural land, plantations, and coastal vegetation, etc. Nearly half of the total area consists of agricultural land comprising plantation, cropland, and fallow land. There are dense rural and urban settlements and sand dunes with vegetative cover in the backshore area, while sandy beaches, salt-affected lands, saltpans and eroded landforms are in various parts of the nearshore coastal area. Mostly in the central and southernmost portions of the Tuticorin's urban settlements, water bodies such as pools and ponds are well spread (Fig. 3).

### Methodology

#### Sample collection and analysis

Water Samples have been obtained from aquifers for the estimation of the biological, chemical and physical characteristics. A reconnaissance survey was undertaken to identify areas of groundwater recharge and the discharge location. On the basis of the topographic sheets through the use of grid map and satellite image, the study area was divided into numerous grids (5 x 10 km) using ARCGIS 10.2.1 environment. To study the spatial distribution of groundwater quality parameters, the water samples were collected by random sampling method. A total of 24 sampling points distributed over the area under study were recorded using GPS and were named GCP

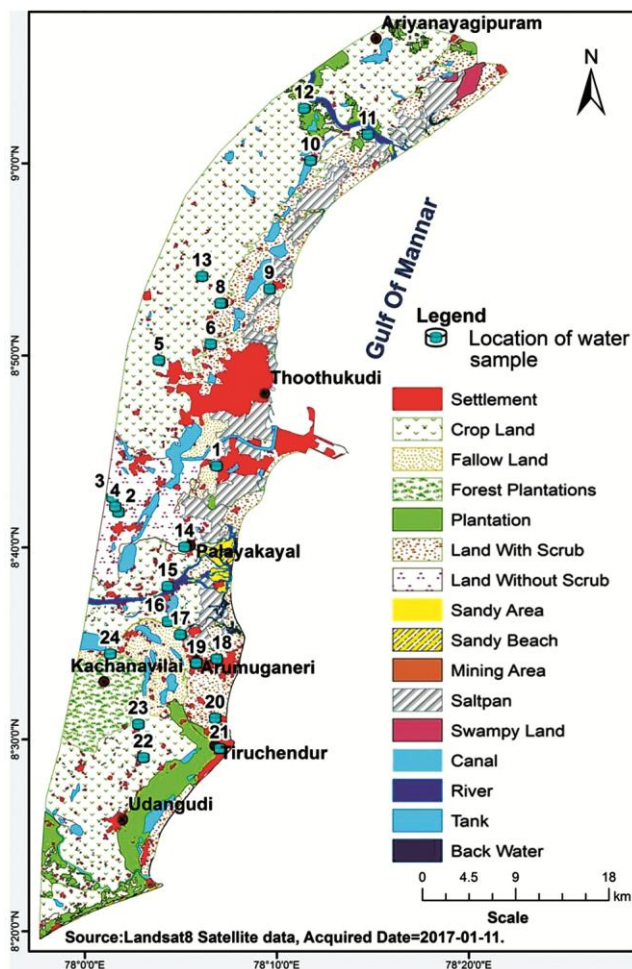


Fig. 3 — Land use/land cover map of the study area

(Ground Control Point) as shown in Figure 2. The descriptions of the water sample collected from the locations are given in Table 1. Representative groundwater samples from 24 locations of Tuticorin coast were collected from aquifers in close proximity to the Tamirabarani river during the summer of 2017. Sampling points were located in and around industries, urban and agricultural areas. The water samples were collected in dirtfree, colorless glass bottles after rinsing twice or thrice with water before the sample has been finally drawn. In the cases of water sample collection from a pump or motor, the samples were collected after about 30 minutes of water flow through the pipe to ensure uniform sampling.

The samples were stored at 4 °C for further analysis in the laboratory to analyze the physico-chemical characteristics of groundwater including EC, pH, Total Dissolved Solids (TDS), cations:  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , anions:  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$

Table 1 — Description of water sample collection locations

Sample No	Location	Latitude (N)	Longitude (E)	Description
1	Muthaiyapuram	8°44'14'	78°06'52'	SPIC area and Agricultural area
2	Pillaiyarkovil	8°41'50'	78°01'45'	Near Coir company
3	Sahalpuram	8°42'36'	78°01'26'	Agricultural area
4	Kamaraj Nagar	8°42'07'	78°01'35'	Agricultural area
5	Therku Veerapandiyapuram	8°49'45'	78°03'51'	Behind Sterlite industries
6	Jothi Nagar	8°50'35'	78°06'33'	Agricultural area
7	K Velayuthapuram	8°52'43'	78°07'08"	Agricultural area
8	Arasadi	8°52'43'	78°07'04'	Saltpan
9	Tamaraikulam	8°53'28'	78°09'37'	Saltpan
10	Kulathoor	9°15'00'	78°14'50'	Agricultural area
11	Vaipar	9°00'09'	78°11'45'	Agricultural area
12	Poossanur	9°02'52'	78°11'25'	Agricultural area
13	Vaalasamuthram	8°54'07'	78°06'06'	Thermal power plant
14	Manjaneerkayal	8°40'01'	78°05'11'	Agricultural area
15	Mukkani	8°37'58'	78°04'19'	Agricultural area
16	Athur	8°36'08'	78°04'20'	Agricultural area
17	Sahupuram	8°35'27'	78°04'58'	DCW industry
18	Kayalpattinam	8°34'11'	78°06'52'	Saltpan
19	Arumuganeri	8°33' 58'	78°05'48'	Agricultural area
20	Veerapandiyapattinam	8°31'06'	78°06'47'	Saltpan
21	Tiruchendur	8°29'31'	78°07'02'	Urban
22	Paramakuruchi	8°29'03'	78°03'03'	Agricultural area
23	Kayalmozhi	8°30'47'	78°02'47'	Agricultural area
24	Vanathiruppathi	8°34'27'	78°01'19'	Agricultural area

are taken into account for the interpretation of geochemical characterization of groundwater. The physico-chemical characteristics were estimated following standard procedures as prescribed by the American Public Health Association (APHA 2005). Electrical Conductivity (EC), pH and TDS have been measured *in-situ* using respective electrodes. Afterwards,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  were determined through titration. Carbonates and bicarbonates were determined by titrating the samples with a standard acid using phenolphthalein and methyl orange as indicators. Titration to the methyl orange end point indicates neutralization of bicarbonates. Chlorides were determined by titrating with standard  $\text{AgNO}_3$  solution using potassium chromate as indicator. Sulphate was determined by adding solid barium chloride in the presence of gum acacia which makes the colloid very stable at pH 4.8. Calcium was estimated by titration with EDTA using murexide as indicator in the presence of sodium hydroxide. Magnesium was estimated with calcium using Eriochrome. Sodium was estimated by flame photometry. Anions ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) were analyzed using ion chromatography (ICS1100) (APHA 2005).

The quality of chemical analyses was carefully monitored by the duplicate samples, standard reference solutions and blank solutions.

Wilcox plot was used to identify various hydrogeochemical characteristics in groundwater to ensure its suitability for drinking and irrigation prepared with Aqua-Chem software<sup>17</sup>.

The data obtained were used to perform Multivariate Statistical Analysis (MSA) with the help of XLSTAT 2016 software. Correlation matrix, Principal Components Analysis (PCA), and Hierarchical Cluster Analysis (HCA) was used to analyze the groundwater parameters. In this study, HCA has analyzed the resemblance in tendencies of water quality variation between the examined target sites.

## Results and Discussion

### Groundwater quality for drinking purpose

Variations in physico-chemical parameters in water from different areas of Tuticorin and its surroundings are shown in Table 2. Water quality parameters with obtained values and standard WHO and BIS limits<sup>18-20</sup> are shown in Table 3. The pH values vary between

Table 2 — Statistical summary of different physico-chemical parameters of the sample (concentration in mg/L except for EC (dS<sup>-1</sup>/M) and pH)

Parameter	Minimum	Maximum	Average	Std. Dev.	WHO 2012	ISI 1983	BIS 1991
pH	7.86	8.54	8.2	0.16	6.5-8.5	6.5-9.2	6.5-8.5
EC	110	14530	3340.8	3781	1500	-	-
TDS	48	4500	1193.7	1214.72	1500	1500	1500
Ca	12	202.4	88.2	61.72	200	200	200
Mg	1.2	687.8	104.9	148.28	150	100	100
Na	6.2	2405	448.42	635.58	200	150	150
K	0.78	138	33	43.63	12	-	-
CO <sub>3</sub>	3	111	26	24.5	200	-	-
HCO <sub>3</sub>	39.6	738.3	286.9	209.4	500	400	400
Cl	10.6	4782.5	985.85	1285.13	600	1000	1000
SO <sub>4</sub>	3.7	669.6	164.35	184	250	400	400
NO <sub>3</sub>	0.46	65.9	14	15.83	45	45	45
Turbidity	0.78	2.75	1.59	0.52	5	5	5

Table 3 — Classification of groundwater samples of the study area based on (BIS, 1991)

S. No.	Groundwater class	TDS range (mg/l)	Number of samples		Sampling locations
			No.	%	
1	Freshwater	< 1000	15	62.5	1-5, 7, 10-12, 14-16, 22-24
2	Slightly saline	1000 – 3000	6	25	6-9, 19, 20, 21
3	Moderately saline	3000 – 10000	2	8.5	13,18
4	Very saline	10000 – 30000	1	4	17
5	Brine	> 30000	-	-	-

7.86 and 8.54, averaging 8.2, to indicate the basic characteristics shown in summary statistics of Table 4. A high pH value is caused by an interaction between rain water and sediments there by producing alkalinity to groundwater<sup>21</sup>. The central part of the study area exhibit higher EC values compared to other areas, because of industrial and saltpan activities. Electrical conductivity ranged between 110 – 14530  $\mu$ S/cm. The higher values of EC signify higher salinity and total dissolved concentration. Results suggest that only 6 samples out of 24 have EC below 500  $\mu$ S/cm (fresh water), 4 water samples have under marginal water (500 – 1500  $\mu$ S/cm), while 8 samples have EC values ranging between 1500 and 5000  $\mu$ S/cm and the remaining 6 of 24 samples have EC values greater than 5000  $\mu$ S/cm (Table 4). The climate of area under study is semi-arid and hence categorized by high evaporation thereby increasing salt content in the groundwater. Overall, high EC (> 1500  $\mu$ S/cm) is observed in the study area. The results shows that EC values are greater in the areas near to the coast compared to the inland areas from northern to southern part of the study area. The values of TDS ranged between 48 to 4500 mg/l in drinking water. The maximum prescribed limit of TDS

concentration in water is below 1000 mg/l which is acceptable to consumers, though the acceptability varies according to WHO and BIS standards. Most groundwater samples come under the freshwater category (62.5 %) and hence the groundwater in such areas are suitable for drinking purposes as shown in Table 3. The groundwater quality in remaining 37.5 % of area ranges from slightly to moderately saline and so it is unsuitable for drinking, and besides its TDS value is higher than 1000 mg/l. Perhaps percolation of channel water containing solids, agricultural waste and industrial seepage has resulted in relatively higher TDS concentrations in groundwater samples 13, 17 and 18. Turbidity variation is reasonably uniform throughout the study area ranging from 0.78 to 2.75 NTU. Also, chloride increases the electrical conductivity of water thereby increasing the corrosivity.

Among the water samples investigated, the magnitude of cations is in the decreasing order as: Na<sup>+</sup> > Mg<sup>2+</sup> > Ca<sup>2+</sup> > K<sup>+</sup> for groundwater; whereas, the order of anions is in the increasing order as: Cl<sup>-</sup> > HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > CO<sub>3</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> for groundwater. Significant variations were observed in the order of ions, based on the locations of water samples. In groundwater,

Table 4 — Results of correlation analysis

Variables	pH	EC	Na	K	Ca	Mg	Cl	HCO <sub>3</sub>	CO <sub>3</sub>	NO <sub>3</sub>	SO <sub>4</sub>	TDS
pH	1	-0.094	-0.119	-0.007	-0.451	0.092	-0.064	-0.276	-0.422	-0.316	-0.304	0.010
Ec	-0.094	1	0.953	0.596	0.683	0.710	0.996	0.354	0.515	-0.017	0.192	0.869
Na	-0.119	0.953	1	0.622	0.622	0.473	0.946	0.378	0.537	0.008	0.197	0.906
K	-0.007	0.596	0.622	1	0.377	0.253	0.576	0.436	0.224	0.330	0.356	0.626
Ca	-0.451	0.683	0.622	0.377	1	0.421	0.657	0.401	0.738	-0.166	-0.078	0.515
Mg	0.092	0.710	0.473	0.253	0.421	1	0.723	0.089	0.170	-0.064	0.126	0.452
Cl	-0.064	0.996	0.946	0.576	0.657	0.723	1	0.270	0.496	-0.030	0.170	0.854
HCO <sub>3</sub>	-0.276	0.354	0.378	0.436	0.401	0.089	0.270	1	0.203	0.172	0.336	0.426
CO <sub>3</sub>	-0.422	0.515	0.537	0.224	0.738	0.170	0.496	0.203	1	-0.135	-0.040	0.493
NO <sub>3</sub>	-0.316	-0.017	0.008	0.330	-0.166	-0.064	-0.030	0.172	-0.135	1	0.857	0.055
SO <sub>4</sub>	-0.304	0.192	0.197	0.356	-0.078	0.126	0.170	0.336	-0.040	0.857	1	0.198
TDS	0.010	0.869	0.906	0.626	0.515	0.452	0.854	0.426	0.493	0.055	0.198	1

there is considerably a large concentration of HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>. The low SO<sub>4</sub><sup>2-</sup> content in groundwater is due to the sulphate reduction process in the aquifer system<sup>5,22</sup>. The concentration levels of Cation viz. Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and K<sup>+</sup> ions vary from 6.2 – 2405 mg/l, 1.2 – 687.8 mg/l, 12 – 202.4 mg/l and 0.78 – 138 mg/l, respectively. Cationic concentration level indicate that the sodium concentration in the groundwater samples exceed the permissible limit of 200 mg/L.

Among the anions, chloride is present in significant proportions in groundwater which is an important inorganic anion. The concentration of chloride ion in the study area is between 10.6 and 4782.5 mg/l; averaging to 985.85 mg/l. Comparatively higher chloride concentration level (1836 – 4782.5 mg/L) is observed in groundwater samples 8, 10, 13 and 17-19 which contribute around 75 to 80 % of total anionic concentration because of the poor sanitation, chemical fertilizers, return flows from irrigated agriculture and effluents from industries. According to WHO and BIS, the chloride concentration level should not exceed 250 mg/l, but a total number of 16 samples from the study area exceeded the prescribed limits and are unfit for drinking, whereas 6 samples (8, 10, 13 and 17-19) exceed 0.25 g/litre due to the reaction with metals ions to form salts thereby increasing metal hardness in drinking water. The consumption of drinking water containing sodium chloride with concentrations more than 250 mg/litre can produce hypertension<sup>23</sup>. This is related to sodium ion concentration. Bicarbonate concentration ranges from 39.6 to 738.3 mg/L. A relatively lower HCO<sub>3</sub><sup>-</sup> concentration when compared to the chloride concentration in groundwater reveals that the dissolution of mineral is insignificant, but 4 samples

(8 and 17-19) exceeded the permissible limits. The box plot of various parameters in groundwater quality is shown in The hardness of groundwater is determined by Ca<sup>2+</sup> and Mg<sup>2+</sup> ions along with HCO<sub>3</sub><sup>-</sup> ion. In soil, precipitation of Ca<sup>2+</sup> and Mg<sup>2+</sup> takes place because of the temporary hardness with the precipitated salts, which contributes to a high concentration of groundwater ions when getting leached from the soil during rain. One sample (1) has exceeded the permissible limit for calcium and 2 samples (13 and 17) have exceeded the permissible limit for magnesium in the spatial groundwater quality distribution parameters as shown in Table 2. The intake of calcium and magnesium are connected with high risks of nephrolithiasis (kidney stones), colorectal cancer, osteoporosis, coronary artery disease, hypertension and stroke, insulin resistance and obesity<sup>17</sup>.

SO<sub>4</sub><sup>2-</sup> ranges from 3.7 to 669.6 mg/l; averaging to 164.35 mg/l. This is a common environmental problem in agricultural regions that are irrigated. The highest sulphate concentration of greater than 400 mg/l in groundwater sample 1 shows the deposition of soluble salts, manmade activity and inclusion of excess sulphate fertilizer in surrounding soil. The 68 % of people intaking water with sulphate levels ranging from 1000 to 1500 mg/litre suffer from laxation<sup>24</sup>. The observed range of NO<sub>3</sub><sup>-</sup> is 0.46 – 65.9 mg/l; averaging to 14 mg/l. The highest nitrate concentration of greater than 45 mg/l has been found in groundwater sample 16. In natural conditions, NO<sub>3</sub><sup>-</sup> concentration will normally not surpass 10 mg/l in ground-water; hence, anything in excess of 10 mg/L, indicates anthropogenic pollution because of poor sanitation, and haphazard use of fertilizers for high crop-yields. Gypsum and anhydrite dissolution might cause SO<sub>4</sub><sup>2-</sup> in groundwater whereas

fertilizers and leaching of municipality waste or agricultural runoff could cause high concentration of  $\text{NO}_3^-$  in groundwater<sup>17</sup>.

Sodium exceeding the permissible limits is seen in 6 samples (8, 10, 13 and 17 – 19) similar to bicarbonate, chloride and EC. Fawell *et al.*<sup>25</sup> have reported that the accidental overdoses of sodium chloride causes vomiting, nausea, convulsions, cerebral and pulmonary oedema, muscular twitching and rigidity. Excessive consumption of salt critically intensifies chronic congestive heart failure<sup>22</sup>.

**Irrigation suitability**

In the study area, agriculture accounts for almost 30 to 40 % comprising of maize, corn, paddy and other crops. During irrigation, the high rate of dissolved salts like magnesium, sodium, bicarbonate and chloride in irrigation areas can affect the plant roots thereby resulting in the lesser yields and interrupting the plant growth<sup>22</sup>. Hence, The methods of Wilcox<sup>26,27</sup> were used to identify and recognise groundwater parameters which in turn depend on water mineralization and its effect on plants and soil.

Water type in the study area is categorized as very hard, moderately hard, hard, and soft. The category of

coastal groundwater established by total hardness indicates that all the samples fall under very hard categories. Values of EC of the groundwater in these areas measure within  $2500 \mu\text{S}/\text{cm}$ . The water is moderately alkaline in 50 percent of samples consisting high salinity. High salinity and sodium levels are unsuitable for irrigation as sodium is the ingredient of a harmful salt and leads to inferior physical status of soil. A high rate of salts in water used for irrigation can alter osmotic pressure in plants root zones which limits the water intake by the plant and thus hinders the growth. The sample no 13 and 17 – 19 contain fluvial marine sediments in the eastern part of the study area. Wilcox diagram of the study area (Fig. 4) drawn using aquachem software shows that the 12.5 % of groundwater samples fall into unsuitable conditions, 15 % samples fall under the doubtful to unsuitable category, whereas 62.5 % of groundwater samples fall within the permissible category.

**Multivariate statistical analyses**

*Correlation analysis (CA)*

Correlation coefficients matrix shows that EC and TDS indicate a good positive correlation with Mg, Ca, Na,  $\text{SO}_4$ , Cl, and  $\text{NO}_3$  (Table 4), thereby inferring that

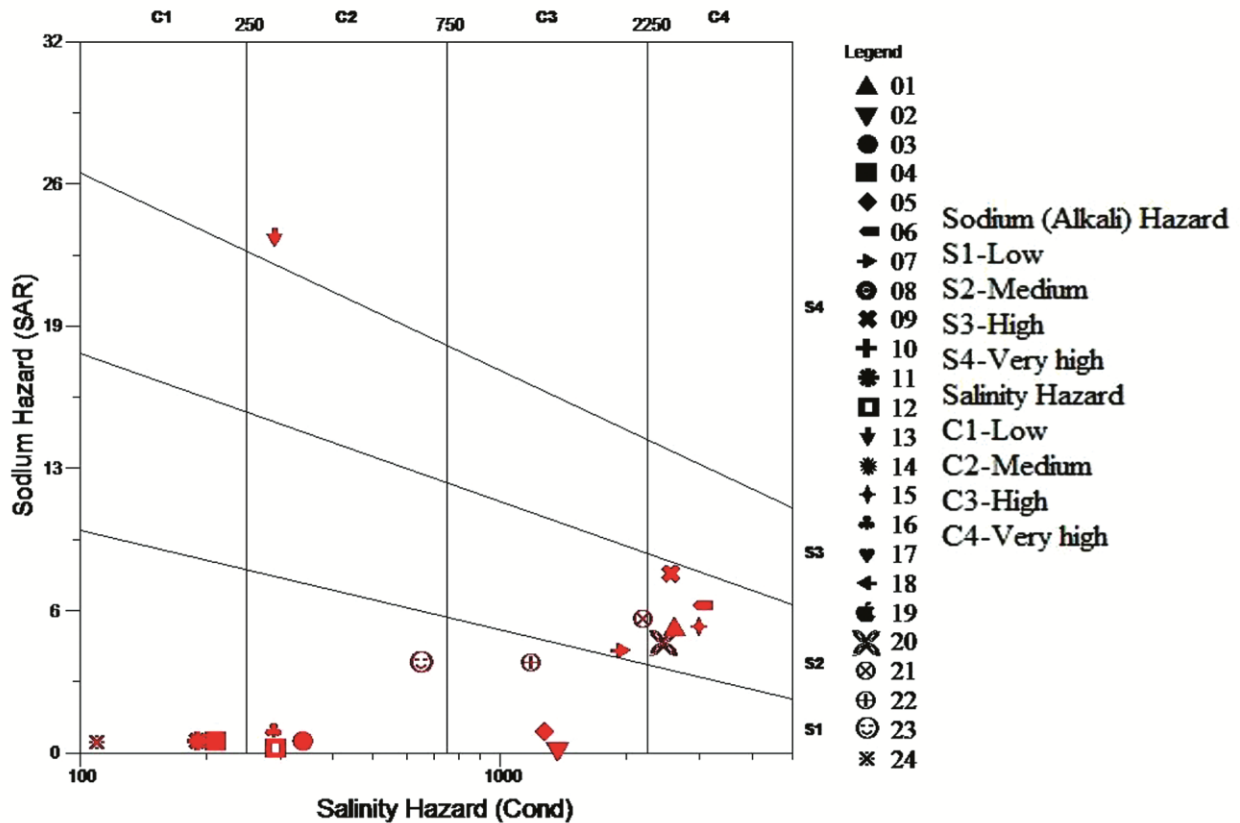


Fig. 4 — Wilcox plot of the groundwater samples

these ions come from the origins of inland salinity and infiltration of seawater.

The correlation matrix subjected to 14 variables including major ions and physical parameter decides the relationship between the variables and controlling factors and helps to recognise the sources of different elements. Firstly, high correlations were resulted between physical parameters like EC and Cl (0.996), Na<sup>+</sup> (0.953), TDS (0.869) Mg<sup>2+</sup> (0.710), Ca<sup>2+</sup> (0.683) and K<sup>+</sup> (0.596; Table 4). This correlation possibly identifies salinity intensification because of the chemical weathering of rock-forming minerals belonging to silicate group in the area. Also, there is a sign of possible correlation between Na and EC (0.953), TDS (0.906) that can be resulted due to the physical pollution, possibly from the salt pans and the discharge of industrial effluents into rivers. Secondly, significantly higher correlations were observed in other major elements. Positive correlation was established between SO<sub>4</sub> and NO<sub>3</sub> (0.857). In the area under study, the origin of groundwater nitrate pollution may be from animal waste, domestic sewage and from septic tank effluents.

#### Principal Component Analysis (PCA)

To investigate groundwater quality, PCA was performed on 14 variables for 24 groundwater samples in and around the coastal region of Tuticorin. The first factor (PC 1) clarified the total variance by 42.22 % and dominated by the EC, Na, K, Ca, Mg, Cl, HCO<sub>3</sub>, CO<sub>3</sub> and TDS (Marked by red colour; Table S2). PH, NO<sub>3</sub>, SO<sub>4</sub>, alkalinity and turbidity show a mild and negative association with factor 1 (PC 1) reflecting chemical components due to the geological function in the water system that confirms previous published scientific findings of Mondal *et al.*<sup>12</sup>. Figures 5 and S1 shows the factor 1 vs. factor 2 plot and their level of relationship to each other. Factor 2 (PC 2) is dominated by NO<sub>3</sub>, SO<sub>4</sub>, turbidity and clarified 17.70 % of the overall variance (Table S3); since nearby local variations in land use, water system rehearses, aquifer type and precipitation can bring about increment nitrate fixations. Factor 3 (PC 3) shows strong positive and negative correlation with pH and CO<sub>3</sub> with 11.93 % of total variation, respectively. Factor 4 (PC 4) is moderately regulated by HCO<sub>3</sub><sup>-</sup>. Factors 4 and 5 could have an impact on the anthropogenic effects of fertilizer use in agriculture, inland salinity, and carbonate mineral dissolution activities.

#### Hierarchical Cluster Analysis (HCA)

HCA analysis is utilized to group the water samples with similar monitoring points of chemical composition. In the current study, a dendrogram chart has been prepared with the help of Ward's method to group the places of sampling. As per the results (Fig. 6), Cluster I (sample no. 1 and 18), cluster II (sample no. 2 – 7, 9, 11, 12, 14 – 16 and 20 – 24) and cluster III (sample no. 8, 10, 13, 17 and 19) confirm to the slightly saline region, fresh water region, and moderately saline region, respectively. Hence, cluster III may be designated with moderate salinization due to industrial activities and inland salinity. Cluster I comprise of slightly saline water and cluster II consist of fresh water in the study area.

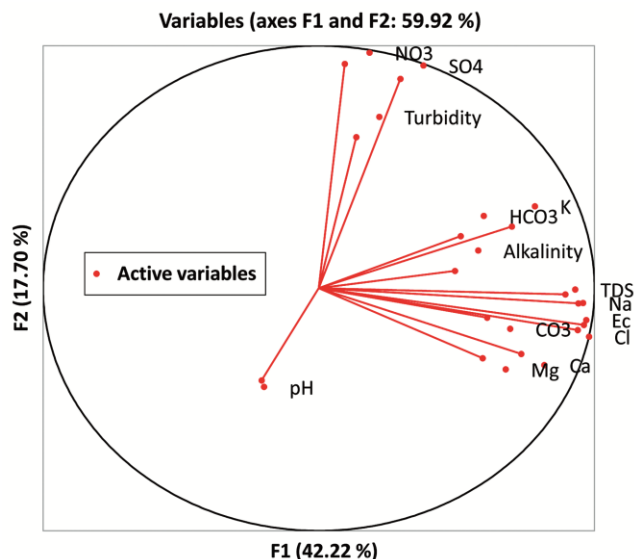


Fig. 5 — Scatter plot of loadings for the three identified PCA components performed on groundwater chemical data

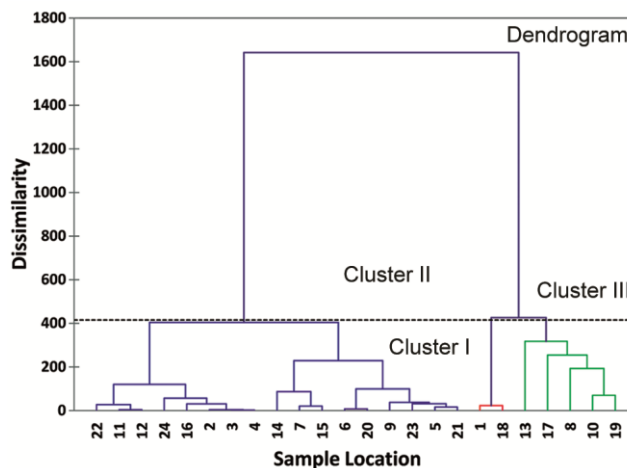


Fig. 6 — Dendrogram of aerial cluster in groundwater samples



## Conclusion

This study provides hydro-geochemical characteristics and their chemical-influencing processes of groundwater that interacts with the coastal region which in turn been evaluated through a geostatistical analysis in the Tuticorin coast of Tamil Nadu, India. The analysis is based on the major physico-chemical characteristics like Ca, Na, Mg, Cl, and HCO<sub>3</sub> as the dominant cation and anion respectively. Based on WHO standards the values of Total Dissolved Solids (TDS) and Electrical Conductivity (EC), the water samples were found to be freshwater (62.5 %), slightly saline (25 %), moderately saline (8.5 %), and extremely saline (4 %), respectively. The findings indicate that the ground water is fresh to salt water.

Principal Components Analysis (PCA) stated that four extracted factors accounted for 81.27 % of the total variance. The PCA findings provided a hint that the water quality in the coastal region is mainly affected by saltpan field inland salinity, ion dissolution and anthropogenic behaviour. HCA classified the 24 groundwater samples into three dominant clusters (C1, C2 and C3) that helped to understand the location of groundwater quality in the investigated area. Both Muthaiyapuram and Kayalpattinam (sample no. 1 and 18) are slightly saline. The stations Pillaiyarkovil, Sahalpuram, Kamarajnagar, Therku Veerapandiyapuram, Jothinagar, K Velayuthapuram, Tamaraikulam, Vaipar, Poosanur, Manjaneerkayal, Mukkani, Athur, Veerapandiyapattinam, Tiruchendur, Paramakurichi, Kayalmozhi and Vanathiruppathi (sample no. 2 – 7, 9, 11, 12, 14 – 16 and 20 – 24) are identified to have freshwater. The remaining sample locations like Aasadi, Kulathoor, Vaalasangam, Sahupuram and Arumuganeri (sample no. 8, 10, 13, 17 and 19) are reasonably saline. These areas are around major industries such as SPIC, Sterlite, TTPS and DCW. Study also reveals that overexploitation has resulted in mixing of highly saline groundwater with freshwater whose availability is depleting. To avert groundwater salinity, recharge well or dug well shall be constructed along the shoreline and freshwater shall be injected into the dug well to push away seawater from intrusion.

## Supplementary Data

Supplementary data associated with this article is available in the electronic form at

[http://nopr.niscair.res.in/jinfo/ijms/IJMS\\_50\(04\)329-338\\_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijms/IJMS_50(04)329-338_SupplData.pdf)

## Acknowledgements

We thank the anonymous referees for their useful suggestions.

## Conflict of Interest

The authors declare no conflict of interests.

## Author Contributions

Conceptualization and job layout: GS & RM. GS: Conceptualization, methodology, collection of data, research, data interpretation, software, and manuscript preparation. RM: The entire analysis, equipment, examination, and supervision of corrections of the manuscript.

## References

- 1 Singh C K, Kumar A, Shashtri S, Kumar A, Kumar P, *et al.*, Multivariate statistical analysis and geochemical modeling for geochemical assessment of groundwater of Delhi, India, *J Geochem Explor*, 175 (2017) 59–71. <http://dx.doi.org/10.1016/j.gexplo.2017.01.001>
- 2 Rhoades J D, Kandiah A & Mashali A M, The use of saline waters for crop production, (Food and Agriculture Organization of the United Nations, Rome), 1992, pp. 145.
- 3 Rina K, Singh C K, Datta P S, Singh N & Mukherjee S, Geochemical modelling, ionic ratio and GIS based mapping of groundwater salinity and assessment of governing processes in Northern Gujarat, India, *Environ Earth Sci*, 69 (2013) 2377–2391.
- 4 Kumar C & Satyanarayan S, Integrating multivariate statistical analysis with GIS for geochemical assessment of groundwater quality in Shiwaliks of Punjab, India, *Environ Earth Sci*, 62 (2011) 1387–1405.
- 5 Barbecot F, Marlin C, Gibert E & Dever L, Hydrochemical and isotopic characterisation of the Bathonian and Bajocian coastal aquifer of the Caen area, *Appl Geochemistry*, 15 (2000) 791-805
- 6 Belkhiri L & Narany T S, Using Multivariate Statistical Analysis, Geostatistical Techniques and Structural Equation Modeling to Identify Spatial Variability of Groundwater Quality, *Water Resour Manage*, 29 (2015) 2073–2089.
- 7 Ledesma-ruiz R, Pastén-zapata E, Parra R, Harter T & Mahlknecht J, Investigation of the geochemical evolution of groundwater under agricultural land: A case study in northeastern Mexico, *J Hydrol*, 521 (2015) 410–23. <http://dx.doi.org/10.1016/j.jhydrol.2014.12.026>
- 8 Reghunath R, Murthy T R S & Raghavan B R, The utility of multivariate statistical techniques in hydrogeochemical studies: an example from Karnataka, India, *Water Res*, 36 (2002) 2437–2442.
- 9 Mahlknecht J, Hernández-Antonio A, Eastoe C J, Tamez-Meléndez C, Ledesma-Ruiz R, *et al.*, Understanding the dynamics and contamination of an urban aquifer system using groundwater age (14C, 3H, CFCs) and chemistry, *Hydrol Process*, 31 (13) (2017) 2365–2380.

- 10 Kundzewicz Z W, Mata L J, Arnell N W, Döll P, Jimenez B, *et al.*, The implications of projected climate change for freshwater resources and their management, *Hydrol Sci J*, 53 (1) (2008) 3–10. <http://www.tandfonline.com/doi/abs/10.1623/hysj.53.1.3>
- 11 Bhadja P & Kundu R, Status of the seawater quality at few industrially important coasts of Gujarat (India) off Arabian Sea, *Indian J Geo-Mar Sci*, 41 (1) (2012) 90–7.
- 12 Mondal N C, Singh V P, Singh V S & Saxena V K, Determining the interaction between groundwater and saline water through groundwater major ions chemistry, *J Hydrol*, 388 (1–2) (2010) 100–11. <http://dx.doi.org/10.1016/j.jhydrol.2010.04.032>
- 13 Roques C, Aquilina L, Bour O, Maréchal J-C, Dewandel B, *et al.*, Groundwater sources and geochemical processes in a crystalline fault aquifer, *J Hydrol*, 519 (2014) 3110–28.
- 14 Yidana S M & Yidana A, Assessing water quality using water quality index and multivariate analysis, *Environ Earth Sci*, 59 (2010) 1461–1473.
- 15 Machiwal D & Jha M K, Identifying sources of groundwater contamination in a hard-rock aquifer system using multivariate statistical analyses and GIS-based geostatistical modeling techniques, *J Hydrol Reg Stud*, 4 (2015) 80–110. <http://dx.doi.org/10.1016/j.ejrh.2014.11.005>
- 16 Suma C S, Srinivasamoorthy K, Saravanan K, Faizalkhan A, Prakash R, *et al.*, Geochemical Modeling of Groundwater in Chinnar River Basin: A Source Identification Perspective, *Aquat Procedia*, 4 (2015) 986–92. <http://dx.doi.org/10.1016/j.aqpro.2015.02.124>
- 17 Gu A D, Lee H, Iida T, Shimizu I, Tominaga M, *et al.*, Heat-Evoked Activation of the Ion Channel, TRPV4, *J Neurosci*, 22 (15) (2002) 6408–14.
- 18 Cloutier V, Lefebvre R, Therrien R & Savard M M, Multivariate statistical analysis of geochemical data as indicative of the hydrogeochemical evolution of groundwater in a sedimentary rock aquifer system, *J Hydrol*, 353 (3–4) (2008) 294–313.
- 19 World Health Organisation, World Health Statistics, 2009.
- 20 Kisan M, Sangathan S, Nehru J, Pitroda S G & Nī tiś atakam B, Vitreous Sanitary Appliances (Vitreous China), Part 6: Specific Requirements of Urinals and Partition Plates [CED 3: Sanitary Appliances and Water Fittings], *Specification BIS*, IS 2556-6 (1995). <https://law.resource.org/pub/in/bis/S03/is.2556.6.1995.pdf>
- 21 Subramanian V & Saxena K K, Hydrogeochemistry of groundwater in the Delhi region of India, *Relat Groundw Quant Qual*, (Proceedings of the Hamburg Symposium, August 1983), (IAHS Publ no 146), pp. 307–316. [http://hydrologie.org/redbooks/a146/iahs\\_146\\_0307.pdf](http://hydrologie.org/redbooks/a146/iahs_146_0307.pdf)
- 22 Farnham I M, Johannesson K H, Singh A K, Hodge V F & Stetzenbach K J, Factor analytical approaches for evaluating groundwater trace element chemistry data, *Analytica Chimica Acta*, 490 (2003) 123–38.
- 23 World Health Organization, Sodium in Drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality, WHO/SDE/WSH/03.04/15. [https://www.who.int/water\\_sanitation\\_health/dwq/chemicals/sodium.pdf](https://www.who.int/water_sanitation_health/dwq/chemicals/sodium.pdf)
- 24 World Health Organization, Sulfate in Drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality, WHO/SDE/WSH/03.04/14. [https://www.who.int/water\\_sanitation\\_health/dwq/chemicals/sulfate.pdf](https://www.who.int/water_sanitation_health/dwq/chemicals/sulfate.pdf)
- 25 Fawell J & Nieuwenhuijsen M J, Contaminants in drinking water, *Br Med Bull*, (2003) 199–208.
- 26 Selvakumar S, Chandrasekar N & Kumar G, Hydrogeochemical characteristics and groundwater contamination in the rapid urban development areas of Coimbatore, India, *Water Resour Ind*, 17 (2017) 26–33. <http://dx.doi.org/10.1016/j.wri.2017.02.002>
- 27 Shrestha S & Kazama F, Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan, *Environ Model Softw*, 22 (4) (2007) 464–75.